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BIOSORPTION OF HEXAVALENT CHROMIUM BY *Spirogyra* spp.: EQUILIBRIUM, KINETICS AND THERMODYNAMICS

A. Yaqub, M. S. Mughal[*], A. Adnan[**], W. A. Khan[***] and K. M. Anjum[****]

Department of Zoology, Government College University, Lahore, Pakistan
*Department of Fisheries and Aquaculture, University of Veterinary and Animal Sciences, Lahore, Pakistan
**Department of Chemistry, Government College University, Lahore, Pakistan
***Department of Wildlife and Ecology, University of Veterinary and Animal Sciences, Lahore, Pakistan
***Pakistan Wildlife Foundation, Islamabad, Pakistan
Corresponding Author email: atifravian@gmail.com

ABSTRACT

Uptake of hexavalent chromium (Cr VI) using dead biomass of green algae, *Spirogyra* spp. to evaluate biosorption capacity with special emphasis on its mechanistic aspect was studied. Optimum biosorption of Cr (VI) was observed at pH 4.0 (265mg/g), biomass concentration of 1mg/g, and temperature 303K.Various adsorption isotherms were employed to analyze the experimental data of which Langmuir isotherm was found most suitable, showing monolayer adsorption. Pseudo-second order model was found suitable for the kinetic interpretation of the data. Various thermodynamic parameters were calculated and the biosorption was found to be spontaneous, endothermic and feasible under the given conditions. Analysis of FTIR spectra indicated the presence and role of electronegative functional groups on algal surface responsible for binding of Cr (VI) ions.

Key words: Biosorption, Green algae, Heavy metals, Kinetic, Thermodynamic, FTIR.

INTRODUCTION

A variety of effluents from industrial sources including toxic heavy metal pollutants, such as Cadmium (Cd), Chromium (Cr), and other heavy metals and burning of fossil fuels are routinely discharged into the environment.These toxic metal ions are non-degradable and tend to not only accumulate in living organisms but also bio-magnify as they travel through food chain (Ahmad *et al.*, 2011; Vandecasteele *et al.*, 2004). More recently, aquatic fauna and flora have been extensively reported to show elevated metal ion bio-accumulation (Mortazavi and Sharifian, 2011; Ahmad and Bibi, 2010).

Chromium, a vital heavy metal pollutant in the aquatic bodies (Congeevaram *et al*., 2007), may be found in hexavalent [Cr (VI)], trivalent [Cr (III)] or divalent [Cr (II)] forms;Cr (VI) being the oxidized form is highly soluble and toxic, as compared to its other forms. Several studies have been undertaken in order to elucidate complex mechanisms of chromium VI toxicity (Beveridge *et al.*, 1997).These toxins tend to bioaccumulate and increasingly become concentrated as they travel through the food chain (Vandecasteele *et al*., 2004; Volesky, 1990). Toxic metal ions are known to pose severe health hazards such as, complications during pregnancy, seminiferous tubule impairment, etc. and have been declared as carcinogens based on a number of studies (US EPA, 1991). The present scenario presents a need to develop effective technology to remove heavy metal ions from the environment.

In this connection, various natural and synthetic adsorbents have been developed for the removal of metal ions from wastewater (Demirbas *et al.*, 2004; Li *et al.*, 2007). But due to poor performance and/or high cost of these materials creates a need for improved and cost-effective alternatives, such as biosorption, the use of dead biomass for the removal of heavy metal pollutants from the aquatic environment (Volesky, 1990, Iqbal and Edyvean, 2007; Volesky, 2007). Biomass of numerous organisms have been tested in this regard but use of algae such as, green algae, brown algae, red algae etc. has shown some promising results in terms of their capacity to remove heavy metal ions from solution (Davis *et al.*, 2003; Volesky, 2007).

On the rise is the need to exploit filamentous green algae in the area of biosorption (Arief *et al.*, 2008). To evaluate the performance of biosorption, various models, such as equilibrium, kinetic and thermodynamic values can be determined with the help of various models (Pahlvanzadeh *et al.*, 2010; Melcakova and Ruzovic, 2010).

The underlying mechanism of biosorption involves the adsorption of toxic metal ions onto the cell surface (wall, membrane or external polysaccharides, etc). The cell wall of algae possesses many electronegative functional groups, such as hydroxyl (OH), phosphoryl (PO_3O_2), amine (NH_2), carboxyl (COOH), sulphydryl (SH), etc., which confer adsorption to heavy metal cations (Davis *et al.*, 2003). Each functional group can dissociate into corresponding anion and proton at a specific pH because of its own specific

dissociation constant (pKa) (Arief *et al.*, 2008). These functional groups are the components of cell wall constituents such as, hetero-polysaccharides and proteins, and are functioning as metal binding sites (Naja and Volesky, 2006). Filamentous green algae can hence be predicted as efficient potential biosorbents due to the biochemistry of their cell wall (Mata *et al.*, 2008; Arief *et al.*, 2008). Freshly available data regarding the capacity of filamentous green algae to biosorb heavy metal ions, such as, Cr (VI) has opened the doors of cost-effective option for biosorption to be employed in the wastewater treatment technology (Melcakova and Ruzovic, 2010). Filamentous green algae, such as species of *Spirogyra* are easily available in terms of amount of biomass especially in tropical freshwater bodies. They are relatively newly known in this context and their potential to establish as better and cost-effective biosorbents in this scenario needs further explanation.

In the present study biosorption of heavy metal ions, such as Cr (VI) by using the dead biomass of green algae, *Spirogyra* spp. was studied. Emphasis was laid on the estimation of kinetic equilibrium and thermodynamic parameters. These studies determined the efficacy of the test biosorbents to evaluate their performance in wastewater technology (Gupta and Rastogi, 2008). Studies at cellular level were also undertaken to improve the understanding of possible binding sites in the cell wall of *Spirogyra* spp. and to understand the extent of biosorption and how various polysaccharides and peptides are possibly involved in binding with Cr (VI).

MATERIALS AND METHODS

Biosorbent: Filaments of Spirogyra spp., belonging to three different species, viz: *S. juergensii, S. elongate*, and *S.piepengensis* were collected from Botanical Gardens of GC University, The Mall, Lahore, Pakistan, and tested for their biosorptive capacity for Cr (VI) ion. The algal biomass was washed thoroughly in running tap water 4–5 times, treated with 0.02 M HNO_3 and again washed with distilled running water, dried overnight at 60°C until a constant weight was achieved.The final weight of the biosorbent was recorded and then crushed through a 300 nm sieve to obtain a uniform particle size and before use in further studies.

Metal Ion Solutions: Stock solution of potassium dichromate ($K_2Cr_2O_7$) was prepared by using $K_2Cr_2O_7$ (Fisher Scientific, USA) in double distilled water; thereafter serial dilutions of this solution were prepared to obtain concentrations of 100, 200, 300, and 400 ppm of Cr (VI) solution.

Glassware and Apparatus: All experiments related to biosorptive potential of algal biomass were conducted by using 125 mL Erlenmeyer flasks. Prior to use, the flasks were heated at 70^0C for 4 hours, followed by one wash with concentrated HNO_3 and then one wash with distilled water.

Biosorption Evaluation: One hundred mL of Cr solutions were taken in 125 mL Erlenmeyer flasks (at concentrations of 1.0, 5.0, 15.0, and 25.0 mg/L). The dosages of 0.1, 0.2, and 0.3g of dead biomass of *Spirogyra* spp. were introduced in the above mentioned flasks separately. These biomass dosages were also introduced in a separate set of flasks containing distilled water only, as control. The flasks were maintained under constant agitation on a rotator shaker (180 rpm) for a period of 3 hrs. The experiments were conducted at varying pH, ranging from 1.0 to 7.0, and pH values solutions were adjustedusing 0.2N HNO_3 and 0.1N NaOH. Thermodynamic studies were also performed under varying temperatures, viz: 10°, 20°, 30°, and 40°C (283, 293,303, and 313K) by maintaining optimum pH as derived from initial experiments.

Transport of Samples for Analysis: A sample of 5 ml from each flask was collected by using an auto-pipette at regular intervals of 0, 30, 60, 90,120,150 and 180 min. After collecting samples, each sample was poured in BD syringe. Each sample was then passed through 0.25 nm Nylon Syringe Filters (Fisher Scientific, USA). The adsorption capacity of the filter for Cr (VI) had already been tested which was less than 5%. The filtrate was then preserved for further analysis.All experiments were repeated three times.

Analysis by Atomic Absorption Spectrometer: All the samples were tested for metal ion concentration by using Atomic Absorption Spectrometer at department of chemistry, University of the Punjab, Lahore, Pakistan for the analysis.

Fourier Transform Infra-red Spectroscopy (FTIR): FTIR spectroscopy was performed at Department of Chemistry, University of the Punjab, Lahore, Pakistan. Tablets of algal biomass (2mg) mixed with potassium bromide (KBr) (1:100 p/p) were prepared in a Graseby-Specac Press. A window characteristic of information of polysaccharides and peptides (between 600 and 5000 cm^{-1}) was selected in order to monitor cell wall structure modifications. Spectra of both, Cr (VI) ion loaded and unloaded biomasses (control) were obtained for comparison at a resolution of $1cm^{-1}$. All spectra were normalized and baseline-corrected with Perkin-Elmer IR Data management software. Data were then exported to Microsoft Excel 2003 and all spectra were area-normalized.

Mathematical Modeling and Interpretation of data: Evaluation of biosorption capacity was performed by subjecting the data obtained from biosorption studies to the following isotherm models and linear plots were drawn by using Microsoft Excel 2007.

Langmuir isotherms were used to correlate the equilibrium data. Langmuir model assumes a monolayer sorption of sorbate from the aqueous solution (Langmuir, 1918; Lawal *et al.,* 2010). The Langmuir equation is given below:

$$q_e = q_{max}\frac{c_e}{(b + c_e)}$$

The linearized form of this equation can be expressed as given below:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{b.q_{max}}.\frac{1}{c_e}$$

Here,
q_e = Equilibrium constant of sorbate ion on surface of the biosorbent (mg/g)
C_e = Equilibrium concentration of metal ion in solution
b = Saturation constant (mg/L)

The values of q_e, and b were calculated from intercept and slope of linear plot of $1/q_e$ versus $1/C_e$. The distribution coefficient (*k*) for metal ions between the sorbent and the aqueous solution at equilibrium stage was determined from the following expression:

$$K = \frac{q_e}{c_e}$$

Freundlich model was also employed to estimate the adsorption intensity of the adsorbent towards the sorbate (Freundlich, 1907; Lawal *et al.,* 2010). This theorem considers multi-layers adsorption on the sorbent surface. This model may be given by the equation below:

$$q_e = K_f C_e^{1/n}$$

This equation can be linearized as follows:

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

Here,
K_F= Freundlich emperical constant
relative to sorption capacity
1/n = emperical constant relative sorption Intensity
The values of the $K_F$and 1/n were calculated from the intercept and slope respectively from a linear plot of *ln*q_e versus *ln* C_e.

Temkin isotherm was also employed as given by the following equation(Lawal *et al.,* 2010):

$$q_e = B\ln(K_T C_e)$$

Where,
K_T = equilibrium binding constant correlated to the maximum binding energy and
B = constant related to the heat of adsorption.
The linearized form of this equation given as follows:

$$q_e = B\ln K_T + B\ln C_e$$

A linear plot of "q_e" versus *ln"*C_e*"* enables the determination of the isotherm constants, B and K_T from the slope and the intercept respectively.

Kinetic Studies: Pseudo-second order kinetic model as developed by Ho and McKay (1999) was employed to evaluate the kinetic parameters for the biosorption studies of Cr (VI) and Cr (VI) ions by biosorption from dead biomass of *Spirogyra communis*, was investigated. The concentration of biomass was kept at 1 g while initial Cr (VI) ion concentration was varied from 100 to 400 ppm.
To explain the correlation between the equilibrium concentration of metal ions in the solid phase (sorbent) and the *aqueous* solution, pseudo-second order model, as developed by Ho and Mckay (1999), was used. Pseudo-second order model considers that the rate of occupation of biosorption sites is proportional to the square of the number of unoccupied sites.

$$\frac{dq_t}{dt} = K_2(q_e + q_t)^2$$

Where,
t = time(min)
q_t= uptake capacity at time 't' ($mg.g^{-1}$)
q_e = Equilibrium constant of sorbate ion on surface of the biosorbent ($mg.g^{-1}$)
K_2 = equilibrium rate constant of pseudo-second-order adsorption ($g.mg^{-1}.min^{-1}$).
The above equation could be integrated and rearranged to give thefollowing expression:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}}$$

The values of the constants were calculated by plotting t/q_t versus $1/q_e$ by using Microsoft Excel 2007.

Thermodynamic parameters: Thermodynamic parameters were also determined form the experimental data. Following equation was used to obtain the values of entropy (ΔH) and enthalpy (ΔS).

$$\ln b = \frac{\Delta S^o}{R} + \frac{\Delta H^o}{RT}$$

Here,
R= gas constant
b= Langmuir's constant.
The linear plot of the *ln* b versus 1/T (Figure 4.9) was drawn by using Microsoft excel 2007 and fromintercept and slope, values of entropy (ΔH) and enthalpy (ΔS) were measured.
Arhenius equation was used to obtain the values of Arhenius constant (A_0) and the activation energy (E_a) by using the following equation.

$$\ln K_2 = \ln A^o - \frac{E_a}{RT}$$

The values of change in free energy (ΔG) for biosorption were determined by using the following equation:

$$\Delta G = -RT\ln b$$

RESULTS AND DISCUSSION

Biosorption Capacity: The effect of varying physico-chemical factors was investigated; these studies are important not only to understand the mechanistic aspect but also helpful for the optimization of the use of test sorbent at industrial scale.

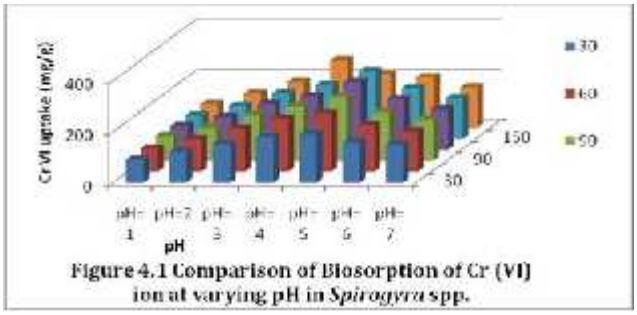

Figure 4.1 Comparison of Biosorption of Cr (VI) ion at varying pH in *Spirogyra* spp.

Effect of pH: The biosorption of Cr (VI) was studied at varying pH values, such as 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 pH units. Increase in biosorption capacity was observed from pH 1.0 through 4.0; optimum pH was recorded at pH 4.0 for biosorption in aqueous solution (265 mg/g). However, further increase in the pH value form 4.0 through 7.0 resulted in decrease in biosorption capacity (Fig. 4.1).Interaction of dissociation sites on the biosorbent surface and sorbate solution chemistrydepends upon the pH of the solution, such as hydrolysis, complexation by ligands (binding sites), precipitation and availability of Cr (VI) ion, etc. (Romera *et al.,* 2007).The increase in biosorption capacity of Cr (VI) ion by *Spirogyra* spp.from 53 to 18% was observed by increasing the pH valuefrom 1.0 to 4.0 pH units. This might be attributed to the fact that at low pH, the solution is protonated due to specific pKa values of the sorbates and the binding sites (functional groups) at the biosorbent surface and competition between protons and metal ions in the solution leads to reduced biosorption (Romera *et al.*, 2006). The hexavalent chromium [Cr (VI)] ions exist in the form of $HCrO_4$ and Cr_2O_7;excess H^+ ions neutralize the negatively charged biosorbent surface, and thereby, reduce the hindrance for diffusion of dichromate ions (Kumar *et al.,* 2008).On the other hand, decrease in biosorption from 42 to 32% was observed by increasing the pH from 4.0 through 7.0 pH units. This might be attributed to precipitation reaction which occurs at pH 5.0-6.0 (Matheickal and Yu, 1999). The formation of insoluble hydroxides of metal ion might reduce the concentration of free sorbate ion available for biosorption.

Other studies regarding biosorption at various pH by using various biosorbentsseem to suggest similar trends (Gupta and Rastogi, 2008; Bishnoi *et al*., 2007; Arief *et al*., 2008).

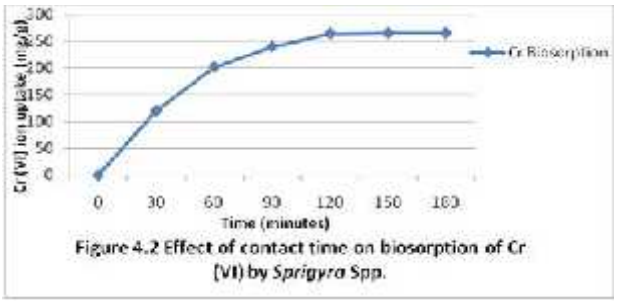

Figure 4.2 Effect of contact time on biosorption of Cr (VI) by *Sprigyra* Spp.

Effect of Contact Time: The maximum Cr (VI) uptake was recorded in the first 30 minutes of contact time, followed by a relatively slower rate up to 120 min and thereafter, no significant uptake of Cr (VI) ion was observed (Fig. 4.2). Rapid uptake of Cr (VI) ion in the first 30 min.might be attributed to freely available binding sites; whereas the biosorbent tends to become saturated with metal ion biosorption at later stages. At 120 min of contact time equilibrium concentration was achieved indicating that all the binding sites seemed to have saturated fully. Previous studies also suggest that equilibrium could be achieved between 60 to 150 min for the biosorption of heavy metal ions depending upon the biosorbent and metal ion species(Onyancha *et al.,* 2008; Arief *et al.,* 2008)."

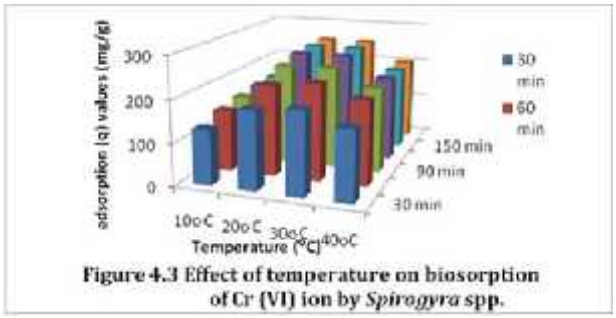

Figure 4.3 Effect of temperature on biosorption of Cr (VI) ion by *Spirogyra* spp.

Effect of Temperature: Temperature effect on the biosorptive capacity was studied at varying temperatures, 10, 20, 30, and 40°C. The extent of biosorption was maximum at 30° C (65%) followed by its capacity at 20°C (64%) (Fig. 4.3). However, lower biosorptionwas found at10°C (40%) and 40°C (50%). Moreover, equilibrium concentration was achieved rapidly at higher temperatures compared tolower temperatures.

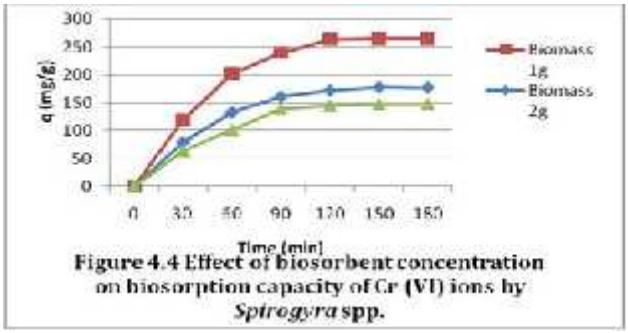

Figure 4.4 Effect of biosorbent concentration on biosorption capacity of Cr (VI) ions by *Spirogyra* spp.

Effect of Biosorbent Quantity: The biosorption capacity was directly proportional tobiomass concentration. However, at 1mg/L biosorbent concentration, maximum metal uptake (q_{max}=135 g/gm) per unit mass of sorbent was observed (Fig. 4.4). This trend could be explained as a consequence of a partial aggregation of biomass at higher biomass concentration, which results in a decrease in effective surface area for the biosorption (Gupta and Rastogi, 2008).

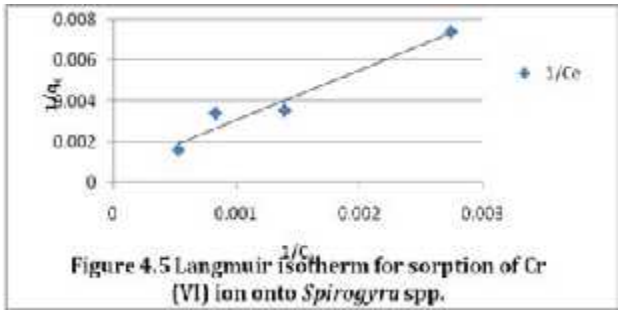

Figure 4.5 Langmuir isotherm for sorption of Cr (VI) ion onto *Spirogyra* spp.

Biosorption Equilibrium Isotherm: The experimental data were fitted to various sorption models to examine the relationship between sorption and aqueous concentrations of Cr (VI) ions.

Langmuir isotherms were used to correlate the equilibrium data by using the already given equation. The linear plot (Figure 4.5) of inverse of equilibrium concentrations of Cr (VI) "$1/q_e$"versus "$1/C_e$" shows a typical equilibrium biosorption isotherm suggesting that biosorption of Cr (VI) ions involves a chemical equilibrated and saturable mechanism resulting in site-specific biosorption on the surface of the sorbent (Table1). The values obtained from the Langmuir isotherm were near the experimental values showing monolayer adsorption on algal surface.

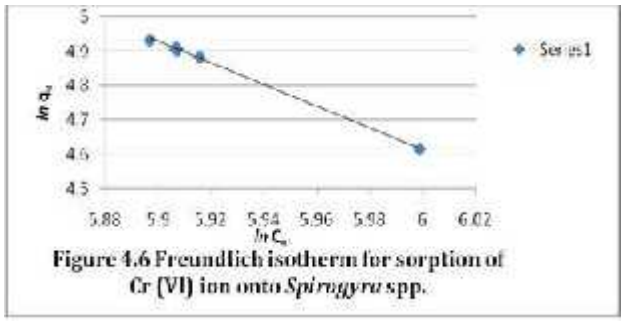

Figure 4.6 Freundlich isotherm for sorption of Cr (VI) ion onto *Spirogyra* spp.

Freundlich isotherm model was employed to estimate the adsorption intensity of the adsorbent towards the sorbate [Cr (VI)]. Figure 4.6 shows a linear relationship of Log q_e versus Log C_e. The values of Freundlich's saturation constants were derived from intercept and slope respectively (Table1).

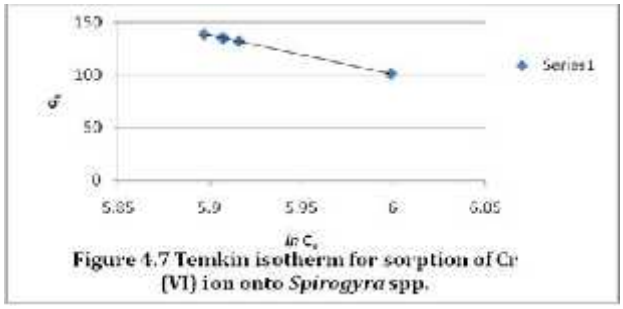

Figure 4.7 Temkin isotherm for sorption of Cr (VI) ion onto *Spirogyra* spp.

Temkin isotherm was used and the values of K_T and B were calculated (Table1). Linear plot of "q_e" versus "C_e"is seen in Figure 4.7.

Table 1. Values of constants of various adsorption isotherms

Langmuir's constants				Freundlich's constants			Temkin's constants		
q_{max} (mgg^{-1})	b ($L\ mg^{-1}$)	R^2	K	N	K_F	R^2	K_T	B	R^2
498	.008	.9012	0.88	0.31	108.76	0.6712	0.024	4.31	0.9999

Kinetic Studies: Pseudo-second order kinetics model was employed for evaluation of Cr (VI) ions biosorprtion by *Spirogyra* spp. (at varying concentrations of sorbate) to explain the correlation between the equilibrium concentration of metal ions in the solid phase (sorbent) and the *aqueous*solution. The values of the constants were derived from the linear plot of 't/q' versus 't' (Fig. 6 and Table 2).

Table 2. Pseudo-second order kinetic constants for the biosorption of Cr (VI) y *Spirogyra* spp.

q_{eq} Cal	K_2	R_2
98.92	0.0009	0.9959

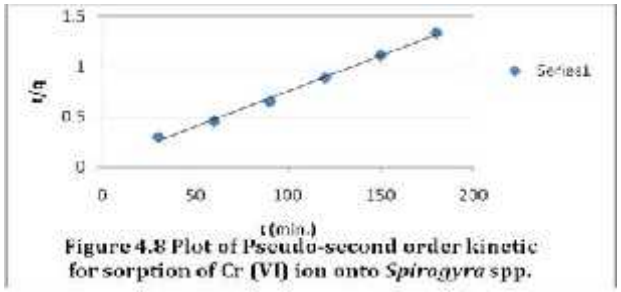

Figure 4.8 Plot of Pseudo-second order kinetic for sorption of Cr (VI) ion onto *Spirogyra* spp.

Thermodynamic studies: Thermodynamic behavior of Cr (VI) ion adsorptionon the surface of *Spirogyra* spp. was studied by calculating various thermodynamic constants. Equation was used to obtain the values of entropy (ΔH) and enthalpy (ΔS).

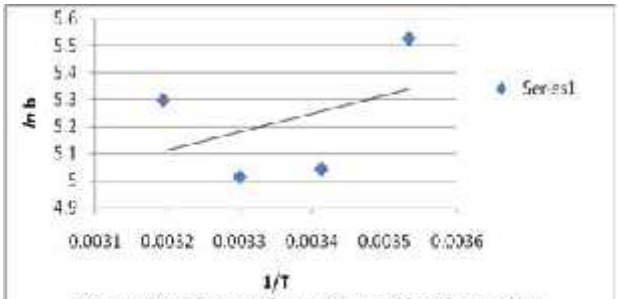

Figure 4.9 Thermodynamic profile of sorption of Cr (VI) ion onto *Spirogyra* spp. for ΔH and ΔS

From a linear plot of *ln* b versus 1/T (Fig. 4.9), values of ΔH and ΔS were determined by using already given equation (Table 3), and ΔG was determined. Values of ΔH and ΔS were found to be positive, whereas values of ΔG were negative (Table 4). This implies that adsorption of Cr (VI) were spontaneous and feasible undergiven conditions. This is in agreement with previously performed studies of biosorption of cations by using other biosorbents (Lawal *et al.*, 2010; Pahalvanzadeh *et al.*, 2010). The ΔG values also decrease in magnitude on increasing the temperature from 283°K through 303°K (Table 4).

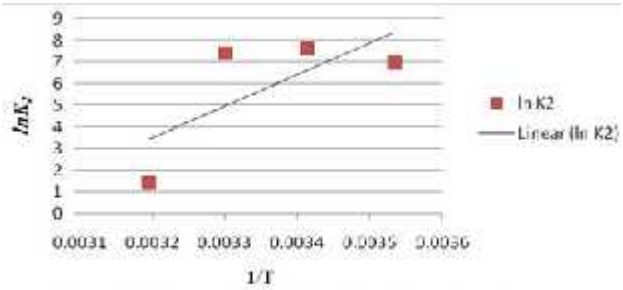

Figure 4.10 Thermodynamic profile of sorption of Cr (VI) ion onto *Spirogyra* spp. for E_a and A_0 values

Values of Arhenius constant (A_0) and the activation energy (E_a) were also determined (Table 1) from a linear plot of "*ln* K_2" versus "1/T" (Fig. 4.10).

Table 3. Thermodynamic parameters

ΔH° (KJmol^{-1})	ΔS° (J mol^{-1}K^{-1})	A_0	Ea (J mol^{-1}g^{-1})
2.73	52.77	18.09	12.76

Table 4. Change in free energy (-ΔG) at varying temperatures

Temperature (K^o)	283	293	303	313
-ΔG (KJmol^{-1})	12.70	11.80	11.73	13.06

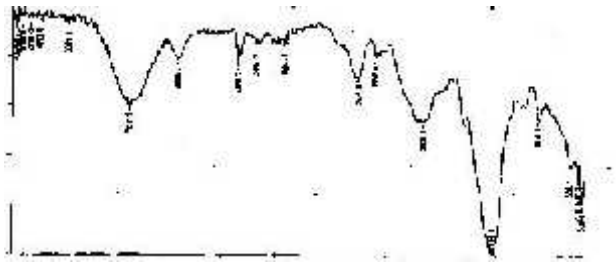

Figure 4.11. FTIR spectra of unloaded *Spirogyra* spp. (control)

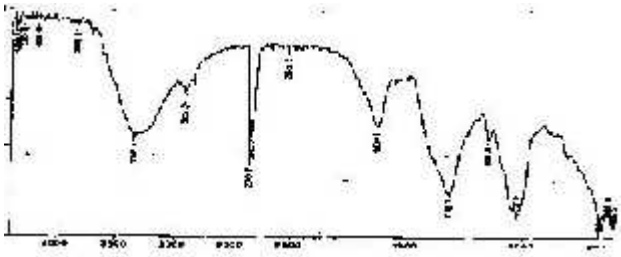

Figure 4.12.FTIR spectra of Cr-loaded *Spirogyra* spp.

Binding sites of Cr (VI) ions on *Spirogyra* spp. surface: FTIR spectra showed shift in peaks, 1020 to 1032, 1650 to 1634, and 3354 to 3352 (Fig. 4.11 and Fig. 4.12). The above mentioned peaks represent electronegative functional groups such as, hydroxyl (-OH), amine (-NH), etc., capable of attracting cations, such as Cr (VI) ion (Table 5).

Table 5. Shifts in FTIR spectra (cm^{-1}) showing binding sites of Cr (VI) biosorption on cell wall of *Spirogyra* spp.

Sr. No.	Unloaded Samples (control)	Cr (VI) loaded Samples	Probable functional group
1.	3354	3352	−OH −NH
2.	1650	1634	−OH
3.	1020	1032	−CH

Biochemical analysis of cell wall of filamentous green algae, such as *Spirogyra* spp. reveals that the above mentioned functional groups are components of organic constitutes, such as aldehyde, ketone, carboxylic acid, alcohols, ethers, esters, etc (Davis *et al.*, 2003).

A number of previously performed studies on cell wall biochemistry ofgreen algae versus biosorption are in agreement with the present findings. (Arief *et al.*, 2008).

Conclusions: The evaluation of the performance of biosorption of Cr (VI) ion by using *Spirogyra* spp. was based on equilibrium modeling, kinetic and thermodynamic studies, and analysis of surface binding sites by performing FTIR spectroscopy. Physicochemical

factors, such as pH, temperature, initial metal ion concentration, biosorbent dosage and contact time, etc. have been found to play a significant role in affecting the capacity of biosorbent. Optimum pH for biosorption was 4.0 (q_{max}= 264 mg/L), biosorbent dosage 1 g/L, and time to attain equilibrium concentration was 120 minutes. Biosorption data were the best fitted to Langmuir and Temkin isotherms, indicating monolayer sorption, and kinetics was found to follow pseudo-second-order rate expression. Thermodynamic studies show negative values of ΔG indicating that biosorption is spontaneous and exothermic in nature. The higher values of ΔS reflect the affinity of the biosorbents to Cr (VI) ions. It can be concluded from the present study that species of *Spirogyra* spp. could be employed as cost-effective and eco-friendly biosorbents, capable of reuse, thereby offering an alternative to expensive sorbents, currently being used in wastewater treatment.

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