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Study of physical chemistry on Biosorption of hexavalant chromium by using Chlorella Pyrenoidosa

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ABSTRACT

Discharge of heavy metals from metal processing industries is known to have adverse effects on the environment. Biosorption of heavy metals by metabolically inactive biomass of microbial organisms is an innovative and alternative technology for removal of these pollutants from aqueous solution. Presence of heavy metals in the aquatic system is posing serious problems and hexavalant chromium has been used in many industrials and removal of Cr (VI) ions from waste waters is significant. Biosorption is one of the economic methods that used for removal of heavy metals. In the present study, the biomass generated from the dried Chlorella pyronoidsa was used for evaluating the biosorption characteristics of Cr (VI) ions in aqueous solutions. Batch adsorption experiments were performed on these leaves and it was found that the amount of metal ions adsorbed increased with the increase in the initial metal ion concentration. In this study effect of agitation time, initial metal ion concentration, temperature, pH & biomass dosage were studied. Maximum metal uptake was observed at pH= 5. Maximum metal uptake (q_{max}) was 142.86 mg/g .The biosorption followed both Langmuir and Freundlich isotherm model but Freundlich isotherm model was better than Langmuir with R^2= 0.985. The adsorption equilibrium was reached in about 1 h. The kinetic of biosorption followed the second – order rate. The biomass could be regenerated using 0.1 M HNO_3. A positive value of $\Delta H°$ indicated the endothermic nature of the process. A negative value of the free energy (ΔG°) indicated the spontaneous nature of the adsorption process. A positive value of $\Delta S°$ showed increased randomness at solid–liquid interface during the adsorption of heavy metals, it also suggests some structural changes in the adsorbate and the adsorbent. FTIR Spectrums of Chlorella pyrenoidosa revealed the presence of hydroxyl, amino, carboxylic and carbonyl groups. The scanning electron micrograph (SEM) clearly revealed the surface texture and morphology of the biosorbent.

Keywords: biosorption, chlorella pyronoidsa, Cr (VI), isotherm models, kinetic.

INTRODUCTION

Chromium ores are mined today in South Africa, Zimbabwe, Finland, India, Kazakihstan and the Philippines. A total of 14 million tonnes of chromite ore is extracted. Reserves are hestimated to be of the order of 1 billion tonnes with unexploited deposits in Greenland, Canada and USA. The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch. Heavy metal pollution has posed a serious threat to the aquatic environment. At high concentrations, metals are toxic to animals and plants alike, as they could be dispersed in water and consequently in human beings through food chain biomagnifications that could cause serious health hazards. Chromium (Cr) water pollution has become of considerable concern due to the fact that chromium has been widely used in metal finishing, electroplating, leather tanning, stainless steel production, textile industries, and chromate preparation[1]. Chromium exists in the environment in either its hexavalent form (Cr (VI)) or trivalent form (Cr (III)). The metal species Cr (VI) is considered as highly toxic in that it could act as a carcinogen, mutagen, and teratogen in the biological system [2].It has also been noted that prolonged exposure to the metal species could cause skin allergies and cancer in human beings [3]. Additionally, chromium can be oxidized to the state of a more carcinogenic and mutagenic Cr (VI) by some bacteria in the environment under certain conditions [4] .Recently, the commonly used methods applied to remove excessive chromium from aqueous solutions have included ion exchange, chemical precipitation, activated carbon adsorption, evaporation and membrane processes. However, these methods were found to be either inefficient or expensive when metal ions exist in low concentrations (<100 mg/L) and may also be associated with the generation of secondary environmental problems from waste disposal[5] .Biosorption is the binding and concentration of heavy metals from aqueous solutions (even very dilute ones) by certain types of inactive, dead, microbial biomass[6] .Some of the advantages of biosorption include competitive performance, heavy metal selectivity, cost-effectiveness, regenerative and no sludge generation. Sources of biomass include seaweeds, microorganisms (bacteria, fungi, yeast, and molds), activated sludge and fermentation waste. Studies using Biosorbents have shown that both living and dead microbial cell are able to uptake metal ions and offer potential inexpensive alternative to conventional absorbents [7, 8]. However, living cell is subject to toxic effect of the heavy metals, resulting in cell death. Moreover, living cell often require the addition of nutrients and hence increase the BOD and COD in the effluent. For these reasons, the use of non-living biomaterials or dead cells as metal binding compounds has been gaining advantage because toxic ions do not affect them. In addition, dead require less care and maintenance, and cheaper [9] .Furthermore, dead biomass could be easily regenerated and reused. The capability of some living microorganisms to accumulate metallic elements has been observed at first from toxicological point of view [10, 11, and 12]. However, further researches have revealed that inactive/dead microbial biomass can passively bind metal ions via various physicochemical mechanisms. Therefore researches on biosorption have become an active field for the removal of metal ions or organic compounds. Biosorbent behavior for metallic ions is a function of the chemical make-up of the microbial cells of which it consists [13]. Mechanisms

responsible for biosorption, although understood to a limited extent, may be one or combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and micro precipitation [14, 15 and 16]. Algae, in common with other microbial groups, can accumulate metals from their external environment by means of physico-chemical and biological mechanisms [17]. The absorption process is being widely used by various researchers for the removal of heavy metals from aqueous solutions. In the recent years the use of various natural products has been widely investigated as an alternative for the currently expensive methods of water treatment. Some of the natural products can be effectively used as a low cost absorbent. Heavy metals can be absorbed by living or non-living biomass [18]. Chromium and its compounds are toxic metals introduced into natural water from a variety of industrial wastes [19]. Chromium has been considered as one of the toxic pollutants and because of its carcinogenic characteristics, it has been become a serious health problem. Extensive use of chromium results in large quantities of chromium containing effluents which need sufficient treatments [20].

MATERIALS AND METHODS

Biomass and culture medium: In this study chlorella pyrenoidosa (2738) obtained from National Collection of Industrial Microorganisms (**NCIM**) from PUNE - INDIA, which was isolated and thoroughly pure. The Chlorella pyrenoidosa was maintained in modified Fog's Media at 28 ^{0}C with using 3000 lx light intensity. After 21 days cultivation period cells were harvested by centrifugation and were washed several times with deionised water in order to remove culture media and was kept on a filter paper to reduce the water content. The biomass dried at 60 ^{o}C in an oven for 24 h and milled to a gritty consistency. The biomass was sieve for particle size smaller than 1 mm and stored in dark bottle and keeps in a dry cabinet for experiments. All of the media are sterilized by autoclaving at 121^{o}C for 20 min.

Preparation of synthetic sample: A stock solution of 1000 mg/l of Cr (VI) was obtained by dissolving potassium dichromate (Merck Company) in distilled water. The test solutions of various concentrations range from 10 mg/L to 100 mg/L were prepared from the stock solution. The solution pH was adjust using 0.1 M HNO_3 and 0.1 M NaOH at the beginning of the experiment and not controlled afterwards. The conical flasks (250 mL) were shaken at 120 rpm in a temperature controlled rotatory shaker.

Analysis of hexavalant chromium ions: hexavalant chromium ions were determined spectrophotometrically by atomic adsorption spectrophotometer (UNICAM, model 929, UK).

Batch biosorption studies: Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, agitation time and pH. Solution containing adsorbate and adsorbent was taken in 250 mL capacity conical flask and agitated at 120 rpm in a shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using whatman No.41 filter paper.

Effect of agitation time and initial concentration: For the determination of rate of metal biosorption by biomasses from 100 ml (at 10, 20, 50, 100 mg/L) on conical flask 250 mL, the

supernatant was analyzed for residual metal at different time intervals. The pH and the adsorbent dosage was kept constant at pH= 5± 0.01, which varied according to the adsorbent and adsorbate under consideration. Amount of biomass dosage was 0.1±0.001 g for biomass (Chlorella pyronoidsa) and temperature was 25 ±1 ˚C and agitation speed of shaker was 120 rpm [21, 22, 23, and 24].

Effect of adsorbent dosage and initial concentration: The effect of adsorbent dosage i.e., the amount of the biomasses on the adsorption of metals was studied at different dosages ranging from 0.1 to 3 g with varied metal concentrations of 10, 20 and 50 mg/L. The equilibrium time and the pH were kept constant depending on the metal under consideration. The pH and the adsorbent dosage was kept constant at pH= 5± 0.01, which varied according to the adsorbent and adsorbate under consideration. Agitation time was 120 minute for biomass (Chlorella pyronoidsa) and temperature was 25 ±1 ˚C and agitation speed of shaker was 120 rpm [21, 22, 23, and 24].

Effect of pH and initial concentration: To determine the effect of pH on the adsorption of metal solutions (100 mL) of different concentration ranges (10, 20 and 50 mg/L) at conical flask 250 mL were adjusted to desired pH values and mixed with constant amount of adsorbent and agitated at preset equilibrium time. The equilibrium time and adsorbent dosage varied with the metal and adsorbent under consideration. Amount of biomass dosage was 0.1±0.001 g for e biomass (Chlorella pyronoidsa) and temperature was 25 ±1 ˚C and agitation speed of shaker was 120 rpm and contact time was 120 min [21, 22, 23, and 24].

Effect of temperature: Optimum biomass concentration with optimum pH was used to monitor the temperature effect on biosorption. Experiments were carried out at different temperatures from 10-40 ^{o}C for each culture and kept on rotary shaker at 120 rpm. The samples were allowed to attain equilibrium. To determine the effect of temperature on the adsorption of metal solutions (100 mL) of concentration 50 mg/L at conical flask 250 mL were adjusted to desired pH values and mixed with constant amount of adsorbent and agitated at preset equilibrium time. The equilibrium time and adsorbent dosage varied with the metal and adsorbent under consideration. Amount of biomass dosage was 0.1±0.001 g for biomass (Chlorella) and pH was 5±0.001 and agitation speed of shaker was 120 rpm and contact time was 120 min [21, 22, 23, and 24].

Desorption studies: After adsorption, the adsorbates – loaded adsorbent were separated from the solution by centrifugation and the supernatant was drained out. The adsorbent was gently washed with water to remove any unadsorbed adsorbate. Regeneration of adsorbate from the adsorbate – laden adsorbent was carried out using the desorbing media – distilled water at pH ranges using dilute solutions of EDTA, HCL and HNO_3 (Stirred at 120 rpm for 120 min at 25 ^{0}C) . Then they were agitated for the equilibrium time of respective adsorbate. The desorbed adsorbate in the solution was separated and analyzed for the residual heavy metals [21, 22, 23, and 24].

FT-IR spectroscopy (Fourier Transform Infrared): In order to determine the functional groups responsible for Cr (VI) biosorption, IR spectroscopy was used that about 0.1 g biomass was mixed with KBr for FT-IR spectra analysis (Shimadzu model 8400).

SEM (Scanning Electron Microscopy): The SEM was used to investigate the morphology of the biosorbent. We used samples with pH=5 and C_0 = 10 mg.L^{-1}. Scanning Electron Microscope (SEM, JEOL, JSM-6360A) used for this study.

RESULTS

Results on the effect of pH of Cr (VI) at different initial metal ion concentrations by Chlorella, present in the **Figures 1**. Maximum percentage of biosorption accursed at the initial concentration of 10 mg/L at the time of 120 minute at pH= 5 for Cr (VI) was 92.51 % and metal ion uptake capacity was 9.25 mg/g and when initial concentration of Cr (VI) increased to 50 mg/L, percentage of biosortion of Cr (VI) was 89.66 % and uptake capacity was 41.82 mg/ for Chlorella. With increase the initial concentration percentage of biosorption decreased and metal ion uptake capacity was increased. Results on the contact time of chromium (VI) at different initial metal ion concentrations by Chlorella present in the **Figure 2**. The time required to reach equilibrium for chromium (VI) adsorption by Chlorella, was 60 minute for all initial metal ion concentrations. In the initial concentration of 10 mg/L at the time of 60 minute percentage of remove of Cr (VI) was 88.93% and metal ion uptake capacity was 8.89 mg/g and when initial concentration of Cr (VI) increased to 100 mg/L, percentage of remove of Cr (VI) was 73.25 % and uptake capacity was 73.25 mg/g for Chlorella. The time taken for Cr (VI) adsorption by chlorella was dependent on initial metal ion concentration and increased with increase in concentration of Cr (VI).With increase the initial concentration percentage of biosorption decreased and metal ion uptake capacity was increased. Results on the effect of biomass dosage of Cr (VI) at different initial metal ion concentrations by Chlorella present in the **Figure3**. Percentage of biosorption accursed at the initial concentration of 10 mg/L at the time of 120 minute at pH= 5 and 0.1± 0.001 g of biomass for Cr (VI) was 92.51 % and metal ion uptake capacity was 9.25 mg/g and when initial concentration of Cr (VI) increased to 50 mg/L, percentage of biosortion of Cr (VI) was 83.64% and uptake capacity was 41.82 mg/g for Chlorella. When amount of biomass increased from 0.1 ± 0.001 g to 3 ± 0.001 g, percentage of biosorption accursed at the initial concentration of 10 mg/L at the time of 120 minute at pH= 5 for Cr (VI) was 99.82% and metal ion uptake capacity was 0.332 mg/g and when initial concentration of Cr (VI) increased to 50 mg/L, percentage of biosortion of Cr (VI) was 95.66% and uptake capacity was 1.59 mg/ for Chlorella. With increase the initial concentration percentage of biosorption decreased and metal ion uptake capacity was increased. With increased the amount of biomass observed that percentage of biosorption increased and metal ion uptake capacity was decreased. Results on the effect of temperature of Cr (VI) at initial metal ion concentration of 50 mg/L by Chlorella present in the **Figures 4**. Maximum percentage of biosorption accursed at the initial concentration of 50 mg/L at the time of 120 minute at pH= 5 for Cr (VI) was 82.36% and metal ion uptake capacity was 41.18 mg/g at the temperature of 30 ^{o}C for Chlorella. The findings of chlorella indicate that the sorption percentage increased with increase in temperature up to 30 ^{o} C and there was a decrease in sorption percentage with further increase in temperature. This may be due to the shrinkage of cells at higher temperature.

Equilibrium isotherms : The isotherm studies were performed in the solution with the initial concentrations ranging from 10 to 100 mg/L at optimum pH values for ions (pH=4.5 or pH = 5) .After shaking the flask containing the mixture of biomass (120 rpm, 25 ºC) and ions for 120 min, the amount of residual ions in the filtrated solution was analyzed. The biosorption

equilibrium uptake capacity for each sample was calculated according to mass balance on the ions expressed in this equation: $q_e = \frac{(C_0 - C_e)}{M} \times V$

where V is the sample volume (L), C_0 is the initial ion concentration (mg/L), C_e is the equilibrium or final ion concentration (mg/L) , M is the biomass dry weight (g), and q_e is the biomass biosorption equilibrium ions uptake capacity (mg/g).Langmuir and Freundlich isotherms, the two classical adsorption models, were used to describe the equilibrium between adsorbed ions on the biomass cell (q_e ,q) and ions in the solution (C_e, q) in this study.

Langmuir isotherm model: $$q_e = \frac{q_{\max} C_e b}{1 + C_e b}$$

That after arrange we have; $$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}}$$

These values q_{max} and b (where b, is the adsorption equilibrium constant) can be obtained from the slopes and the intercepts of the linear plots respectively, where experimental data of Ce/qe as the function of C_e. as shownin **Figure 5** .The empirical Freundlich equation based on sorption on a heterogeneous surface, on the other hand, is as follows:

$q_e = K_f (C_e)^n$

K is an indication of the adsorption capacity of the adsorbent; n indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. The equation can be linearized in the following logarithmic form:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$

These values n & K_f can be obtained from the slopes and the intercepts of the linear plots respectively, where experimental data of Ln q_e as the function of Ln C_e. .The equilibrium experimental results of hexavalant chromium ions have been fitted in the Langmuir and Freundlich models. For biosorption of Hexavalant chromium using chlorella pyrenoidosa the coefficient of determination (R^2) of both models was mostly close to 1 as shown in **Figure 6.** This indicates that both models adequately describe the experimental data of the biosorption of Hexavalant chromium. In the biosorption of hexavalant chromium by chlorella, most of the metal ions were sequestered very fast from the solutions in the first phase of contact time 60 minutes and almost no increase in the level of bound metal have been occurred after this time interval. Biosorption equilibrium isotherms were plotted for metal uptake q against the residual metal concentration in the solution. The q verses C_f sorption isotherm relationship was mathematically expressed by Langmuir and Freundlich models. The higher the values of k and n; lower the value of b, the higher the affinity of the biomass. **Table1** describes summaries of linear regression data for Langmuir and Freundlich isotherms for Hexavalant chromium biosorption using chlorella pyrenoidosa biomass. Langmuir and Freundlich constant k were obtained from the linear equations of both models. As indicated in the **Table 1**, the coefficients of determination (R^2) of both models are close to 1. In the **Table 1** the values of K_f, n, q_{max} and b were given.

Kinetic modeling: Figure 7 shows the experimental break through curves for the effects of contact time on a bound rate of Cr (VI). It can be observed that the adsorption of hexavalant chromium ions quickly increased at the beginning of biosorption, but after 15 min, the adsorption slowed down. The result indicated that the maximum adsorbed amount of the hexavalant chromium ions was achieved within 60min, and then followed by a longer equilibrium period. After this equilibrium period, the amount of adsorbed ions did not significantly change with the adsorption time. Therefore, for the following experiments, the contact time was maintained for 60 min to ensure that equilibrium was fully achieved.

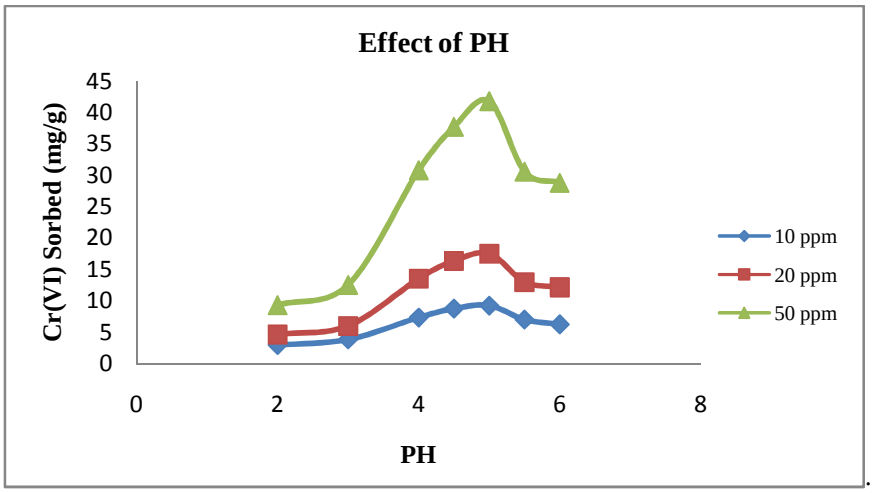

Fig.1 Effect of pH on biosorption of chromium by Chlorella pyrenoidosa (biomass dose=0.1 g, initial chromium ion concentration = 10, 20 and 50 mg l^{-1}; temperature = 25 ˚C; agitation speed = 120 rpm; contact time = 120 min).

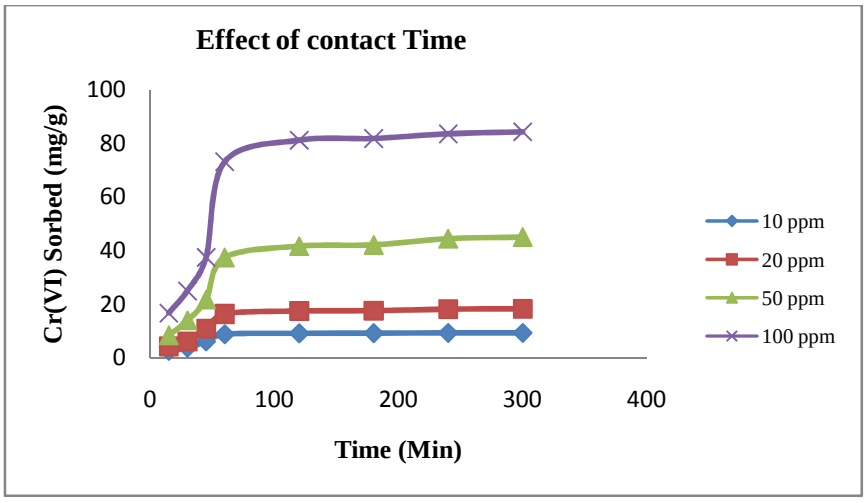

Fig.2 Effect of Contact Time on biosorption of chromium by Chlorella pyrenoidosa (biomass dose=0.1 g, pH=5, initial chromium ion concentration = 10, 20 50 and 100 mg l^{-1}; temperature = 25 ˚C; agitation speed = 120 rpm).

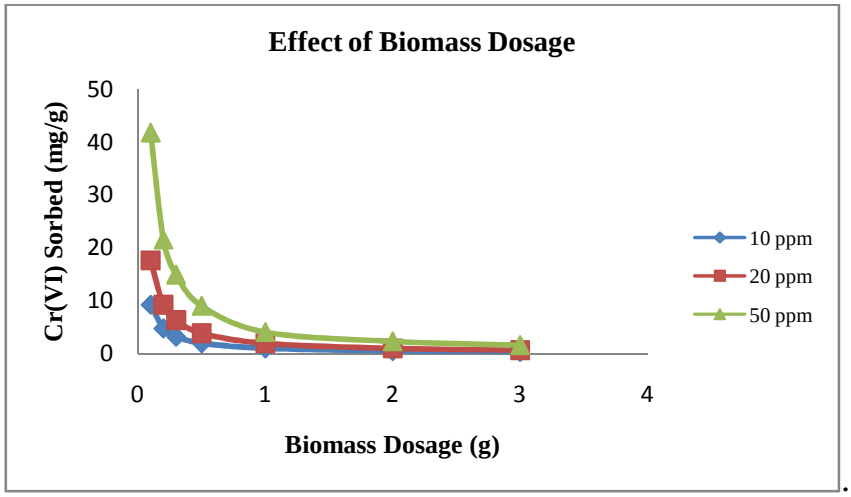

Fig.3Effect of Biomass Dosage on biosorption of chromium by Chlorella pyrenoidosa (pH=5, initial chromium ion concentration = 10, 20 and 50 mg l^{-1}; temperature = 25 °C; agitation speed = 120 rpm; contact time = 120 min).

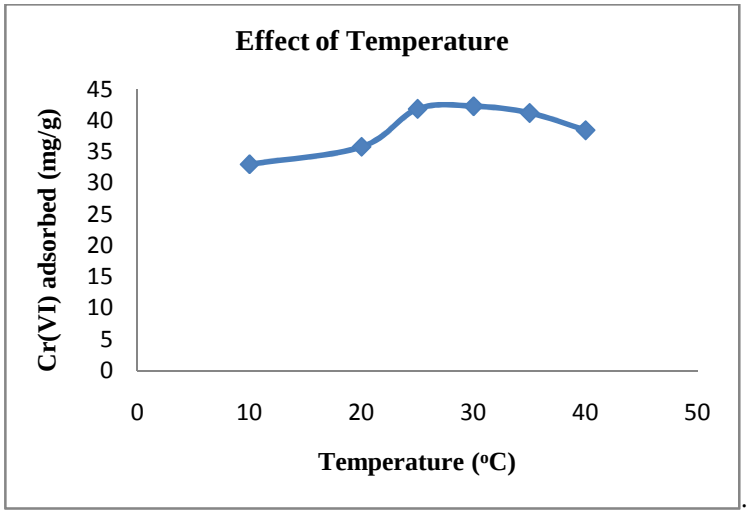

Fig.4 Effect of Temperature on biosorption of chromium by Chlorella pyrenoidosa (biomass dose=0.1 g, pH=5, initial chromium ion concentration = 50 mg l^{-1}; temperature = 25 ◦C; agitation speed = 120 rpm; contact time = 120 min).

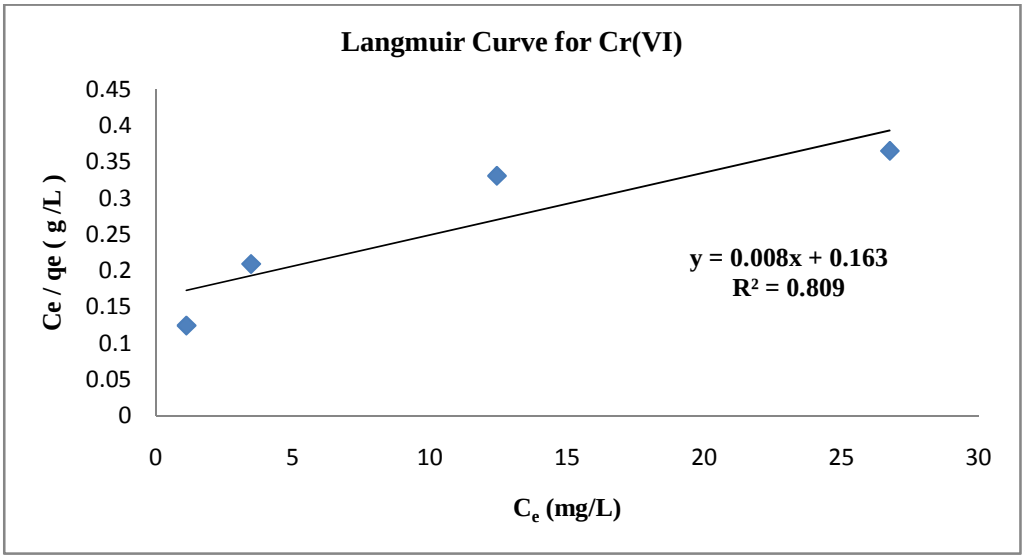

Fig.5 Langmuir adsorption isotherm for chromium by Chlorella pyrenoidosa (q_{max}= 142.86 mg/g , b= 0.041 L/mg).

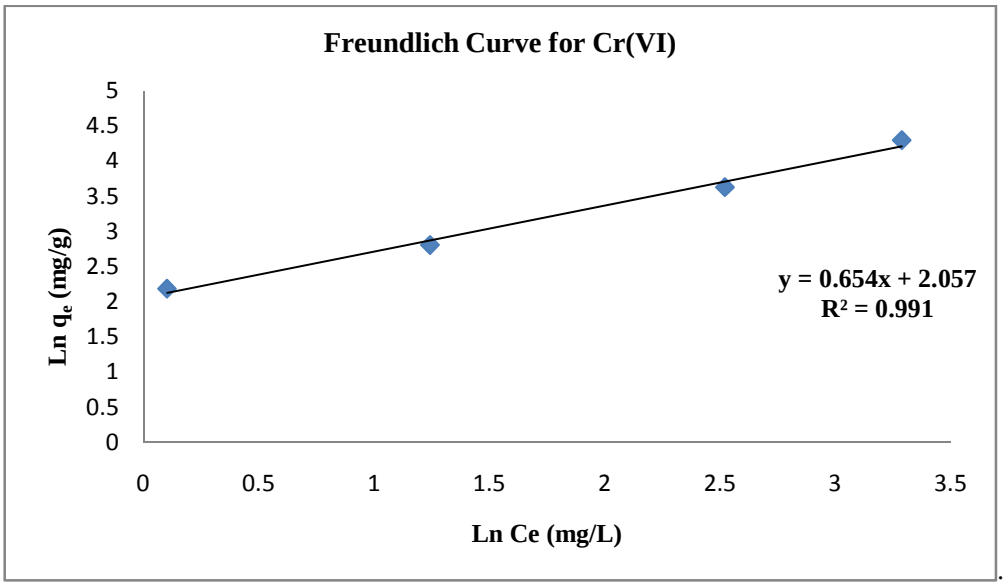

Fig.6 Freundlich adsorption isotherm for chromium by Chlorella pyrenoidosa (n=1.42, K= 7.04).

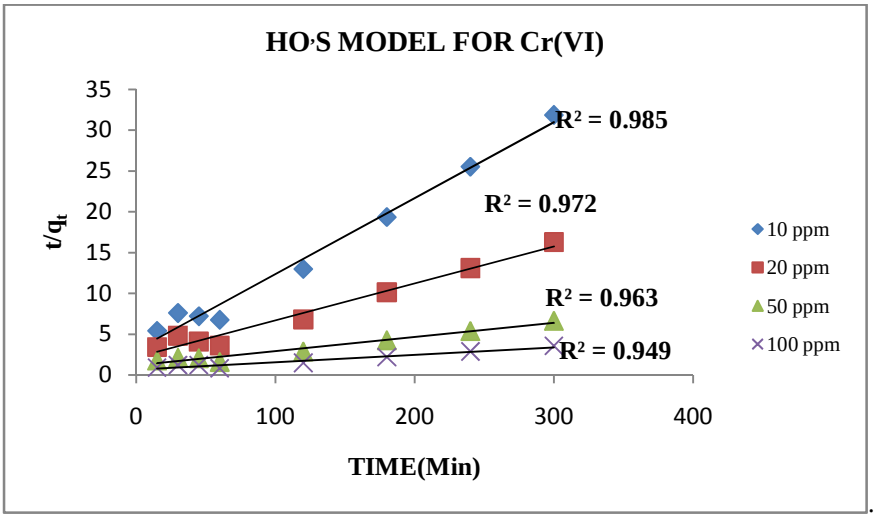

Fig.7 Plot of HO'S Model (Pseudo Second Order Rate) for chromium by Chlorella pyrenoidosa

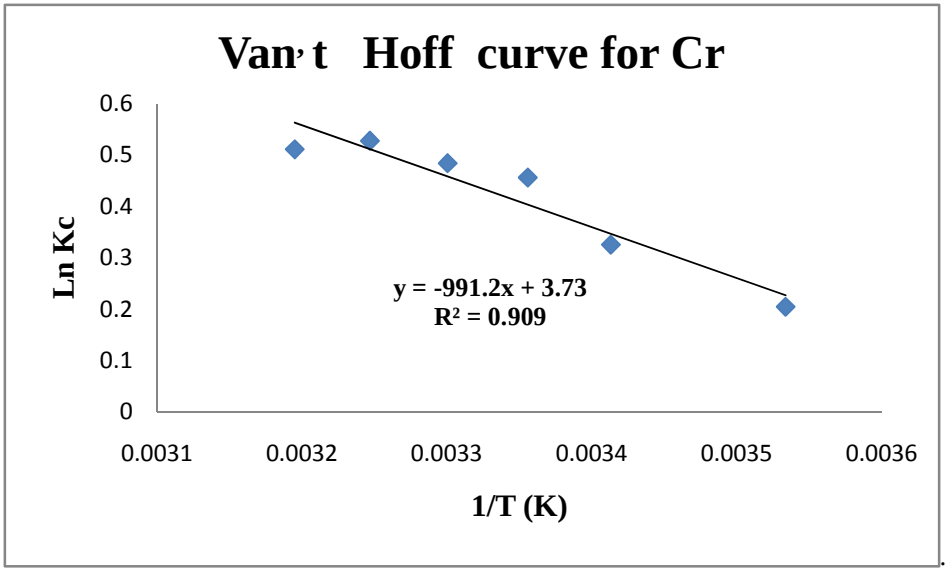

Fig. 8 Plot of Van' t Hoff equation for the estimation of thermodynamic parameters for biosorption of chromium by Chlorella pyrenoidosa.

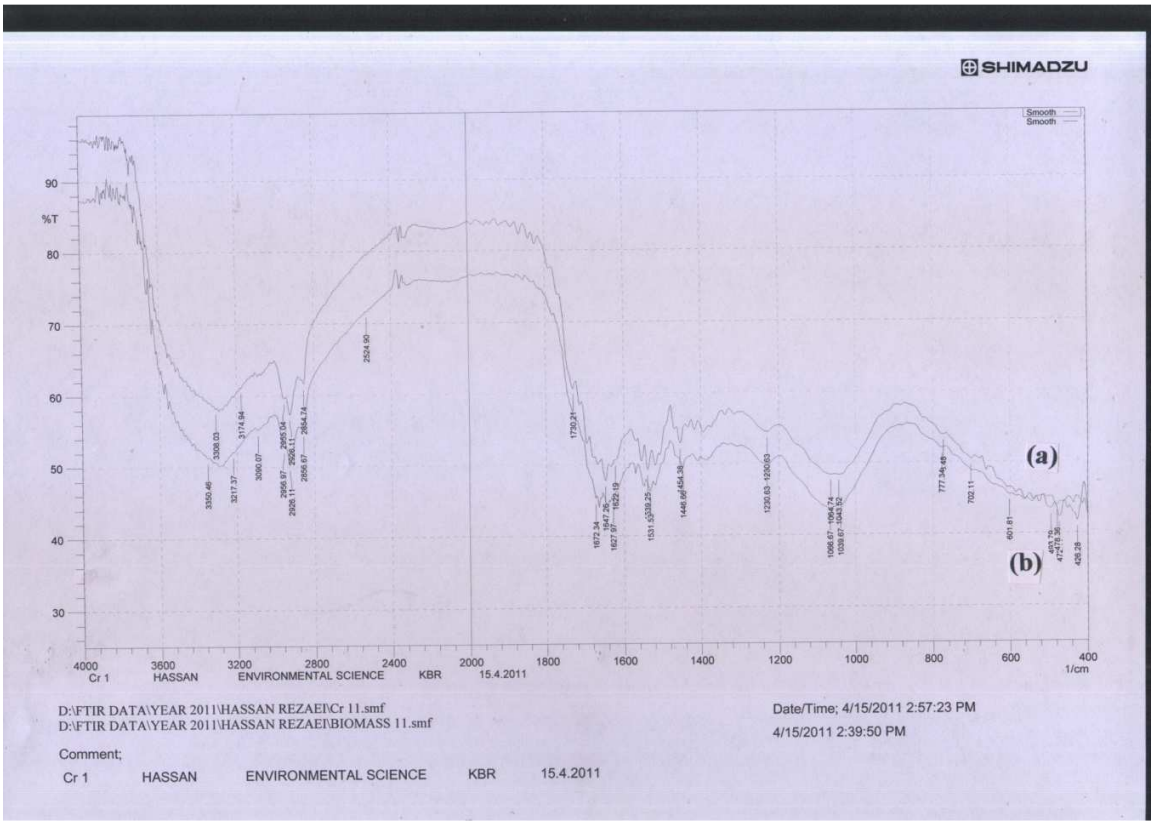

Fig.9 FTIR Spectrum of the Chlorella pyrenoidosa (before (b) and after (a) biosorption of chromium).

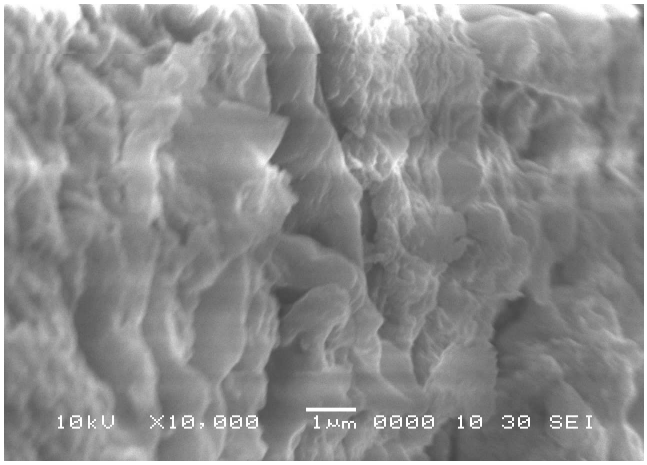

Fig.10 Scanning electron microscopy (SEM) micrographs of the Chlorella pyrenoidosa before biosorption.

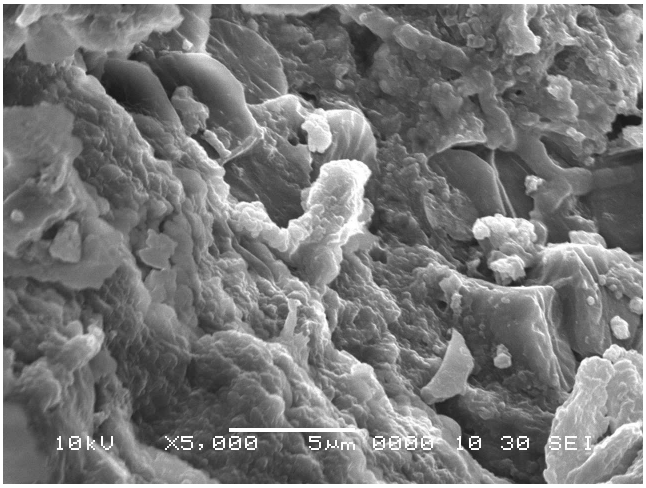

Fig.11 Scanning electron microscopy (SEM) micrographs of the Chlorella pyrenoidosa after biosorption of chromium.

Table. 1 Parameters of isotherm models for chromium

Biomass	Langmuir Parameters			Freundlich parameters		
	q_{max} (mg/g)	b(L/mg)	R^2	K_f	n	R^2
Chlorella pyrenoidosa	125	0.049	0.809	7.82	1.53	0.991

Table .2 Type of isotherm for various R_L

R_L	R_L>1	R_L=1	0< R_L<1	R_L = 0
Type of isotherm	Un favorable	Linear	Favorable	Irreversible

Table .3 Parameter of kinetic model for chromium of Chlorella pyrenoidosa

Concentration of Cr	Equation	R^2	K_2
10 mg/L	y = 0.093x + 3.054	0.985	2.83×10^{-3}
20 mg/L	y = 0.045x + 2.189	0.972	9.25×10^{-4}
50 mg/L	y = 0.017x + 1.182	0.963	2.44×10^{-4}
100 mg/L	y = 0.009x + 0.637	0.949	1.27×10^{-4}

Table. 4 Thermodynamic parameters for the adsorption of heavy metals by Chlorella pyrenoidosa.

Heavy Metals	ΔH° ($J\ mol^{-1}K^{-1}$)	ΔS° ($J\ K^{-1}mol^{-1}$)	-Δ°G ($J.mol^{-1}K^{-1}$)					
			283 K	293 K	298 K	303 K	308 K	313 K
Cr	8240.83	31.01	17.06	54.21	94.86	120.81	153.60	170.05

Table .5 The desorption efficiency of different desorbent

Desorbent	EDTA (0.1M)	HCL(0.1M)	HNO_3(0.1M)
% Desorption of Cr	72.23 ± 3.15	89.57 ±3.39	95.04 ±3.10

The pseudo-second-order equation is also based on the sorption capacity, which is expressed as:

$$\frac{t}{q_t} = \frac{1}{\left(K_2 q^2{}_e\right)} + \frac{t}{q_e}$$

Where K_2 is the rate constant of pseudo-second-order sorption (g· mg^{-1}·min^{-1}). K_2qe^2 is the initial rate constant (represented by h, mg·g^{-1}·min^{-1}). Plotting t/q_t versus t will give a straight line. The values of qe and K_2 can be determined from the slope and intercept of the plot, respectively. The results showed that the pseudo-second-order model fitted the simulation curve much better than the pseudo-first-order model for Cr (VI). The results of pseudo-second-order model showed on the **Table 2**.The coefficient of determination (R^2) and K_2 HO˙S Model for the different metal ion concentration under study for has been established as:10 ppm > 20 ppm > 50 ppm > 100 ppm With increase the initial concentration coefficient of determination (R^2) and K_2 decreased.

Equilibrium parameter R_L: The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by the equeation : **R_L = 1/1+bC_o**

Where C_o is the initial adsorbate concentration (mg/L) and b is the Langmuir constant (L/mg). The parameter indicates the shape of the isotherm as follows (**Table3**).The R_L values at different initial adsorbate concentrations indicate favorable adsorption for all the adsorbents and adsorbates studied.

Thermodynamic studies: Adsorption, studies in the temperature range 283–313 K were conducted to determine thermodynamics constants such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the system and to ascertain the sorption mechanism. For this study, adsorbent dosage selected was 0.1 gr. and hexavalant chromium concentration was 50 mg L^{-1} with pH= 5 in a conical flask and allowed to equilibrate for 1 h at the different temperatures ranging from 283 to 313 K. In order to determine thermodynamic parameters, experiments were carried out at different temperatures in the range of 283–313 K for heavy metals adsorption. The thermodynamic parameters such as standard Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were estimated to evaluate the feasibility and nature of the adsorption process. The Gibbs free energy change, of the process is related to equilibrium constant by the equation: $\Delta G^\circ = -RT \ln K_C$

where, T is temperature in K, R is ideal gas constant having value as 8.314, J mol^{-1} K^{-1} and K_C is thermodynamic equilibrium constant. The thermodynamic equilibrium constant, was determined as: $K_C = \frac{C_a}{C_e}$

Where, C_a is mg of adsorbent adsorbed per liter and C_e is the equilibrium concentration of solution, mg/L. According to thermodynamics, the Gibbs free energy change is also related to the enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by the following Van˙t Hoff equation:

$$\ln K_C = \frac{-\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R}$$

The values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot lnKc versus, 1/T. Results on the Plots of Van' t Hoff equation for the estimation of thermodynamic parameters by Chlorella pyrenoidosa present in the **Figures 8**.The calculated values of thermodynamic parameters are reported in **Table 4**.A positive value of ΔH° indicated the endothermic nature of the process. A negative value of the free energy (ΔG°) indicated the spontaneous nature of the adsorption process. It was also noted that the change in free energy, increases with increase in temperature, which exhibits an increase in adsorption with rise in temperature. This could be possibly because of activation of more sites on the surface of biomasses with increase in temperature. A positive value of ΔS° showed increased randomness at solid–liquid interface during the adsorption of heavy metals, it also suggests some structural changes in the adsorbate and the adsorbent.

FTIR Spectroscopy of Chlorella pyrenoidosa: Spectrums of Chlorella pyrenoidosa present in the **Figure 9** that revealed the presence of hydroxyl, amino, carboxylic and carbonyl groups. The presence of OH group along with carbonyl group confirmed the presence of carboxylic acid groups in the biosorbent. The presence of NH group and OH group along with carbonyl group might be attributed the presence of amino acid groups in the biosorbent.

Scanning electron microscopy (SEM): Scanning electron microscopy (SEM) of Chlorella pyrenoidosa at before and after biosorption of hexavalant chromium present in the **Figures 10** and **11** respectively. The scanning electron micrograph clearly revealed the surface texture and morphology of the biosorbent at different magnifications. The SEM analysis revealed important information on surface morphology. In these micrographs structures with large surface area were evident.

Desorption studies : Desorption and regeneration studies of the adsorbates showed that regeneration and recovery of the adsorbates is possible. Chemisorption/ion exchange was the main mechanism by which the adsorbates (metals) were attached to the adsorbents. Physical adsorption played a minimal role in the process .The result of desorption studies of Cr (VI) in a batch system showed that HNO_3 (0.1 M) was more efficient in Cr (VI) desorption, which remove 95% hexavalant chromium ions (**Table 5**).

CONCLUSION

The batch experiment conducted with the biosorption demonstrated that biomass of chlorella pyrenoidosa exhibited the potential for Cr (VI) removal from aqueous solution. Optimum pH and temperature for biosorption in this study were 5 and 25 ^oC, respectively. The time taken for Cr (VI) adsorption by chlorella pyrenoidosa was dependent on initial metal ion concentration and increased with increase in concentration of Cr (VI). With increase the initial concentration percentage of biosorption decreased and metal ion uptake capacity was increased. With increased the amount of biomass observed that percentage of biosorption increased and metal ion uptake capacity was decreased. The findings of chlorella pyrenoidosa indicate that the sorption percentage increased with increase in temperature up to 30 ^{o} C and there was a decrease in

sorption percentage with further increase in temperature. The removal of Cr (VI) increase with increase in biosorbent .The biosorption process was followed both Langmuir and Freundlich isotherm model but Freundlich isotherm model was better than Langmuir with R^2= 0.991. The pseudo second-order kinetics described the experimental data well. The equilibrium time was 60 min. The R_L values at different initial adsorbate concentrations indicate favorable ($0<R_L<1$) adsorption for all the adsorbents and adsorbates studied.HNO_3 (0.1M) had higher efficiency of Cr (VI) desorption than EDTA (0.1M) and HCL(0.1M) with 95% efficiency desorption.A positive value of ΔH° indicated the endothermic nature of the process. A negative value of the free energy (ΔG°) indicated the spontaneous nature of the adsorption process. A positive value of ΔS° showed increased randomness at solid–liquid interface during the adsorption of heavy metals, it also suggests some structural changes in the adsorbate and the adsorbent. **FTIR** Spectrums of Chlorella pyrenoidosa revealed the presence of hydroxyl, amino, carboxylic and carbonyl groups. The scanning electron micrograph (**SEM**) clearly revealed the surface texture and morphology of the biosorbent.

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