Studies on bisorption of trivalent Chromium using *Caulerpa fastigiata*

ABSTRACT

Chromium is one of the toxic elements in different types of industrial effluents responsible for environmental pollution. Traditional removal methods like chemical precipitation and ion exchange resins for Cr (III) ion removals are costly and labour intensive. Biosorption is a promising alternative due to its higher metal binding capacity, and low cost. This study aims to report batch adsorption study of trivalent chromium with marine macro *algae* *Caulerpa fastigiata* an abundantly available biomass.. Various pre set parameters studied include initial metal ion concentration, pH, temperature, sorbent dosage and biomass particle size. Testing the sorption data with isotherm models quoted in the literature for Cr^{3+} proved that Freundlich model is the best fit with correlation co-efficient in between 0.995-0.999 .Kinetic study results prompt that the sorption data on Cr^{+3} with correlation coefficients $R^2=0.999$, can best be represented by pseudo second order . Free energy change (ΔG^0) with negative sign reflects the feasibility and spontaneous nature of the process. The SEM studies showed Cr(III) biosorption on selective grains of biosorbent. The FTIR spectra indicated bands corresponding to –OH, COO^-, -CH, C=C, C=S and –C-C- groups. After Cr(II) biosorption, the bands were shifted by 5 to 20 cm^{-1}. The XRD pattern of the *Caulerpa fastigiata* was found to be mostly amorphous in nature. After Cr(III) biosorption shift in d-values and % RI were noticed

Keywords: Biosorption, Free energy change (ΔG^0) , Chromium(III), *Caulerpa fastigiata*

INTRODUCTION

Though industrial progress is a landmark of civilized development, harmful industrial effluents, polluting the environment have become an unpleasant price mankind is paying, Heavy metal pollution of water sources is a dangerous environmental hazard; with impending risk of chronic ill health to man and beasts, as the toxic metal ions dissolved in water ultimately reach the top of the food chain[1-4]. Chromium has the dual distinction of being a necessary microelement on one hand and toxic ion with capabilities of inducing severe mucosal irritation and even malignancy on the other hand. Electroplating, dye, cement, leather tanning and painting industries basically discharge effluents rich in chromium[5,6,7]. Maximum permissible limit of Chromium 0.1 mg/L in drinking water was set by U.S. authorities[8]. The recommendations of WHO are much more stringent in this context as the maximum permissible limit of Chromium in drinking water is fixed at .05 mg/L[9]. In the light of the above, heavy metal removal and recovery from waste waters of various above industries has become just not a societal or moral obligation but an essential legal requirement too. A number of techniques were developed for this purpose, namely, chemical precipitation, solvent extraction, ion exchange, membrane separation, photo extraction electro dialysis reverse osmosis and ultra filtration[10-15]. When heavy metals are present in low concentrations almost all of these methods were found to be either prohibitively costly or unacceptably inefficient[16]. This situation hastened the research for alternatives in this direction and biosorption emerged as an efficient, cost effective method with the added advantage of minimal volumes of sludge chemical and or biological for disposal. One more important plus point here is the higher efficacy of biosorption in detoxifying extremely dilute industrial effluents[17]. The favourable cost benefit equation too was confirmed by many researchers[18-21]. Deng et al found marine green microalgae to be very promising natural biological adsorbent with a surplus availability. Presence of polysaccharides, proteins, or lipids in the cell wall surface of these algae containing functional groups such as amino hydroxyl carboxyl and sulphate, which act as binding sites for the pollutant heavy metals, was found to be the most plausible explanation for the high metal binding capacity of the marine algae[22-27]. FTIR (Fourier Transform Infra Red Spectrophotometry) is a new technique to analyze and confirm that the functional groups are responsible for metal complexation. FTIR determines the functional groups responsible for the metal ions complexation [28]. There are several chemical groups that would attract and sequester the metals in biomass. Amino and phosphate groups of nucleic acids, amide, amine, sulfhydryl and carboxyl groups in the proteins and hydroxyls in polysaccharides of marine algae, plants etc are some such groups

Caulerpa fastigiata is abundant, renewable nontoxic algae which could be obtained very economically on a large scale locally from oceans. In the present study, the biosorption capacity of dried algae has been investigated as the function of environmental parameters, adsorption time, pH values and solid/liquid ratio. In addition, equilibrium and kinetic studies were carried out. Langmuir and Freundlich isotherm models were applied to fit experimental data. The biosorbent was characterized by employing instrumental techniques, viz., Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). .

2.EXPERMENTAL

2.1 Preparation of biosorbent *Caulerpa fastigiata*

The biomass used in the present study a green macro algae, *C. fastigiata,*was collected from the East coast of India. After harvesting from sea, the samples were washed with demineralised water thrice, to remove debris, particulate matter and salts from the surface. Dried the biomass in hot air oven at 70°C for 24 hours and size reduction was undertaken by domestic mixer. The dead powdered algal biomass was kept in humidity control oven to maintain the humidity for entire equilibrium studies. The algae was identified and authenticated by the botanist, Dept. of Botany, Andhra University, Visakhapatnam.

2.2 Preparation of stock solutions: All the chemicals used were of analytical reagent grade. In order to avoid interference with other elements in the waste water, the experiments were conducted with aqueous solution of Chromium (III). Stock Cr(III) solution (1000 mg/L) was prepared by dissolving appropriate amount of $CrCl_3$ $6H_2O$ in Milli-Q water. All the working solutions were prepared by diluting the stock solution. The pH of the test solutions was adjusted using reagent grade hydrochloric acid and sodium hydroxide solutions. pH measurements were made using a pH meter (Systronics 361).The heavy metal in solution was analysed by using Atomic Absorption Spectrophotometer.(Model:AA 100) , Characterization of biomasses was carried out by using Scanning Electron Microscope (model Shimazdu), . Fourier Transform Infra red Spectroscope (model Perkin-Elmer 1600), . X-Ray Diffractometer (model Lab X-6000)

2.3 Equilibrium Studies

The experiments were carried out in 250 mL Erlenmeyer conical flasks, at a constant agitation speed (160 RPM) with 100 mL solution with various metal concentrations (6.885,23.664,85.221,97.41

mg L^{-1}) and required amount of adsorbent (2.5, 5.0, 7.5 and 10.0 g L^{-1}) using orbital shaker. Initially the effect of contact time (0-90min) on the sorption capacity of *C. fastigiata* was evaluated. The equilibrium time obtained was used in all experiments and the experiments were repeated thrice for all conditions of study.

2.4 Analytical procedure

The concentrations of un-adsorbed Cr (III) ions in the sample supernatant liquid were determined using an atomic absorption spectrophotometer (Perkin Elmer AA200) with an air acetylene flame. C and C_T were determined and tabulated for subsequent analysis of the data. The metal uptake (q_e) was calculated using the general definition:

$$q_e = \frac{V(C_0 - C_e)}{M} \qquad (1)$$

where q_e is the metal uptake mg g^{-1} biomass, V is the volume of metal containing solution in contact with the biosorbent in L, $C_0$and C_e are the initial and equilibrium (residual) concentration of metal in the solution mg L^{-1}, respectively, and M is the amount of added biosorbent in g. Metal % of removal by *C. fastigiata* was determined by equation 2 as follows:

$$R(\%) = \frac{C_0 - Ct}{C_t} \times 100 \qquad (2)$$

Where R is the percentage of Cr (III) adsorbed by biomass, C_0 is the initial concentration of metal ions in mg L^{-1} and C_t is the concentration of metal ions at time t in mg L^{-1}.

2.5 Characterization of Biomass

2.5.1 FTIR studies

The biomass prior and after adsorption, was air dried, and demoisturized at 60°C in humidity control oven. The powder was analyzed by FTIR (Perkin-Elmer 1600) by Potassium Bromide (KBr) pellet method in the wave number range of 400 cm^{-1} to 4000 cm^{-1}. The FTIR study is intended to provide a deeper understanding of the interaction between the biomass cell surface and the metal ions.

2.5.2 X-ray Diffraction Analysis

The X-ray Diffractogram (XRD) of each of the biomass powder sample was obtained using XRD-6000 Shimadzu, Japan Model. The diffracted X-ray intensities were recorded as a function of 2Θ, at a scan speed of 1.2°/ min and pattern was recorded from 10° to 70°.

2.5.3 SEM studies

The dried biomass powders and the corresponding metal ion loaded powders were first coated with ultra thin film of gold by an ion sputter (JFC-1100) and then were exposed under electron microscope (JEOL, JXA-8100). For this purpose the working height was kept 15 mm with working voltage ranging between 10 kV to 25 kV.

3 Results and Discussion

3.1 Effect of contact time

Experiments were conducted to estimate the time required to reach the sorption equilibrium by taking an initial charge of 100 mL of aqueous solution containing Cr (II) ions and required quantities of biomass. The mixture was shaken in an orbital shaker, the samples were drawn at regular time intervals and the metal concentration was estimated using AAS. The data of concentration of metal ion C_t, in solution with time are shown for different quantities of biomass in Fig 1.

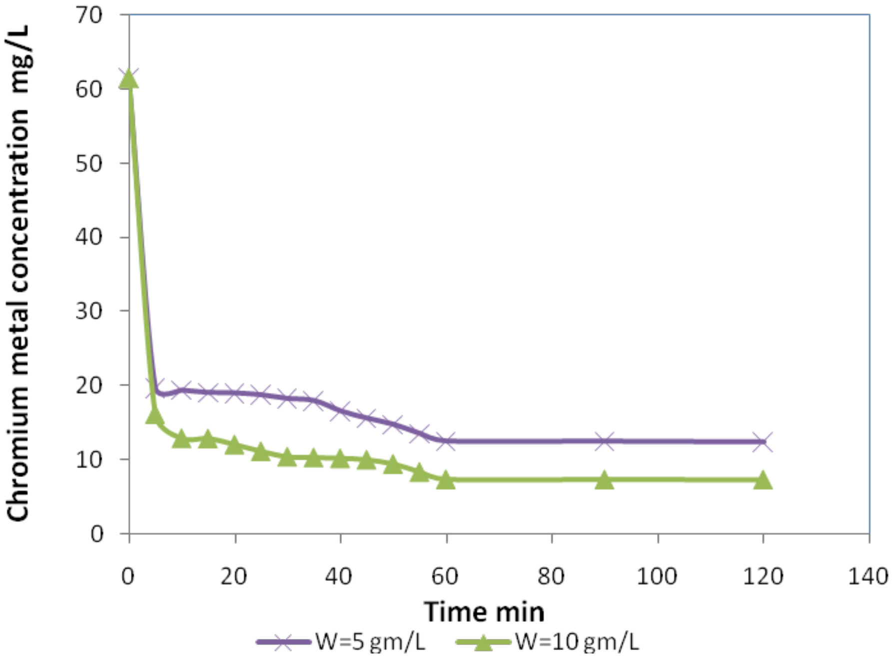


Fig.1 Variation of metal (Cr^{+++}) concentration in solution with time at different biosorbent concentrations at 30°C, dp 0.074mm, C_0 61.506 mg/L and pH 4 using *Caulerpa fastigiata* as biosorbents.

Experimental results show a faster uptake at initial stages of contact, and subsequent slowing down as the equilibrium is approached. In the initial stages of contact, large numbers of vacant sites are available and hence the uptake is faster. The slowing down of metal uptake later is due to difficulty in occupying the remaining vacant sites. Repulsive forces between the adsorbed Cr(III) ions and aqueous Cr(III) may also most probably contribute to the slowing down of uptake of metal at equilibrium.[28,29]

The effect of contact time on % adsorption of Chromium was studied over a duration time period of 5 - 90 min, using l g of *C. fastigiata* biomass powder, (dp = 0.074mm); and 61.506 mg/L of aqueous Chromium solution at pH 4 at temperature 303 K and at 190rpm orbital shaking speed. Chromium removal more than 50% was observed within first 15 min, the rate of percent removal declined gradually till the end of 60 min contact time (optimum contact time) and remained constant thereafter.

The Percentage adsorption increased from 73.65 to 88.03% from 5 min to optimum contact time of 60min with 61.506mg/L of starting Chromium solution[30]. Similar procedure was adopted for 2.5,5,7.5 g/L of biomass concentrations in aqueous solutions and the results indicated the same contact time of 60 minutes as optimum time for different concentrations used.

3.2 Effect of pH

pH of the biosorption medium is one of the essential parameter affecting the uptake of heavy metal ions from aqueous solutions by biosorbent[31,32,33]. One of the factors significantly affecting biosorption of metal ions is its acidic nature. This parameter directly related to the ability of hydrogen ions with that of the metal ions to bind themselves to active sites on the biosorbent surface[34,35]. Generally, metal biosorption involves complex mechanisms of ion exchange, chelation, adsorption by physical forces, and ion entrapment in inter and intra fibrillar capillaries and spaces of the cell structural network of a biosorbent[36,37,38,39]. The FT-IR spectroscopic analysis showed that the moss biomass contains variety of functional groups, such as carboxyl, hydroxyl, and amine and these groups are involved in almost all potential binding mechanisms. Moreover, depending on the pH value of the aqueous solution these functional groups participate in metal ion binding[40]. The effect of pH can be explained by ion-exchange mechanism of sorption in which a significant role is played by the functional groups of biomass that have cation-exchange properties[31,32,33,41].

The effect of pH on the biosorption of Cr(III) ions onto *C. fastigiata* biomass was studied in the pH range 2–8 and the results were presented in fig 2

The adsorption was very low at the initial pH of 2.0(23.83%) for initial concentration of Chromium (62.373mg/L) in solution. with an increase in pH from 2.0 to 4.0, the %Cr(III) biosorption increased from 23.83% to 88.03% . A metal uptake of 34.6 mg .g^{-1} at pH 4 could be realized[42]. For pH beyond 4 the % biosorpion was reduced to 31.2% drastically. At high pH value (>4.0), the binding ability of ions to the sites decreased on account of repulsive forces between the biosorbent and Cr (III) ions. Adsorption of Cr(III) was marginal at pH values more than 6 due to dual complexation of the anions to be adsorbed on to the surface of the adsorbents[43].

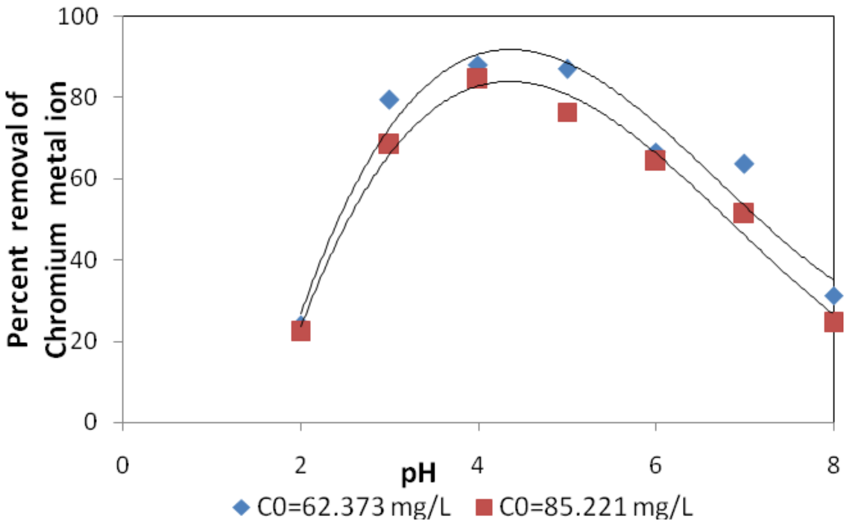


Fig.2 Effect of pH on percent adsorption at different initial metal (Cr^{+++}) concentrations at a temperature of 30°C, dp 0.074mm and L/S ratio 100 using *Caulerpa fastigiata as biosorbent.*

3.3 Effect of metal ion concentration

In aqueous solutions, the initial metal ion concentration influences the metal uptake process significantly. The specific sites in the biosorbents adsorb the metal ions. These specific sites get saturated with increasing metal ion concentration. Equilibrium adsorption data at different concentrations of metal ions in solutions are necessary to establish the efficiency of an adsorbent. Adsorption isotherm models quantify and qualify the capacity of an adsorbent, and the equilibrium adsorption data are necessary to obtain the best fit among different isotherm models available in literature.

The effect of initial Cr(III) concentration on the sorptive removal of Cr(III) is presented in (Fig .3)With the increase in initial Cr(III) concentration from6.88.5mg/L to 97.41mg/L a significant decrease was observed in the percent of removal from 89.12 to 79.43 and adsorption capacity (q_e) increased from 0.61359.mg/L to 7.7373 mg/L at sorbent dosage of 10g/L and pH 4, temperature 40^0c. Similar observations have been made by earlier reporters[43,44].

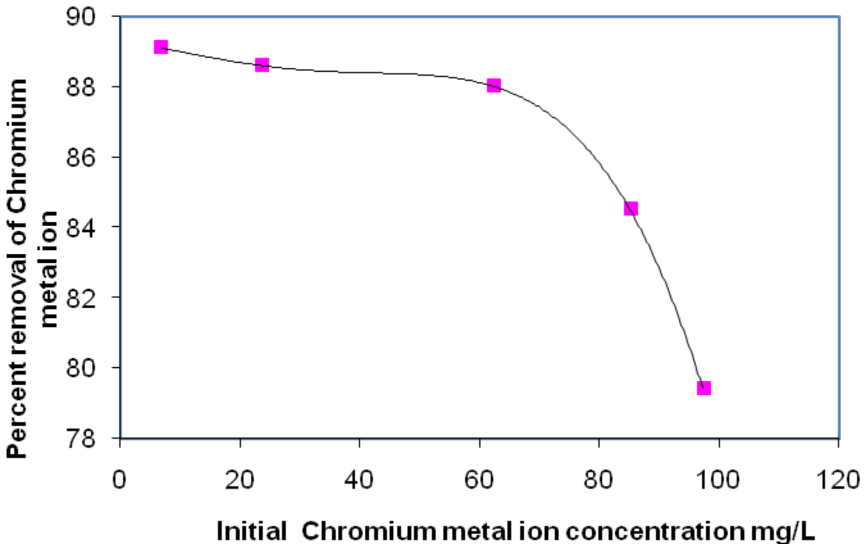


Fig.3 Variation of %Removal of Chromium metal ion with Initial concentration of Cr(III) in solution at temperature of 40°C, pH 4, dp 0.074mm and L/S ratio 100.

3.4 Effect of adsorbent dosage

Biosorbent dosage determines the potential of biosorbent through the number of binding sites available to remove metal ions at a specified initial metal ion concentration. The effect of amount of biomass added to the aqueous solution on the biosorption of Cr(III) using *C. fastigiata* as biosorbent was studied and is shown through the plots of (Fig.4) At equilibrium, metal uptake capacity decreased with an increase in biomass dosage. This decrease could be due to the concentration gradient between the sorbent and the sorbate; an increase in biomass caused a decrease in the amount of metal sorbed onto a unit weight of the algae biomass. Moreover, the increase in percent biosorption of metals by increasing the biomass dosage is due to an increase in the number of active sites and surface area available for biosorption. Similar trends have been reported in the literature[45-49].The % removal of Cr^{3+} on *C. fastigiata* ranged from77.2 to 87.98 at a pH value of 4 and uptake capacity has decreased from 5.4 to 3.159 mg/g.

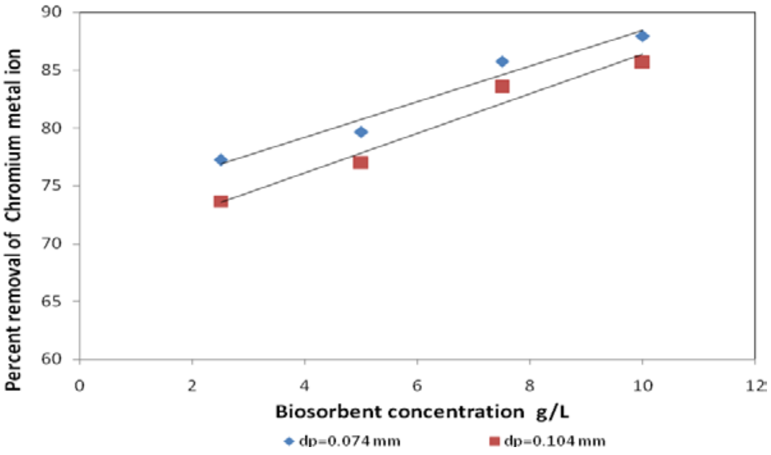


Fig.4 Variation of % Chromium metal ion sorption with biomass concentration at temp 30^0 C, pH= 4 and C_0=61.506 mg/L using *Caulerpa fastigiata* as biosorbent

3.5 Effect of adsorbent size

The effect of Particle size in the range 0.074 mm to 0.150 mm on (Fig 5) adsorption percentage of Cr (III) on *C. fastigiata* was investigated. A decrease of about 10-12% in the % adsorption was found with an increase in the particle size by two fold. The decrease in the average particle size of the adsorbent increased the surface area. The ion-exchange capacities much depends on the specific surface area available for solute–surface interaction, which is accessible to solute. Consequently, it is expected that the ion-exchange capacity had increased with increasing surface area of adsorbent. The rate of exchange is generally controlled by the rate of ion diffusion within the particle and this is related to the size of particles [50,51]

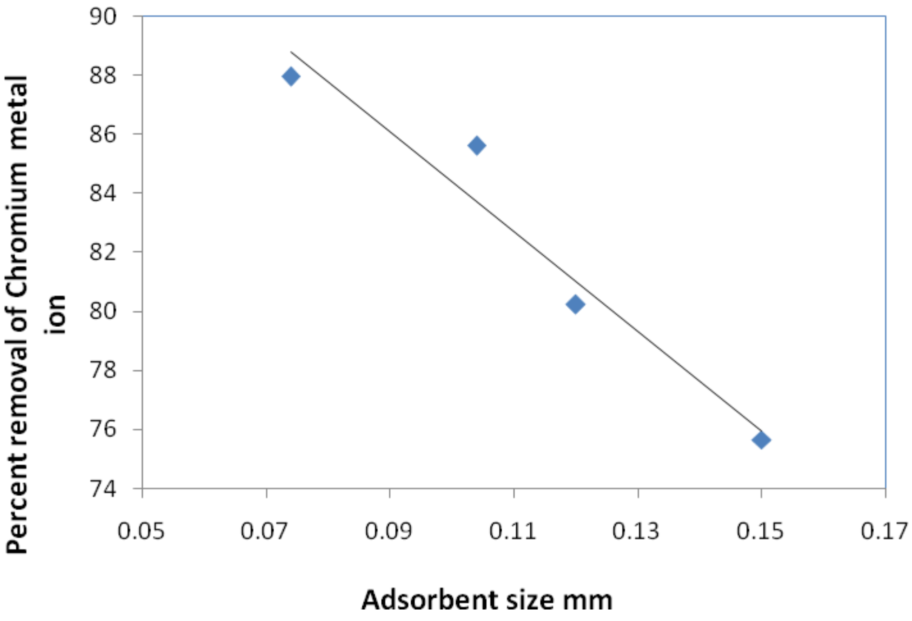


Fig.5 Variation of % Chromium metal ion sorption with Adsorbent size at temp 30^0 C, pH= 4 and C_0=61.506 mg/L using *Caulerpa fastigiata* as biosorbent

3.6 Effect of temperature

In most of the chemical reactions the temperature is expected to activate the process increasing the heat or mass transport processes.

An increase in Cr(III) metal sorption by macro algae was found to increase with temperature by 8%. As shown in (Fig.6) .% sorption increased from 82.25 to 90.16 % with increase in temperature in the range 15-50^{0}C at initial concentration of 6.885 mg/L. The increase can be attributed to the affinity of *C. fastigiata* for Cr(III) ions due to the reorientation of cell wall component of *C. fastigiata*[52].

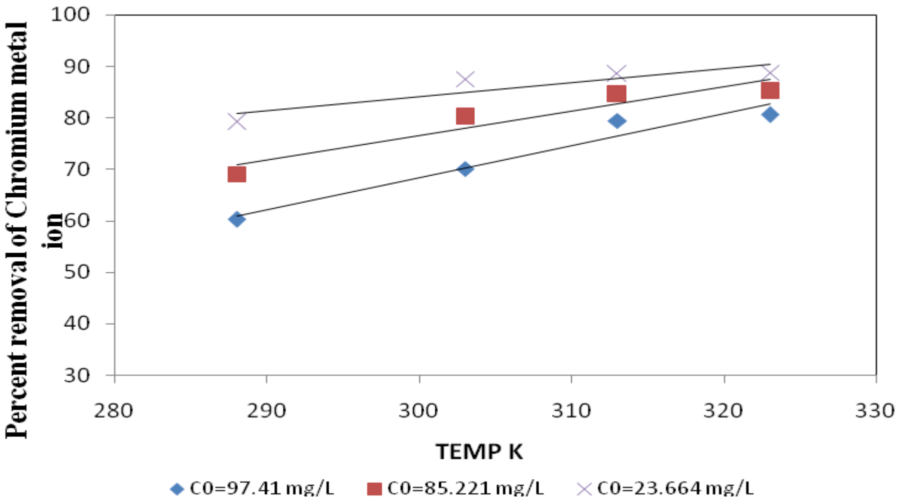


Fig.6 Variation of percent adsorption of Cr^{+++} metal ion with temperature at different initial metal ion concentrations L/S ratio 100 and a pH of 4. using *Caulerpa fastigiata* as biosorbent

3.7 Equilibrium isotherms

3.7.1 Langmuir Isotherm

The equation proposed by Langmuir is universally applicable to chemisorption with some limitations involving physical adsorption[54]. This equation is applicable to the physical or chemical adsorption on solid surface with one type of adsorption active centre

. As long as the limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for adsorption behaviour in different adsorbate-adsorbent systems or for varied conditions within any given system. Linear form of the Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{3}$$

Where q_m (mg/g) is the maximum amount of the metal ion per unit weight of adsorbent to form a complete monolayer on the surface . 'q_e' is equilibrium adsorption capacity (mg g^{-1}), 'C_e' is the equilibrium concentration of the adsorbate in solution (mg L^{-1}), and b is a constant which accounts for the affinity of the binding sites (L mg^{-1}). q_m represents the limiting adsorption capacity when the surface is fully covered with metal ions and helps in the evaluation of adsorption performance, particularly in cases where the sorbent did not reach its full saturation during contact. It is the most widely used simple two parameter equation (Langmuir, 1918). From the plots between (C_e/q_e) and C_e the slope ($1/q_m$) and the intercept ($1/ q_m b$) can be calculated.

The Langmuir constant used to determine the suitability of the adsorbent to adsorbate by using dimensionless factor R_L (Hall separation factor) calculated by:

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

0 <R_L <1 indicates favorable for adsorption, R_L> 1indicates un-favorable for adsorption R_L = 1 indicates linear adsorption, R_L = 0 indicates irreversible adsorption.

The linearized Langmuir adsorption isotherms of Cr (III) onto *C. fastigiata* were obtained at different temperatures (Fig.7). Adsorption constants and correlation coefficients are shown in (Table 1a.) C_e / q_e *vs* C_e plot yielded a straight line with R^2 (0.966) indicating the sorption data could be represented by the Langmuir model. The higher adsorption capacity, q_m(»1) indicated the strong electrostatic force of attraction and b is a constant which accounts for the affinity of the binding sites (L/mg)

Moreover, the b values are 0.067, 0.072 Lmg^{-1} indicating that biosorption capacity of *C. fastigiata* biomass for Cr(III) is higher. From the value of b, a dimensionless factor R_L at different initial metal ion concentrations was calculated and the values are shown in (Table 1b). The adsorption of Cr(III) on algal surface is thus a highly favourable process.

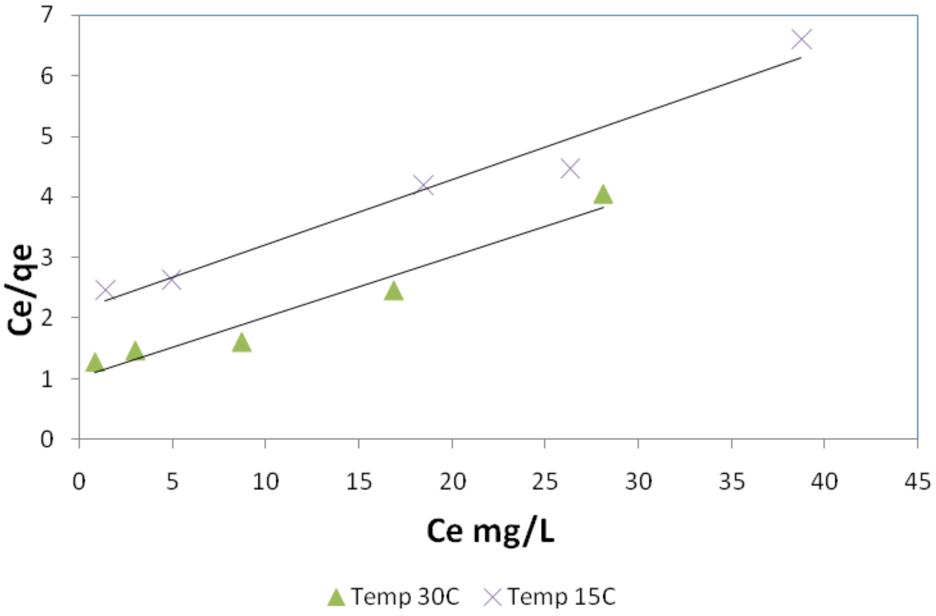


Fig.7 Langmuir plot for adsorption of Chromium ion over macro algae *Caulerpa fastigiata* as biosorbent at different temperatures for an L/S ratio of 100 and at pH 4.

Table.1a

$TEMP^0$ K	**q_m(mg g^{-1})**	**b (L mg^{-1})**	**R^2**
293	9.345	0.2299	0.966
303	9.708	0.1037	0.952

313	14.493	0.072	0.923
323	14.425	0.067	0.937

Table.1b

C_0 (mg/L)	R_L
6.885	0.6843
23.664	0.3832
62.373	0.193
85.221	0.149
97.41	0.1328

3.7.2 Freundlich Isotherm

An adsorption isotherm was proposed by Boedecker [55] which was later modified by Freundlich . The Freundlich adsorption equation can be written as:

$$q_e = K_f C_e^{\frac{1}{n_f}} \tag{5}$$

Taking logarithm on both sides,

$$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e \tag{6}$$

where 'q_e' is equilibrium adsorption capacity (mg g^{-1}), 'C_e' is the equilibrium concentration of the adsorbate in solution, 'K_f' and n_f are constants related to the adsorption process such as adsorption capacity and intensity respectively. This empirical model has shown best fit for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution.

The plot in (Fig .8) gives the isotherm drawn for biosorption of Cr^{+3} on to macro algae *Caulerpa fastigiata*. The coefficient of determination for this case is 0.9835 and the values of n_f and K_f are found to be (1.467) and (1.353*)* at 25^0 C.n_f and K_f values at 35,45^0 C were also calculated and shown in Table 2 . Freundlich constant n_f between 1 and 10 indicates a trend more favourable for bio sorption by macro algae *C. fastigiata*. This is also suggestive that the metal ion under study could well be separated from its aqueous solution with high adsorption capacity.

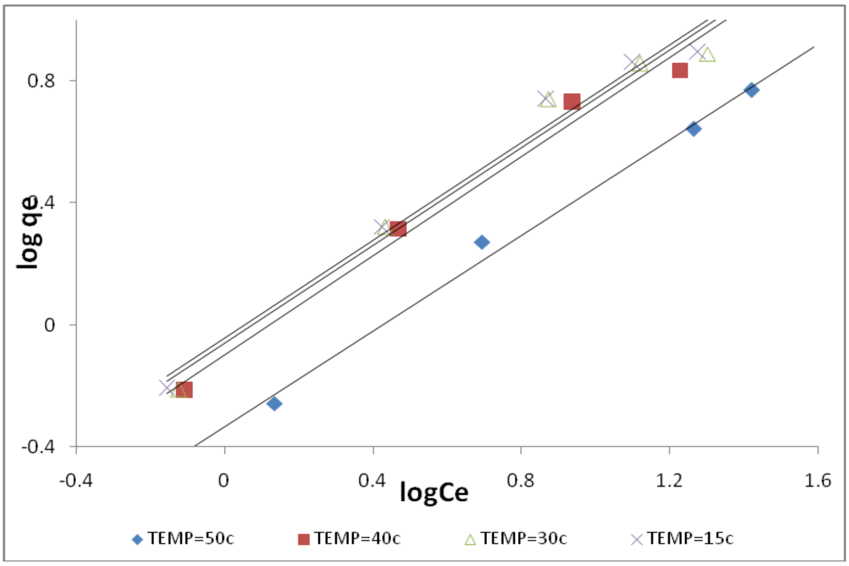


FIG.8 Freundlich plot for adsorption of chromium ion over macro algae *Caulerpa fastigiata* as biosorbent at different temperatures for an L/S ratio of 100 and at pH4.

Table 2

TEMP **(^{0} K)**	**K_F** **$\{(mgg^{-1})(mg\ L^{-1})^n\}$**	**n_f**	**R^2**
288	0.9114	1.246	.9929
303	0.8736	1.232	.9848
313	0.8026	1.246	.9738
323	0.4673	1.277	.9798

3.8 Adsorption Kinetic Models

Several kinetic models have been proposed earlier to identify the mechanism of solute adsorption from aqueous solution onto the adsorbent. They are Pseudo first order/Lagergren kinetic model, First order reversible kinetic model, Ritchie' second order kinetic model and Pseudo second order kinetic model. In the present study Pseudo first order and Pseudo second order kinetic models have been attempted to fit the present biosorption data .

3.8.1 Pseudo-first-order/Lagergren kinetic model

The Pseudo-first-order or Lagergren kinetic rate equation for the adsorption of liquid-solid system was derived based on solid adsorption capacity. It is one of the most widely used adsorption rate equations for adsorption of a solute from a liquid solution [56,57,58]

The pseudo first order kinetic equation can be expressed as:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{7}$$

Where 'q_e' is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg g^{-1}), 'q_t' is the amount of solute adsorbed at any given time 't' and 'k_1' is the rate constant. By using the boundary conditions and simplifying, the equation 7 yields.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{8}$$

'k_1' can be computed from the slope of the linear plot between ln (q_e-q_t) vs. 't' for different adsorption parameters such as pH, temperature, adsorbate concentration, adsorbent dose, and particle size. The pseudo first order rate constant $k_1$could be obtained from the slope of the plot between $\log(q_e - q_t)$ and time 't'. Fig. 9 shows that the Lagergren pseudo-first order kinetic plot does not fit well for the adsorption of Cr (III) onto *C. fastigiata*, as it does not follow a straight line.

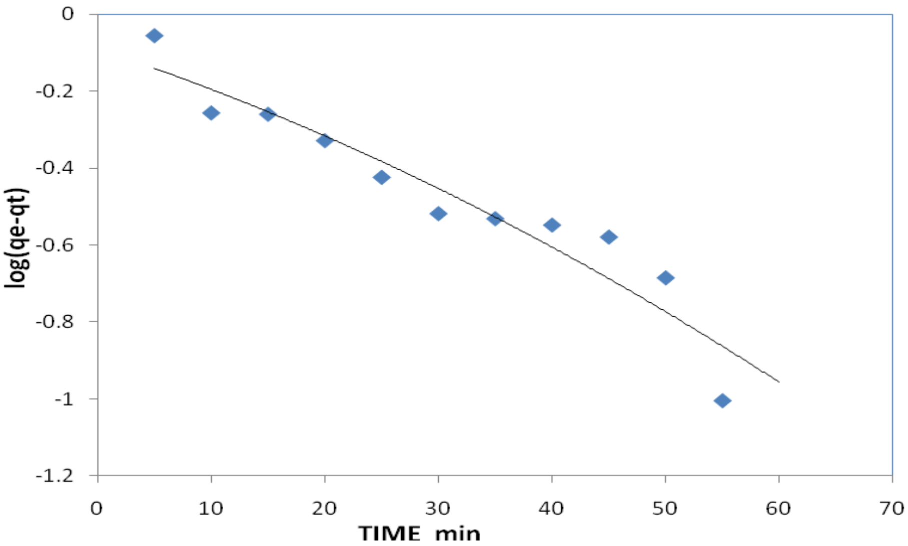


Fig.9 First order kinetic plot for biosorption of metal ion (Cr^{+++}) at 30°C, Co 61.506 mg/L and pH 4 using *Caulerpa fastigiata* as biosorbents.

3.8.2 Pseudo- second- order kinetic model

In view of the above the fitness of the sorption data was tested using pseudo- second- order reaction model .The pseudo-second-order reaction model could be expressed by the rate expression as [59,60,61]

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \qquad (9)$$

On integration for boundary conditions when t=0 to t>0 and q_t=0 to q_t>0 and further simplifications, equation 9 becomes,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (10)$$

The plot (Fig. 10) of t/q_t versus t of Eq. (10) gave a linear relationship from which the q_e and k_2 values were determined. The rate constants and the correlation coefficients for *Pseudo-second-order kinetic model* were calculated and summarized in Table 3 These values showed that the pseudo-second order kinetic plot fits well the adsorption data. The value of correlation coefficient R^2 for the pseudo-second-order adsorption model is relatively high (>0.9994), and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for the pseudo-first-order are not satisfactory. Therefore, it has been concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of lead over this algal biomass.

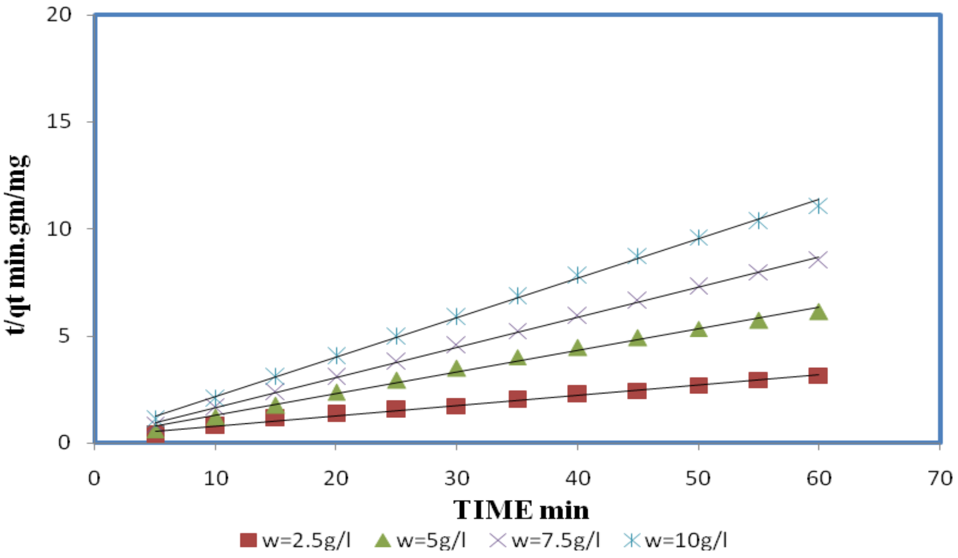


Fig.10 Second order kinetic plot for biosorption of metal ion (Cr^{+++}) at 30°C , C_0 61.506 mg/L and

pH 4.

Table 3

W g/L	**qe(cal) (mg/gm)**	**K_2 (g/mg-min)**	**R^2**	**qe(exp) (mg/gm)**
2.5	**20.40**	**9.468*10-3**	**0.997**	**18.99**
5	**10.10**	**0.0287**	**0.998**	**9.8012**
7.5	**7.246**	**0.059**	**0.999**	**8.767**
10	**5.525**	**0.086**	**0.999**	**5.409**

3.9 Thermodynamic parameters

Gibbs Free Energy ΔG is the Thermodynamic criterion at constant P and T for deciding whether the chemical process does occur/proceed or not. The spontaneity of the reaction can also be judged by the sign and magnitude of ΔG^0. A negative sign for ΔG^0 is an indicative of the spontaneity of any chemical process. To design any chemical process system one should have the knowledge of changes that are expected to occur during chemical reaction. The rate and extent of changes are more informative in the design of process equipment.

In view of the above, analysis has been carried out on the values of thermodynamic parameters on the biosorption of Cr (III) by *C. Fastigiata(*Fig.11). The thermodynamic parameters such as changes in standard free energy change ΔG°, Enthalpy ΔH°, Entropy ΔS° for any given adsorption process could be determined from the Equations:

$$\Delta G^0 = -RTInK_C \tag{11}$$

where ΔG° is the free energy change, expressed as J/mol. Kc is the apparent equilibrium constant for the process. Kc can be derived from:[62,63]

$$K_C = \frac{C_S}{C_e} \tag{12}$$

$$\log\left(\frac{C_S}{C_e}\right) = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} \tag{13}$$

$\frac{C_S}{C_e}$ can be defined as 'adsorption affinity'**.** C_s is the concentration of metal ion (mg) in solid adsorbent. C_e is equilibrium metal Concentration mg/L **.**The enthalpy changes (ΔH°) and entropy changes (ΔS°) for the adsorption process for all the initial metal concentrations in the aqueous solutions were obtained from the plots of $\log\left(\frac{C_S}{C_e}\right)$drawn against 1/T. The calculated thermodynamic data are compiled in Table 4

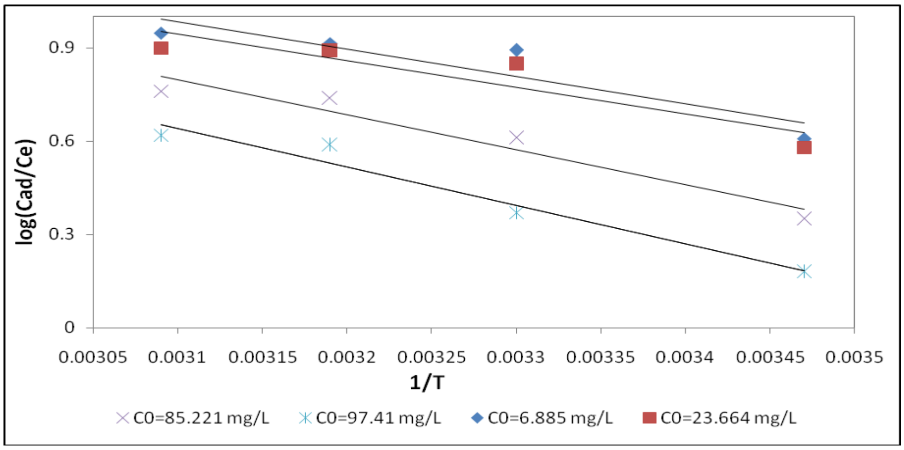


Fig.11 Vant Hoff plot for adsorption of Chromium ion over macro algae *Caulerpa fastigiata* as biosorbent at different temperatures for an L/S ratio of 100 and at pH4.

Table 4a

C_0 (mg/L)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol ^{0}K)
6.885	22.019	88.58
23.664	22.281	88.825
85.221	21.486	81.857
97.41	23.612	85.442

Table 4b

ΔG^0 (KJ/mol)	**TEMPERATURE (^{0}K)**
-0.995296	**288**
-2.276	**303**
-3.131	**313**
-3.985	**323**

Large negative value for ΔG^0 indicates the spontaneity of biosorption process at a given temperature. The free energy values increased positively with decrease in temperature for the biosorption of Cr^{+3}, shows that the spontaneity of the biosorption process increases with increase in temperature

And for Chromium the positive values for ΔH^0 indicated that the biosorption process is endothermic and the positive ΔS^0 confirms the randomness at solid/liquid interface during the biosorption process and this probably suggests that the ready replacement of the ions at solid/liquid interface [64,65].

The data revealed that they are in conformity with the earlier reports on biosorption of metals on biomass

.

.

3.10 Characterization of Biomass

3.10.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infra Red Spectroscopy (FT-IR):

Infrared spectroscopy belongs to the group of molecular vibrational spectroscopies, which are molecule-specific and give direct information about the functional groups, their kind, interactions and orientations. It`s sampling requirements allow the gain of information from solids, liquids and gases, and in particular from solid surfaces. Historically IR has been mostly used for qualitative analysis, to obtain structural information. The instrumental evolution of the day, makes non-destructive and quantitative analysis possible, with significant accuracy and precision. The shift of the bands and the changes in signal intensity allow the identification of the functional groups involved in metal sorption.

The FTIR differences of spectra in pure algal biomass adsorbent were compared to the spectra obtained in metal ion loaded algal biomass to determine whether the observed differences are due to interaction of the metals ions with functional groups (Fig. 12).

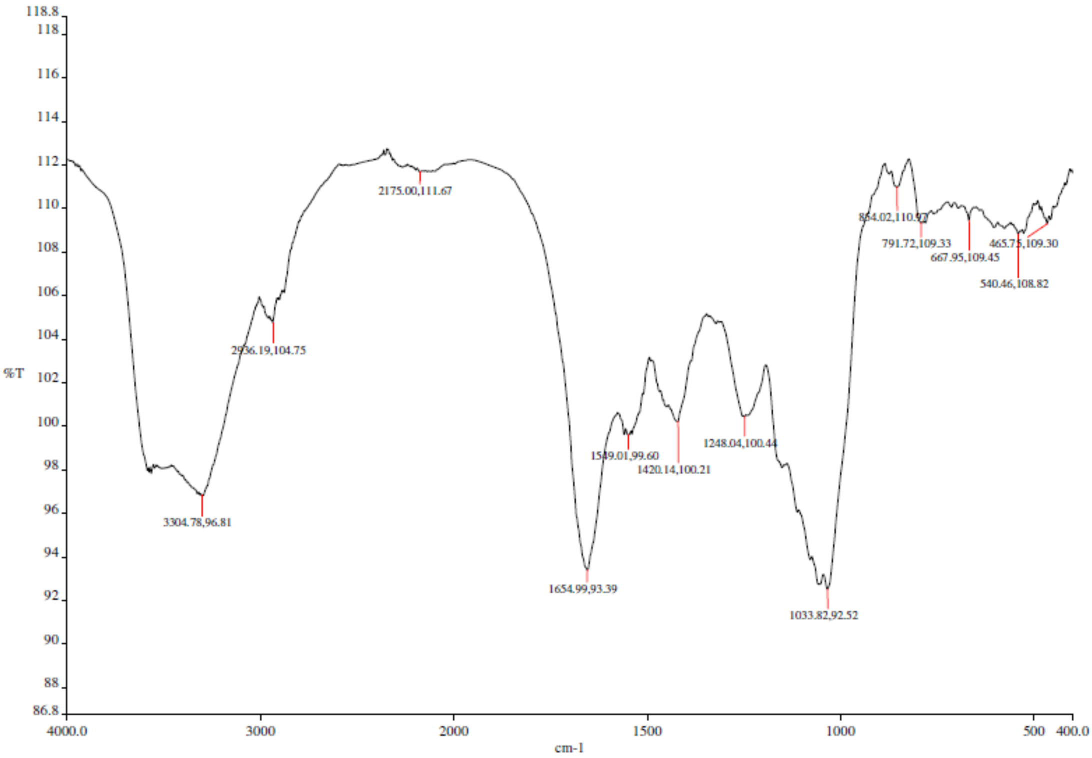


Fig.11. FT-IR Spectrum of unloaded algal biomass

The absorption peaks were tabulated in (Table. 5) for pure biomass and Cr^{+3} loaded algal biomass. The FT-IR spectrum of the Cr^{+3} loaded algal biomass also represented in (Fig.12). The band peak at 3304.78 Cm^{-1} was assigned to the binding –OH and binding –NH groups and the peak slightly shifted to 3306.53 Cm^{-1} , indicated that these groups were slightly involved in the biosorption process. The band at 2936.13 cm^{-1} was due to the – C–H stretching vibrations and was shifted to 2920.41 cm^{-1} for Cr^{+3} loaded biomass. The band at 1654.99 cm^{-1} is due to –C=O of carboxylic acid and was shifted to 1653.04 cm^{-1} for Cr^{+3} loaded biomass.

Table.5

S.No	**Band Position Cm^{-1}**		**Description**
	Un loaded Biomass	**Loaded with Cr^{+3}**	

1	3304.78	3306.53	bounded -OH and -NH groups
2	2936.13	2920.41	C–H stretching vibrations
3	2175.00	---------	C ≡ N in the polyacrylonitrile
4	1654.99	1653.04	C=O of carboxylic acid
5	1549.01	---------	Amide N-H bending vibrations
6	1420.14	1422.40	C–N Stretching (Leila Chebil Ajjabi and Lassaad Chouba, 2009)
7	1248.04	1236.56	-SO_3 stretching (Vítor et al, 2009)
8	1033.82	1034.24	–C–O benzene ring stretching (Tong et al)
9	854.02	---------	S = O and C–S–O bands, from ester sulfonate
10	791.72	780.30	presence of siliceous (Si–C) (Vítor et al, 2009)
11	667.95	694.82	N containing bioligands
12	540.46	532.45	N containing bioligands

The bands at 1420.14 cm^{-1}, 1248.04 cm^{-1} and 1033.82 cm^{-1} were due to C–N, –SO_3 and C–O in benzene ring groups[67] and the peaks were slightly shifted to 1422.40 cm^{-1}, 1236.56 cm^{-1} and 1034.24 cm^{-1} respectively for Cr^{+3} loaded biomass. These results indicated the involvement of –SO_3 functional group in biosorption process.

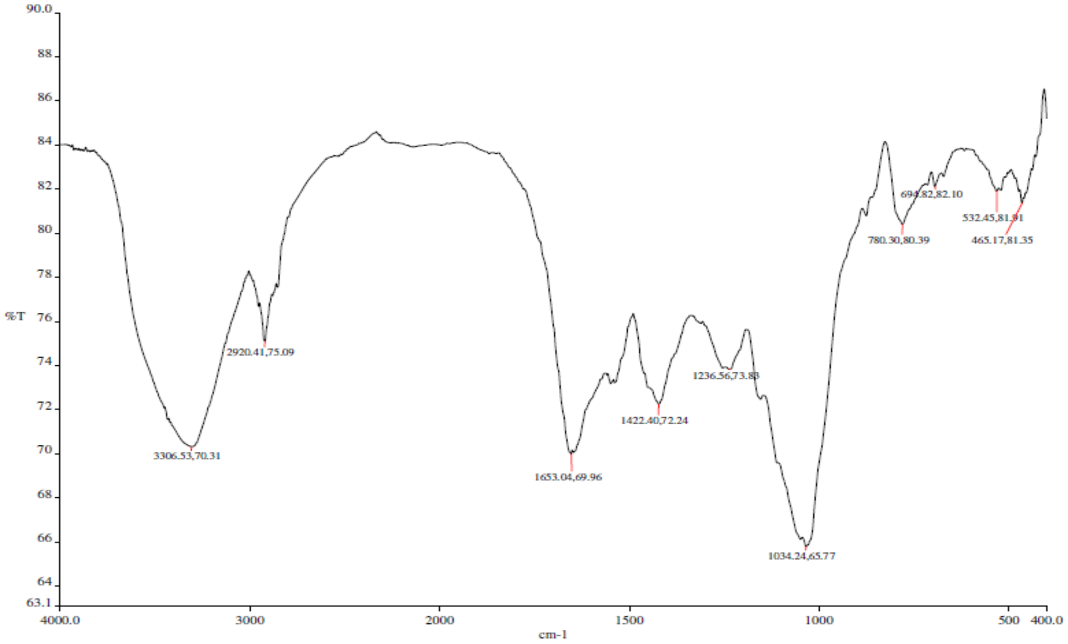


Fig.12 FT-IR Spectrum of Cr^{+3} loaded algal biomass

The characteristic absorption peaks detected in the pure biomass at 2175.00 cm^{-1}, 1549.01 cm^{-1} and 854.02 cm^{-1} were representing C ≡ N in the polyacrylonitrile, amide (N-H) and S = O and C–S–O bands, from ester sulfonate were not detected in metal loaded biomass. Because of changes in metal-loaded biomass, it could be concluded that N-H was involved in binding the metal. Similar results were shown in case of *Pleurotus ostreatus,* reported earlier[68]. Further, the involvement of S = O and C–S–O bands, from ester sulfonate functional groups, in biosorption process by algal biomass was also reported.

The presence of siliceous from diatomaceous earth, in algal waste and composite material, can justify for the absorbance peak at 791.72 cm^{-1} (Si–C). The same results were also seen in the biosorption of divalent metal ion Cu^{+2} on the alga *Gelidium sesquipedale* [69]. The bands present below 800cm^{-1} were finger print zone of phosphate and sulphur functional groups and N containing bioligands. The significant changes in the wave numbers of the specific peaks suggested that hydroxyl, amide, bounded –OH, bounded –NH, C=O stretching vibrations, S = O and C–S–O bands, from ester sulfonate and –C–O benzene ring stretching[70] groups could be involved in the biosorption of Cr^{+3} onto *C. fastigiata*. Similar results were reported for the biosorption of different heavy metals on various algal species[71].

Scanning electron microscopy (SEM)

SEM is a useful technique in the study of both the natural sorbent morphology and its modification derived from sorbate interactions. SEM is an electron microscope which provides images of the sample surface by scanning it with a high energy beam of electrons. The electron interactions with the atoms of the sample produce signals that contain information about topography, morphology, and composition of the sample surface [74]. Magnification of the imaging can be controlled over a range of up to 6 orders of magnitude from about ×25 to 250,000 times. SEM-EDAX gave evidence both of the presence of metals on the sorbent surface and of metal micro precipitation[75,76]. In this investigation, possible mechanisms involved in the sorption of the toxic elements in the biomasses and differences due to the application of the amendments were investigated using scanning electron microscopy.

The SEM images were taken by applying 10 kV voltage with different magnification times for the clarification of surface. The SEM micrographs of *Caulerpa fastigiata* powder before and after biosorption were studied and are depicted in (Fig.13 & Fig.14). It is evident from analysis that the surface area of algal biomass is uneven, heterogeneous with pores on the surfaces.

SEM images of native biomass shows that number of pores with different diameters and different pore areas. Further, pores facilitate the good possibility for metal ions to be adsorbed

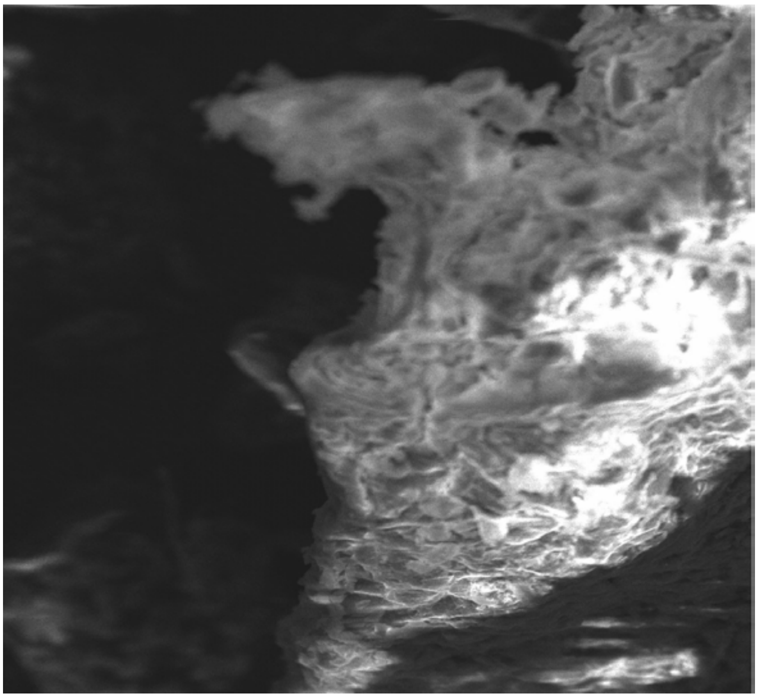
. 

Fig .12 Algae powder *C.fastigiata* without metal ions

.

The following figure (Fig. 5.15) shows the SEM analysis of algal powder loaded with Chromium.

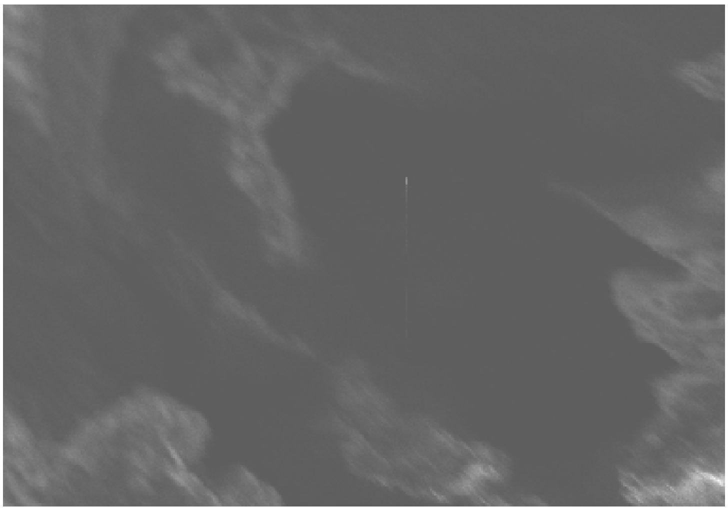


Fig.13 SEM pattern of chromium treated *C. fastigiata leaf powder*

The Scanning electron micrographs of *Caulerpa fastigiata* before metal biosorption shows particles of irregular shape and size. After Cr $^{3+}$ biosorption the biopolymer surface showed a completely different morphology. The same results were shown in case of gum kondagogu [78]when treated with Ni $^{2+}$ and Cr $^{3+}$.

X-RAY Diffraction:

Crystalinity of the material was determined by X-ray diffraction using XRD-6000 Shimadzu, Japan Model. The diffracted X-ray intensities were recorded as a function of 2Θ by using Copper target, at a scan speed of 1.2 ^{0}/ min. XRD patterns were recorded from 10^{0} to 70^{0}. XRD patterns of macro algae *Caulerpa fastigiata* before and after biosorption were depicted in figures (14&15) respectively.

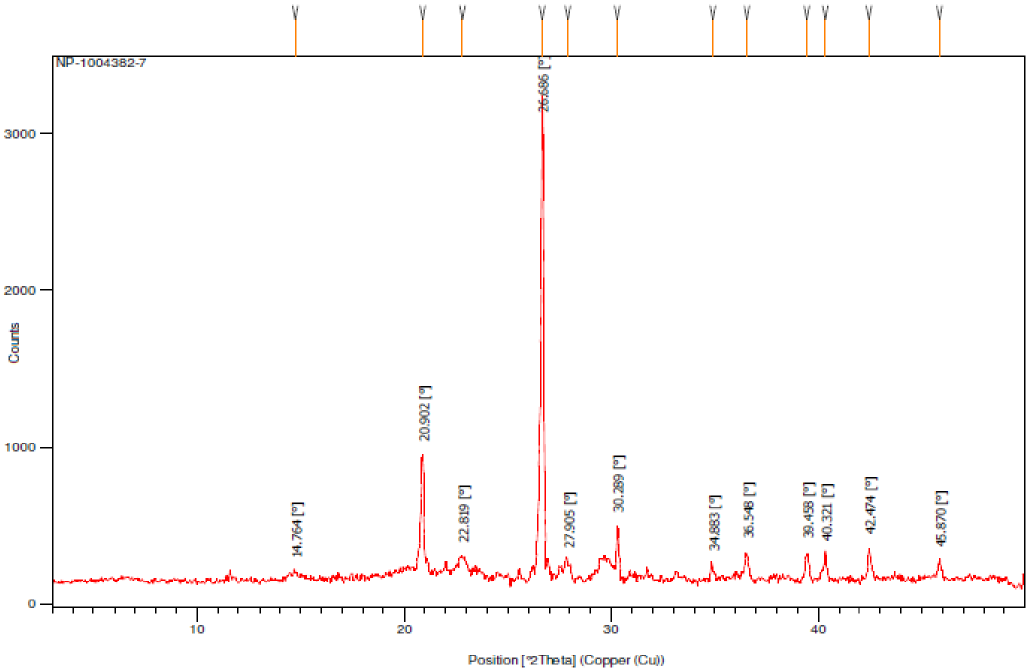


Fig.14 XRD pattern of untreated macroalgae *Caulerpa fastigiata*

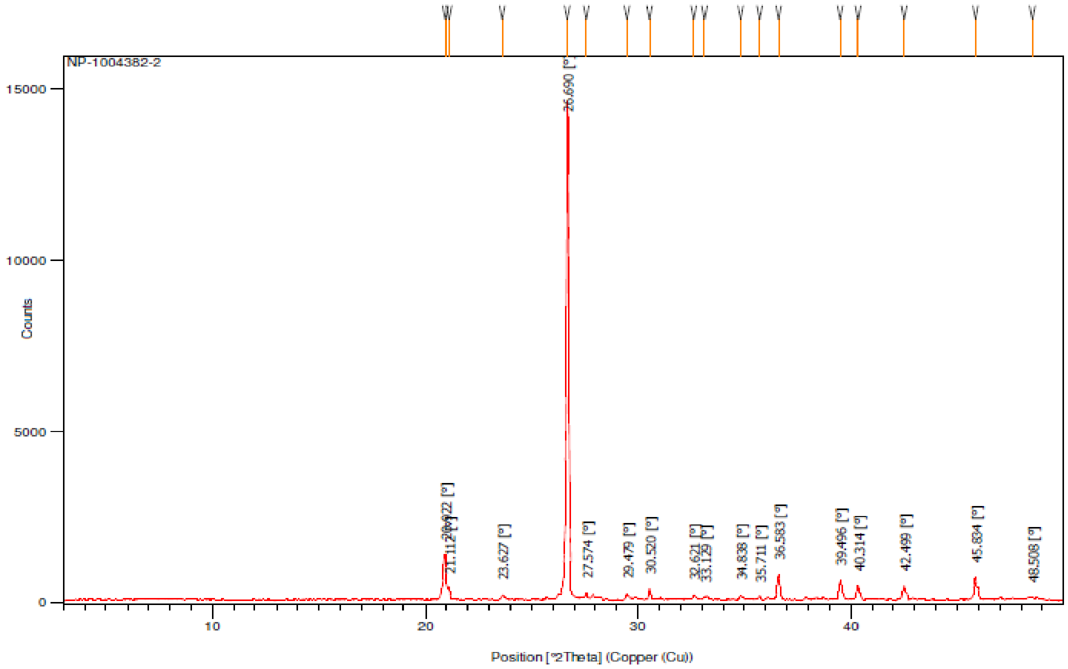


Fig. 15 XRD pattern of Chromium treated macroalgae *Caulerpa fastigiata*

Figure (14) is indicating poor crystallinity of pure biomass*Caulerpa fastigiata*[79,80].

Further the shift in 2θ and d-spacing values were observed in Chromium metal ions loaded biomass. From these observations we can conclude that there was a change in Crystallinity of biomass *Caulerpa fastigiata* after the biosorption.

CONCLUSIONS

Chromium, metal ion biosorption for *Caulerpa fastigiata* macro algae is strongly affected by parameters such as contact time, initial metal ion concentration, pH, Temperature, biosorbent dosage and biosorbent particle size. With an increase in pH from 2.0 to 4.0, the % Cr(III) biosorption increased from23.83% to 88.03% .A metal uptake of 34.6 mg $.g^{-1}$ at pH 4 could be realized. For pH value beyond 4 the % bio sorpion was reduced to 31.2% drastically. With the increase in initial Cr(III) concentration from88.5mg/L to 97.41mg/L a significant decrease was observed in the percent of removal from 89.12 to 79.43 at sorbent dosage of 10g/L and pH 4 , temperature 40^0c.The adsorption capacity(q_e) increased from 0.61359.mg/L to 7.7373 mg/L .

The % removal of Chromium ranged from 77.2 to 87.98 at a pH value of 4 and uptake capacity has decreased from 5.4 to 3.159 mg/g with biomass dosage varying from 2.5 g/L to 10 g/L of adsorbate at initial concentration of 62.373 mg/L . The effect of Particle sizes in the range 0.074mm to0.150mm on percentage adsorption of Chromium was investigated. About 10-12% decrease in the % adsorption was found with an increase in the particle size by two fold .The capacity of Chromium sorption by *caulerpa fastigiata* biomass increased from 82.25 to 90.16 % with increase in temperature in the range 15-50^{0}c at initial concentration of 6.885 mg/L. Freundlich equilibrium isotherm model proved to be good fit for the experimental data of Cr(III) biosorption on *caulerpa fastigiata* .The kinetics of the biosorption of Cr(III) could be described by a second-order kinetic model. Free energy change (ΔG^0) with negative sign reflects the feasibility and spontaneous nature of the process. With *Caulerpa fastigiata* the enthalpy and entropy changes were 22.3495 kJ mol^{-1} and 86.176 J mol^{-1} K^{-1} respectively . The positive enthalpy values indicate endothermic nature and positive entropy values point towards increase in randomness at solid liquid interface. The SEM studies showed Cr(III) biosorption on selective grains. The FTIR spectra indicated bands corresponding to –OH, COO$^-$, -CH, C=C, C=S and –C-C- groups. After Cr(III) biosorption, the bands were shifted by 3 to 20 cm^{-1}. The XRD pattern of the *caulerpa fastigiata* was mostly amorphous in nature with a few peaks. After Cr(III) biosorption shift in d-values and % RI were noticed.

.

REFERENCES

1.B. Volesky , removal and recoveryof heavy metals by biosorption of heavy metals , CRC Press , Boca Raton FL, 1990 , pp 3-43

2.Victor JPV , Cidalia MSB, Rui ARB (2007) Chromium and zinc uptake by algae Gelidium and agar extraction agal waste: Kinetics and equilibrium. J Hazard Mater 149:643-649 B.volesky, Removal and recovery of heavy metals by biosorption , Biosorption of heavy metals , CRC Press, Boca Raton, FL, 1990, pp 3-43.

3. Liu Y, Xu H(2007) Equilibrium, thermodynamics and mechanisms of Ni^{2+} by aerobic granules. Biochem Eng J.35: 174-182

4.K.Kadirvelu, K.Thamaraiselvi, C.Namasivayam, Removal of heavy metals from industrial waste waters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresource Technol. 76(2001) 63-65

5.M.Mohapatra, S.Anand, Studies on Sorption of Cd(II) on Tata Chromite mine overburden. J. Hazard. Matter.148(2007) 553-559

6.E.I.Unuabonah, K.O.Adebowale, B.J.Olu-Owolabi, L.Z.Yang, L.X.Kong. Adsorption of of Pb(II) and Cd(II) from aqueous solutions onto Sodium tetraborate-modified Kaolinite Clay: equilibrium and thermodynamics studies. Hydrometallurgy 93(2008) 1-9.

7.K.Bedoui, I.Abbes-Bekri, E.Srasra, Removal of Cd(II) from aqueous solutions using pure Smectite and Lewatite S 100. The effect of time and metal concentration. Desalination 223(2008) 269-273

8.U.S.Department of Health and Human Services, Agency for toxic substances and Disease Registry. Toxicological profile for Cadmium. 1999

9.B.volesky, Removal and recovery of heavy metals by biosorption , Biosorption of heavy metals , CRC Press, Boca Raton, FL, 1990, pp 141-160

10.M.Ajmal, R.A.K.Rao, R.Ahmed, M.A.Khan, Adsorption studies on Parthenium hysterophorus weed: Removal and recovery of Cd(II) from waste water. J.Hazard.Matr.B.135(2006) 242-248

11.C.Namasivayam, K.Ranganathan, Removal of Pb(II), Cd(II) and Ni(II) and mixture of metal ions by adsorption onto waste Fe(III) Cr(III) hydroxide and fixed bed studies, Environ.Technol.16(1995) 851-860

12.L.Nouri, I.Ghodbane, O.Hamdaoui, M.Chiha, Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran. J.Hazard.Matr.149(2007) 115-125

13.Korchagin VI, Poluektov PT(2006) Integrated utilization of spent ion exchange resins in waste water treatment and in polymer composites. Russ.J.Appl chem..79:1238-1247

14.Terashima Y, Ozaki H, Sekine M(1986) Removal of dissolved heavy metals by chemical coagulation, magnetic seeding and high gradient magnetic filtration. Water res. 20:537-545

15.Antonina P, Kryvoruchko D, Atamanenko I (2004) Concentration/Purification of Co(II) ions by reverse osmosis and ultra filtration combined with sorption on clay mineral montmorillonite and cation- exchange resin KU. 2-8n. J.Member.Sci.228:77-81

16.Blocher C. Dorda J, Mavrov V (2003) Hybrid flotation -membrane filtration process for the removal of heavy metal ions from waste water water. Res. 37: 4018-4026

17.Deng LP,SU,YY,SU H,Wang XT,Zhu XB (2007a) Sorption and desorption of lead (II) from waste water by green algae *Cladophora fascicularis*. J Hazard Mater 143:220-225

18.Marques PASS, Rosa MF, Pinheiro HM (2000) pH effects on the removal of Cu^{2+}, Cd^{2+},and

Pb^{2+} from aqueous solutions by waste brewery waste. Bioproc Eng 23:135-141

19.Choong J, Kwang HP (2005) Adsorption and desorption characteristics of mercury (II) ions Using aminated chitosan bead. Water Res 39:3938-3944

20.Nuria L, Asuncion LS, Susana M et al (2003) Heavy metal biosorption by gellan gum gel beads. Water Res 37:2118-2126

21.Saadet S, Osman G, Erman SI et al (2005) Adsorption of Cd(II) .Cu(II) and Ni(II) ions by Lemna Minor L.: effect of physicochemical environment. J Hazard Mater B 126:96-104

22.Yekta G, Sibel U, Ulgar G (2005) Biosorption of cadmium and lead by ethanol treated waste

Baker’s yeast biomass. Bioresour Technol 96:103-109

23. Deng LP, Zhu XB, Wang XT et al (2007b) Biosorption of copper (II) from aqueous solutions by green alga *Cladophora fascicularis*. Biodegradation 18:393-402

24 Olga MMF Ramiro JEM,Cristina M et al (2008) Removal of Cd(II), Zn (II) and Pb(II) from aqueous solutions by brown marine macro algae: kinetic modelling. J Hazard Mater 153:493-501

25. Patricia M, Andrea S, Alicia FC (2006) Simultaneous heavy metal removal mechanism by dead macrophytes. Chemospher 62:247-254

26. Sheng PX, Ting YP, Paul Chen J et al (2004) Sorption of cadmium , copper, cadmium, zinc, and nickel by marine algal biomass: charecterization of biosorptive capacity and investigation of mechanisms. J Colloid Interf Sci 275:131-141

27. Victor JPV , Cidalia MSB, Rui ARB (2007) Chromium and zinc uptake by algae *Gelidium* and agar extraction agal waste: Kinetics and equilibrium. J Hazard Mater 149:643-649 C.C.V

28. Figueira, M. M., Volesky, D., Mathieu, H. J., Instrumental analysis study of iron species biosorption by *Sargassum* biomass. Environmental Science & Technology 33 (11) (1999) 1840–1846.

29.Mohammad Mehdi Montazer-Rahmati, Parisa Rabbani, Atefeh Abdolali, Ali Reza Keshtkar, Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae, Journal of Hazardous Materials 185 (2011) 401–407.

30.Anna Witek-Krowiak, Roman G. Szafran, Szymon Modelski Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent **Desalination** 265 (2011) 126–134.

31. Sibel Tunli Akar ,Asli Gorgulu, Burcu Anilan, Zerrin Kaynak, Tamer Akar, Investigation of the biosorption charecterestics of lead(II) ions onto Symphoricarpus albus: Batch and dynamic flow studies**, Journal of hazardous materials** 165(2009) 126-133.

32. P.R. Puranik, K.M. Paknikar, Biosorption of lead and zinc from solutions using *Streptoverticillium cinnamoneum* waste biomass**, J. Biotechnol**. 55 (1997)113–124.

33. P. Yin, Y. Qiming, B. Jin, Z. Ling, Biosorption removal of cadmium from aqueous solution by using pretreated fungal biomass cultured from starch wastewater, **Water Res**. 33 (1999) 1960–1963.

34. María Mar Areco, María dos Santos Afonso, Copper, zinc, cadmium and lead biosorption by Gymnogongrus torulosus. Thermodynamics and kinetics studies**. Colloids and Surfaces B: Biointerfaces** 81 (2010) 620–628.

35. T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, **Water Res**. 37 (2003) 4311–4330.

36. Ahmet Sari, Durali Mendil, Mustafa Tuzen, Mustafa Soylak, Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (*Hylocomium splendens*) biomass:Equilibrium, kinetic and thermodynamic studies**, Chemical Engineering Journal** 144 (2008) 1–9.

37. Y. Zhang, C. Banks, A comparison of the properties of immobilized *Sphagnum* moss, seaweed, sunflower waste and maize for the biosorption of Cu, Pb, Zn and Ni in continuous flow packed columns, **Water Res**. 40 (2006) 788–798.

38. K. Chojnacka, A. Chojnacki, H. Gorecka, Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue–green algae *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process, **Chemosphere** 59 (2005) 75–84.

39. B. Volesky, Z.R. Holan, Biosorption of heavy metals, **Biotechnol. Prog**. 11(1995) 235–250.

40. K. Chojnacka, Biosorption of Cr(III) ions by eggshells, **Journal of Hazardous Materials B** 121 (2005) 167–173.

41. I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, **J. Am. Chem**. Soc. 40 (1918) 1361–1403.

42.Izabela Michalak, Biosorption of Cr(III) by Microalgae and Macroalgae: Equilibrium of the process, **American Journal of Agricultural and Biological Sciences** 2 (4)(2007): 284-290.

43.Biswajit Singha, Sudip Kumar Das, Biosorption of Cr(VI) ions from aqueous solutions: Kinetics, equilibrium, thermodynamics and desorption studies, **Colloids and Surfaces B: Biointerfaces** 84 (2011) 221–232

44.K.A.Krishnan, T.S.Anirudhan, Removal of cadmium (II) from aqueous solutions by steam activated sulpherised carbon prepared from suger cane bagasse pith; kinetics and equillibrium studies ,**Water SA**,29(2003)147-156.

45.M. Riaz, R. Nadeem, M.A. Hanif, T.M. Ansari, K.U. Rehman, Pb(II) biosorption from hazardous aqueous streams using *Gossypium hirsutum* (Cotton) waste biomass, **J. Hazard. Mater.** 161 (2009) 88–94.

46.N. Nasuha, B.H. Hameed, A.T. Mohd Din, Rejected tea as a potential low-cost adsorbent for the removal of methylene blue**, J. Hazard. Mater**. 175 (2010) 126–132.

47.Vahid Javanbakht, Hamid Zilouei, Keikhosro Karimi, Lead biosorption by different morphologies of fungus *Mucor indicus*, **International Biodeterioration & Biodegradation** 65 (2011) 294-300.

48.S. Ozdemir, E. Kilinc, A. Poli, B. Nicolaus, K. Guven, Biosorption of Cd, Cu, Ni, Mn and Zn from aqueous solutions by thermophilic bacteria, *Geobacillus toebii* sub.sp. *decanicus* and *Geobacillus thermoleovorans* sub.sp. *stromboliensis*: equilibrium, kinetic and thermodynamic studies, **Chem. Eng. J.** 152 (2009) 195–206.

49.B. Alyuz, S. Veli, Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, J. Hazard. Mater. 167 (2009) 482–488.

50.Sari, M. Tuzen, Biosorption of cadmium(II) from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies**, J. Hazard. Mater**. 157 (2008) 448–454.

51.y. Kumar, P. King, V. Prasad, Zinc biosorption on Tectona grandis L.f. leaves biomass: equilibriumand kinetic studies. **Chemical Engineering Journal** 124(2006), 63-70.

52.V.K. Gupta, A. Rastogi, Sorption and desorption studies of chromium(VI) from nonviable cyanobacterium, *Nostoc muscorum* biomass**, Journal of Hazardous Materials** 154 (2008) 347–354.

53.C.C.V Cruz, C.A. Henriques, A.S. Luna, Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. biomass. **Bioresour.technol**.91(2004), 249-257.

54.I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, ***J. Am. Chem. Soc.,*** 40 (1918) 1361-1403.

55 A. Dabrowski, Adsorption-from theory to practice, ***Advance in colloid and interface Science,*** 93 (2001)135-224.

56.S. Lagergren, S. Kungliga, **Band.**24(4) (1898)1-39.

57.S. I. H. Taqvi, M. I. Bhanger and S. W. Shah, Exploitation of beach sand as a low cost adsorbent for the removal of Pb(II) ions from aqueous solutions, ***Sepn. Sci. Technol***., 41(2006) 531-547.

58.P. Suddhodan and V. Mishra, Inorganic particulates in removal of heavy metal toxic ions-Part X: Rapid and efficient removal of Hg(II) ions from aqueous solutions by hydrous ferric and hydrous tungsten oxides***, J. Colloid Interf. sci.,*** 296 (2006) 383-388.

59.Y. S. Ho and G. Mckay, Pseudo-second-order model for adsorption process***, Process Biochem.,*** 34 (1999) 451-465

60.Y. S. Ho, Adsorption of heavy metals from waste streams by peat, Ph.D. Thesis, Birmingham, U. K. University of Birmingham, 1995.

61.Y. S. Ho and G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, ***Water Res.,*** 34 (2000) 735-742.

62.R. Aravindhan, J.R. Rao, B.U. Nair, Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*, **J. Hazard.Mater**. 142 (2007) 68–76.

63.Sarı, M. Tuzen, M. Soylak, Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay**, J. Hazard. Mater. B** 144 (2007) 41–46.

64.Y. Liu, Y.-J. Liu, Biosorption isotherms, kinetics and thermodynamics, **Sep. Purif. Technol.** 61 (2008) 229–242.

65.S.I. Lyubchik, A.I. Lyubchik, O.L. Galushko, L.P. Tikhonova, J. Vital, I.M. Fonseca, S.B. Lyubchik, Kinetics and thermodynamics of the Cr(III) adsorption on the activated carbon from co-mingled wastes**, Colloid Surf. A: Physicochem. Eng. Aspects** 242 (2004) 151–158.

66.Ahmet Sari, Durali Mendil, Mustafa Tuzen, Mustafa Soylak. Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (*Hylocomium splendens*) biomass: Equilibrium, kinetic and thermodynamic studies .**Chemical Engineering Journal** 144 (2008) 1–9.

67.Sibel Tunali Akar, Asli Gorgulu, Burcu Anilan, Zerrin Kaynak, Tamer Akar, Investigation of the biosorption characteristics of lead (II) ions onto *Symphoricarpus albus*: Batch and dynamic flow studies, Journal of Hazardous Materials 165 (2009) 126–133.

68.Amna Javaid, Rukhsana Bajwa, Umer Shafique, Jamil Anwar, Removal of heavy metals by adsorption on Pleurotus ostreatus, biomass and bioenergy 35 (2011) 1675 -1682.

69.Vítor J.P. Vilar, Cidália M.S. Botelho, José P.S. Pinheiro, Rute F. Domingos, Rui A.R. Boaventura, Copper removal by algal biomass: Biosorbents characterization and equilibrium modeling, Journal of Hazardous Materials 163 (2009) 1113–1122.

70.K.S. Tong, M. Jain Kassim, A. Azra, Adsorption of copper ion from its aqueous solution by a novel biosorbent *Uncaria gambir*: Equilibrium, kinetics, and thermodynamic studies, Chemical Engineering Journal 170 (2011) 145–153.

71.Leila Chebil Ajjabi and Lassaad Chouba, Biosorption of Cu^{+2} and Zn^{+2} from aqueous solutions by dried marine green macroalga *Chaetomorpha linum*, Journal of Environmental Management 90 (2009) 3485–3489.

72.Mubeena Akhtar, Shahid Iqbal, Abida Kausar, M.I. Bhanger, Muhammad Ashraf Shaheen, An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk, Colloids and Surfaces B: Biointerfaces 75 (2010) 149–155.

73.Suleman Qaiser, Anwar Rasheed Saleemi, Muhammad Umar, Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: Batch and column study, Journal of Hazardous Materials 166 (2009) 998–1005.

74.Valeria Marina Nurchi, Guido Crisponi, Isabel Villaescusa, Chemical equilibria in wastewaters during toxic metal ion removal by agricultural biomass, Coordination Chemistry Reviews 254 (2010) 2181–2192.

75.G.C. Panda, S.K. Das, S. Chatterjee, P.B. Maity, T.S. Bandopadhyay, A.K. Guha, Colloids Surf. B: Biointerfaces 50 (2006) 49.

76.S. Tunali, T. Akar, J. Hazard. Mater. B 131 (2006) 137.

77.V.T.P. Vinod, R.B. Sashidhar, B. Sreedhar, Biosorption of nickel and total chromium from aqueous solution by gum kondagogu (*Cochlospermum gossypium*): A carbohydrate biopolymer, Journal of Hazardous Materials 178 (2010) 851–860.

78.Adan Khan, Syed Badshah, Claudio Airoldi, Biosorption of some toxic metal ions by chitosan modified with glycidylmethacrylate and diethylenetriamine, Chemical Engineering Journal 171 (2011) 159-166.

79.Chun-Shui Zhu, Li-Ping Wang, Wen-bin Chen, Removal of Cu(II) from aqueous solution by agricultural by-product: peanut hull, Journal of Hazardous Materials 168 (2009) 739-746.

, .