

## SPIROGYRA AS AN EFFICIENT BIOSORBENT OF CADMIUM: A MECHANISTIC APPROACH

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### Abstract

The biosorption capacity of *Spirogyra* sp. biomass was evaluated for removal of cadmium (Cd) from wastewater. Batch experiments were conducted to optimize various parameters, such as pH, contact time and biomass concentration which affect biosorption. The recorded maximum biosorption capacity was 47 mg/g, while the optimum values for pH, temperature, contact time, and biosorbent concentrations were 5.0, 30°C, 120 min, and 1mg/L, respectively. The data were fitted for various adsorption isotherms, such as Langmuir, Freundlich, and Temkin; Langmuir theorem was found to be the most suitable, showing monolayer adsorption. Pseudo-second order kinetic model was fitted for the interpretation of kinetic modeling and was found to be compatible with interpretation of the data. Various thermodynamic parameters, such as entropy ( $\Delta H$ ), enthalpy ( $\Delta S$ ), Arrhenius constant ( $A^\circ$ ) and the energy of activation ( $E_a$ ) were calculated which indicated that the process was spontaneous, endothermic and feasible under the experimental conditions. FTIR spectra showed the presence of a number of electronegative functional groups on algal surface that were capable of binding to Cd (II) ion.

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

### Introduction

Discharges of industrial effluents, in recent decades, have resulted in the dumping of various toxic pollutants, such as heavy ions. Heavy metal pollutants, such as cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), etc., are non-degradable and thereby tend to accumulate within the biotic components of aquatic ecosystems and tend to increasingly concentrate as they travel through aquatic food chain (Akguc *et al.*, 2008). These toxic metal ions have shown severe health hazards to humans, such as long-lasting impairment of kidney, lungs, immune system, and bone function; the LC50 value of 1.6-3.9 g/kg of Cd (II) in rats shows the high toxicity potential of this heavy metal to mammals (Anon., 1991). Similarly, the rest of the organisms are at stake as well.

Thus, the present scenario necessitates an urgent action for the removal of toxic heavy metals, such as Cd (II) from the environment. Recently, adsorption process has emerged as the most promising technique and has attracted the attention of many researchers in the sector of wastewater treatment by employing both natural inorganic and organic materials (Ghassabzadeh *et al.*, 2010). Moreover, a great variety of synthetic adsorbents, such as silica gel have also been tested (Li *et al.*, 2007); however, poor adsorption of heavy metal ions, and the high cost by these materials necessitate the search for improved and cost-effective alternatives, such as biosorption (Iqbal & Edyvean, 2007; Volesky, 2007), and the use of dead biomass for the removal of heavy metal pollutants from the environment (Volesky, 1990). Among the various types of organisms that have been tested for biosorption of heavy metal ions, the use of algae has shown great promise specifically during the last decade. This is because of the capacity of these algae in removing heavy metal ions from solution (Askari *et al.*, 2007; Volesky, 2007; Andrade *et al.*, 2005; Ahalya *et al.*, 2003; Akhtar *et al.*, 2003; Davis *et al.*, 2003a, b). Use of filamentous green algae in particular had been

ignored initially but now is increasingly capturing attention as indicated by a number of recent studies (Arief *et al.*, 2008; Melcakova & Ruzovic, 2010). Recently, biosorption efficiency has been evaluated by determining equilibrium, kinetic and thermodynamic parameters by using various biosorbents in this context (Gupta & Rastogi, 2008; Melcakova & Ruzovic, 2010).

The mechanism of accumulation and adsorption of metals by algae involve adsorption onto the cell surface (wall, membrane or external polysaccharides) and binding to cytoplasmic ligands, phytochelatins and metallothioneins, and other intracellular molecules. Localization of metal ions on algal cell has been carried out by electron microscopy and Fourier Transform Infra-red Spectroscopy (FTIR) analysis (Mehta & Gaur, 2005; Arief *et al.*, 2008). The algal cell wall has many functional groups, such as hydroxyl (OH), phosphoryl ( $PO_3O_2$ ), amino ( $NH_2$ ), carboxyl (COOH), sulphhydryl (SH), etc., which confer negative charge to the cell surface and facilitate metal ions adsorption; toxic metals generally exist in the cationic form. Each functional group can dissociate into corresponding anion and proton at a specific pH level because of their own specific pKa (dissociation constant) (Arief *et al.*, 2008). These functional groups have been found to be associated with various cell wall components of green algae, such as heteropolysaccharides and proteins, functioning as metal binding sites (Davis *et al.*, 2003; Naja & Volesky, 2006; Melcakova & Ruzovic, 2010). Filamentous green algae, such as *Spirogyra*, *Cladophora*, etc. can therefore be predicted as efficient potential biosorbents due to the biochemistry of their cell wall (Andrade *et al.*, 2005; Arica *et al.*, 2005; Mata *et al.*, 2008; Arief *et al.*, 2008; Onyancha *et al.*, 2008; Yaqub *et al.*, 2009). Freshly available data regarding the capacity of filamentous green algae to adsorb heavy metal ions, such as Cd and Cr have opened the doors of cost-effective biosorption technology (Melcakova & Ruzovic, 2010). Filamentous green algae, such as species of *Spirogyra* are easily available in terms of amounts 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 investigation.

In the present study, biosorption of heavy metal divalent cations, such as Cd (II) by using the biomass of green algae, *Spirogyra* spp. was conducted, with emphasis on the estimation of kinetic equilibrium and thermodynamic parameters. Studies at cellular level were also undertaken to improve the understanding of possible binding sites of Cd (II) ions in the cell wall of the used biosorbents.

## Materials and Methods

**Biosorbent:** Filaments of *Spirogyra* species viz., *S. juergensii*, *S. elongate* and *S. piepengensis* were collected in polythene bags from Botanical Gardens of Government College University (GCU) Lahore, Pakistan, and were tested for their biosorptive capacity for Cd (II) ion. The algal biomass was washed thoroughly in running tap water 4–5 times, treated with 0.02 M HNO<sub>3</sub> and again washed with distilled running water. The washed biomass was dried overnight at 60°C until a constant weight was achieved; the final weight of the biosorbent was recorded. The biosorbent was then crushed and sieved through a 300nm sieve to obtain a uniform particle size of biosorbent used for further studies.

**Metal ion solutions:** Stock solution of Cadmium Nitrate (CdNO<sub>3</sub>) was prepared by using CdNO<sub>3</sub> (Fisher Scientific, USA) in double distilled water; thereafter serial dilutions of this solution were prepared to obtain concentrations of 10, 20, 30, and 40 ppm of cadmium. All experiments related to biosorptive potential of algal biomass were conducted by using 125 mL Erlenmeyer flasks. Prior to use, the flasks were baked at 70°C for 4 hours, followed by one wash with concentrated HNO<sub>3</sub> and then one wash with distilled water.

**Biosorption evaluation:** One hundred mL of Cd (II) ion solutions of 10, 20, 30, and 40 ppm concentration were transferred in 125 mL Erlenmeyer flasks. Biomass concentrations of dead *Spirogyra* spp. were separately taken as 0.1, 0.2, and 0.3g in the above -mentioned flasks. The flasks were maintained under constant agitation on a rotator shaker (200 rpm) for a period of 3 hours. The experiments were conducted at varying pH levels, such as 1, 2, 3, 4, 5, 6 and 7 and the optimum pH was derived. During the experiment, the values of pH of the solutions were adjusted by using 0.2 N HNO<sub>3</sub> and 0.1 N NaOH. The entire experiment was performed at varying temperatures, such as 10, 20, 30, and 40°C by maintaining optimum pH as had been calculated in the above-mentioned experiments.

**Transport of samples for analysis:** A sample of 5 mL from each flask was collected by using auto pipette at regular intervals of 0, 30, 60, 90, 120, 150 and 180 minutes. After collecting samples, each sample was poured in BD (Becton Dickinson) syringe. Each sample was then passed through Osmonics/MSI\* Cameo\*

Glass/Nylon Syringe Filters 0.25 nm (Fisher Scientific, USA). The adsorption capacity of the filter for Cd (II) ion that had already been tested amounted to less than 5% for both of the ions. The filtrate was then preserved for further analysis. All the experiments were conducted in triplicate.

**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.

**Fourier transform infra-red spectroscopy (FTIR):** FTIR spectroscopy was performed at the Department of Chemistry, University of the Punjab. Tablets of algal biomass were prepared in a Graseby-Specac Press, using algal mass (2 mg) mixed with KBr (1:100 p/p). A window characteristic of information of polysaccharides (between 900 and 1800 cm<sup>-1</sup>) was selected in order to monitor cell wall structure modifications. Spectra of both, Cd (II) ion loaded and unloaded biomasses (control) were obtained for comparison at a resolution of 1 cm<sup>-1</sup>. 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. This analysis was conducted at the Department of Chemistry, University of the Punjab, Lahore, Pakistan.

**Scanning electron microscopy (SEM):** The microscopic studies of the surface of biosorbents under investigation [Cd (II) treated as well as non-treated (control)] were carried out by Scanning Electron Microscopy (SEM). Specimens were fixed in a solution of one part Karnovsky's fixative (4% paraformaldehyde and 0.5% glutaraldehyde), one part 2% osmium, and one part culture medium [Bold N1 medium, UTEX] for 10 min, followed by six 4-min rinses in distilled water (Cook, 1998). Specimens were left in rinse water overnight, dehydrated in a graded ethanol series, dried, using a Tousimis Samdri-780-A critical-point drier, mounted on aluminum stubs with double-sided tape, sputter-coated using a Bio-Rad E5000M gold coated, and viewed using a Hitachi S570 scanning electron microscope at either 10 or 20 kV.

**Mathematical modeling and interpretation of data:** The data collected as a result of biosorption studies were tested by conventionally used adsorption isotherms, such as Langmuir and Freundlich isotherms, for adsorption. Additionally, kinetic modeling and thermodynamic studies were also carried out.

**Equilibrium isotherm modeling:** Langmuir isotherm was used to correlate the equilibrium data. Langmuir model assumes a monolayer sorption of sorbate from the aqueous solution (Dursun, 2006; Mashilah *et al.*, 2008; Yaqub *et al.*, 2009). The Langmuir equation is given below:

$$q_e = q_{max} \frac{c_e}{(b + c_e)} \quad (1)$$

The linearized form of equation 1 can be expressed as given below:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{b \cdot q_{max}} \cdot \frac{1}{C_e} \quad (2)$$

Here,

$q_e$  = Equilibrium constant of sorbate ion on surface of the biosorbent (mg/g)

$C_e$  = Equilibrium concentration of metal ion in solution

$K_2$  = Saturation constant (mg/L)

The values of  $q_e$ ,  $C_e$ , and  $K_2$  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:

$$K = \frac{q_e}{C_e} \quad (3)$$

The Freundlich model was also employed to estimate the adsorption intensity of the adsorbent towards the sorbate. This theorem considers multi-layers adsorption on the sorbent surface. This model may be given by the equation below:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

Here,

$K_F$  = Freundlich empirical constant

relative to sorption capacity

$1/n$  = empirical constant relative sorption Intensity

The linearized form of equation 4 is given as follows:

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**, as given by the following equation, was also employed

$$q_e = B \ln(K_T C_e) \quad (5)$$

$K_T$  = equilibrium binding constant correlated to the maximum binding energy and

$B$  = constant related to the heat of adsorption.

The linearized form of equation 5 is given as follows:

$$q_e = B \ln K_T + B \ln C_e \quad (6)$$

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 & McKay (1999), was employed to evaluate the kinetic parameters for the biosorption studies of Cd (II) ions by biosorption from dead biomass of *Spirogyra* spp. The biomass dose was kept at 1 g/L,

whereas kinetics was evaluated by studying biosorption at 10, 20, 30, and 40 mg/L of initial Cd (II) ion solution.

To explain the correlation between the equilibrium concentration of metal ions in the solid phase (sorbent) and the aqueous solution, pseudo-second order model, 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.

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (7)$$

where,

$t$  (min) = time

$q_t$  (mg/g) = uptake capacity at time 't'

$K_2$  (g/mg/min) = equilibrium rate constant of pseudo-second-order adsorption. After being integrated and rearranged, the following expression could be derived:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_{eq}} \quad (8)$$

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

**Thermodynamic parameters:** Biosorption studies were performed at varying temperatures such as, 283°K, 293°K, 303°K, 313°K. Thermodynamic parameters were also determined from the experimental data. The following equation was used to obtain the values of entropy ( $\Delta H$ ) and enthalpy ( $\Delta S$ ).

$$\ln b = \frac{\Delta S^\circ}{R} + \frac{\Delta H^\circ}{RT} \quad (9)$$

where  $R$  is gas constant and  $b$  is the Langmuir's constant. The linear plot of the  $\ln b$  versus  $1/T$  (Fig. 9) was drawn and by determining the intercept and slope, values of entropy ( $\Delta H$ ) and enthalpy ( $\Delta S$ ) were measured.

Arrhenius equation was used to obtain the values of Arrhenius constant ( $A^\circ$ ) and the activation energy ( $E_a$ ) by using the following equation.

$$\ln K_2 = \ln A^\circ - \frac{E_a}{RT} \quad (10)$$

The values of change in free energy ( $\Delta G$ ) for biosorption were determined by using the following equation:

$$\Delta G = -RT \ln b \quad (11)$$

## Results

**Effect of pH:** Biosorption of Cd (II) ions was low at pH value of 1.0 ( $q_{eq} = 23$  mg/g), increasing gradually with the increase in pH value. The maximum biosorption was achieved at pH 5.0 ( $q_{eq} = 65$  mg/g), beyond this pH value biosorption of Cd (II) ion declined (Fig. 1).

**Effect of contact time:** Contact time of the exposure of biosorbent to the sorbate was observed as an important factor in biosorption application. Fig. 2 shows the biosorption efficiency of Cd (II) ion by *Spirogyra* spp., as a function of contact time. The maximum Cd (II) uptake was recorded up to 30 minutes of contact time, followed by a slower uptake up to 120 minutes and thereafter, no significant uptake of Cd (II) ion was observed. After 120 minutes, equilibrium concentration ( $q_{eq} = 47$  mg/g) was achieved indicating the saturation of binding sites of cations in algal cell wall.

**Effect of temperature:** Studies of biosorption of Cd (II) ion at varying temperatures, such as 10, 20, 30, and 40°C (283, 293, 303, and 313°K) showed that the optimum temperature was 30°C ( $q_{eq} = 47$  mg/g), followed by that at 20°C ( $q_{eq} = 46$  mg/g) (Fig. 3). However, lower adsorption occurred at 10 and 40°C. Additionally, equilibrium concentration was found to be achieved rapidly at higher temperatures, as compared to that at lower temperatures.

**Effect of biosorbent concentration:** The biosorption capacity of Cd (II) by *Spirogyra* spp., was found to be directly proportional to the biomass concentration. However, at 1g/L biosorbent concentration, optimum metal uptake per unit mass of sorbent ( $q_{eq} = 47$  mg/g) was

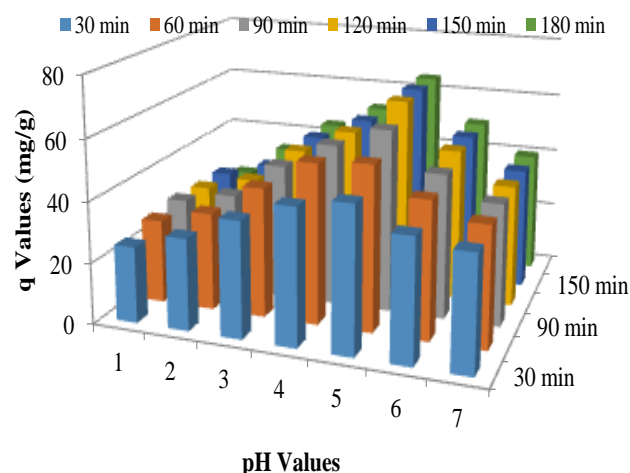


Fig. 1. Comparison of biosorption of Cr (VI) ions at various pH values by *Spirogyra* spp.

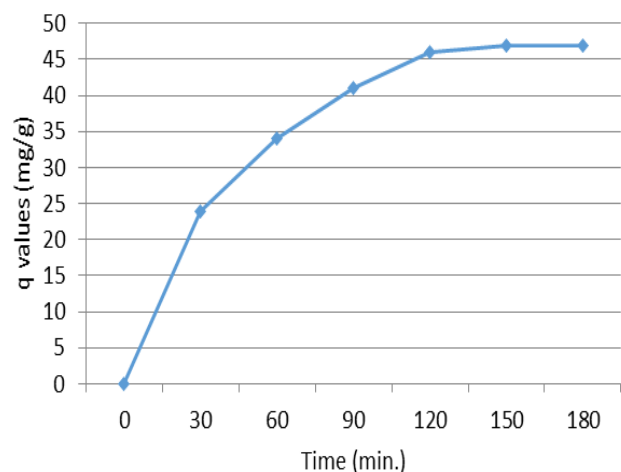


Fig. 2. Effect of contact time on Cd (II) biosorption by *Spirogyra* spp.

observed (Fig. 4), followed by 2 and 3g/L, respectively ( $q_{eq} = 25$  and 18 mg/g respectively).

**Biosorption equilibrium isotherm:** Various sorption models were employed for fitting the data to examine the relationship between sorption and aqueous concentrations of Cd (II) ions:

Langmuir isotherm was used to correlate the equilibrium data by using equation 2. The linear plot (Fig. 5-a) of inverse of equilibrium concentrations of Cd (II) ions,  $1/q_e$  versus  $1/C_e$  showed a typical equilibrium biosorption isotherm, suggesting that biosorption of Cd (II) ions involves a chemical equilibrated and saturable mechanism which reflects site-specific biosorption on the surface of the sorbent (Table 1).

Freundlich isotherm model (Eq. 5-b) was employed to estimate the adsorption intensity of the adsorbent towards the sorbate [Cd (II)]. Linear plot of  $\text{Log } q_e$  versus  $\text{Log } C_e$  can be seen in Fig 5b. The values of Freundlich's saturation constants were derived from intercept and slope, respectively (Table 1).

Temkin isotherm (equation 5c) was used and the values of  $K_T$  and  $B$  were calculated (Table 1). Linear relationship of ' $q_e$ ' versus  $\ln C_e$ ' can be seen in Fig. 5c.

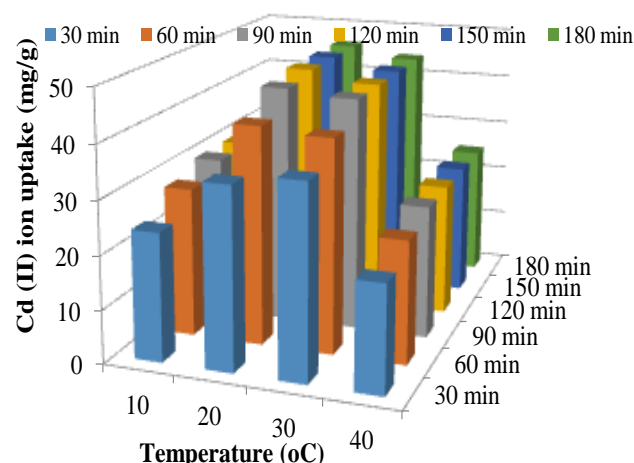


Fig. 3. Effect of temperature on biosorption of Cd (II) ions by *Spirogyra* spp.

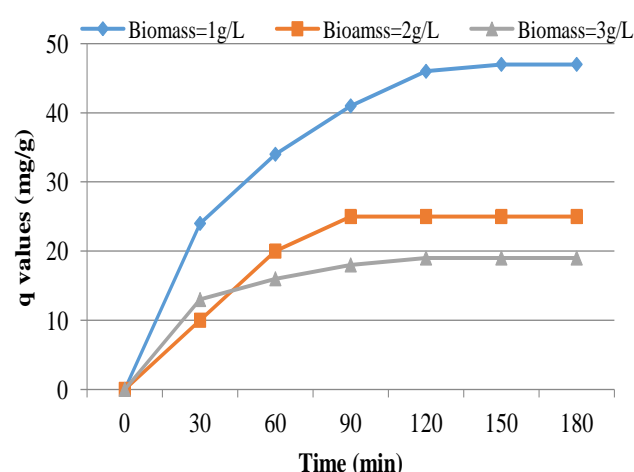


Fig. 4. Effect of biosorbent (biomass) concentration of biosorption of Cd (II) by *Spirogyra* spp.

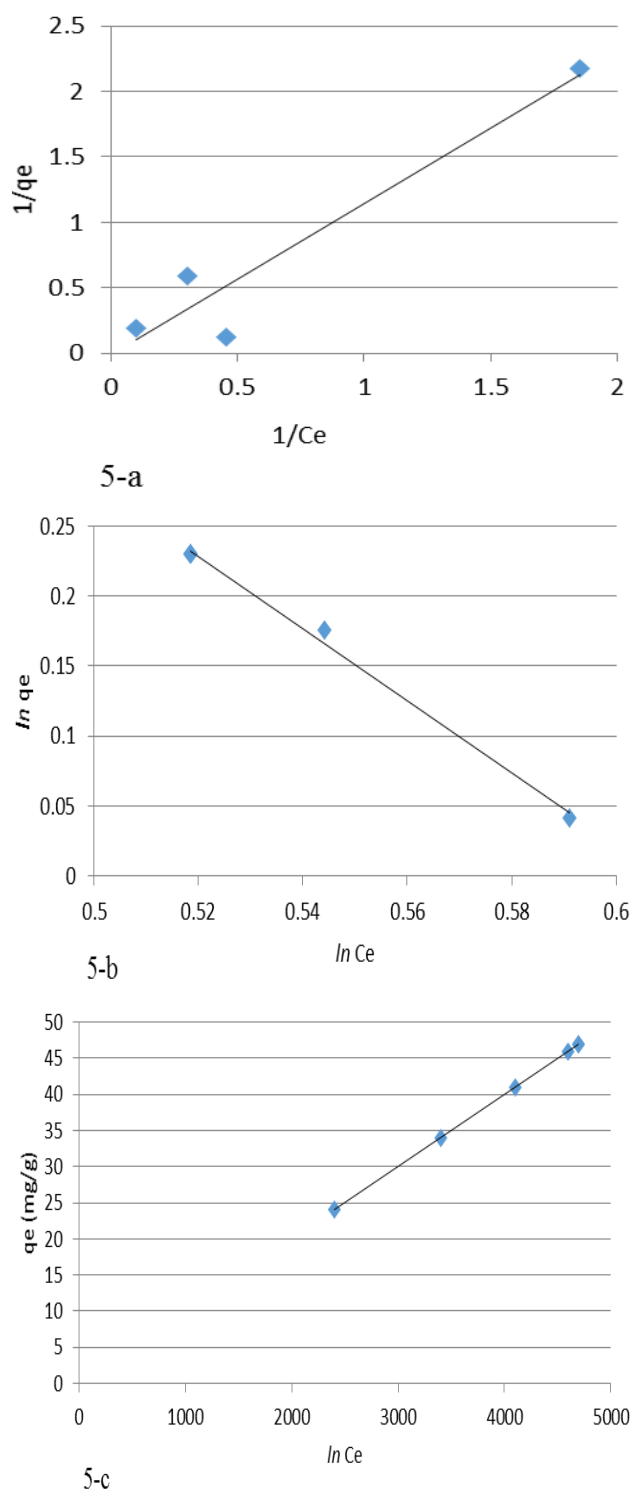


Fig. 5. Plot of Isotherms sorption of Cd (II) for *Spirogyra* spp. Surface.

5-a. Langmuir isotherm

5-b. Freundlich isotherm

5-c. Temkin Isotherm

**Kinetic studies:** Pseudo-second order kinetic model (equation 9) was employed for evaluation of Cd (II) ions sorption 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. From the linear plot of  $t/q$  versus  $t$  (Fig. 6), the values of the constants were derived (Table 2).

**Thermodynamics studies:** Thermodynamics behavior of the adsorption of Cd (II) ion on the surface of *Spirogyra* spp. was studied by calculating various thermodynamics constants. Equation 10 was used to obtain the values of entropy ( $\Delta H$ ) and enthalpy ( $\Delta S$ ).

From a linear of  $\ln b$  versus  $1/T$  (Fig. 7), values of  $\Delta H$  and  $\Delta S$  were determined by using equation 9 (Table 2), and  $\Delta G$  was determined by equation 10. Values of  $\Delta H$  and  $\Delta S$  were found to be positive, whereas values of  $\Delta G$  were negative (Table 2). The  $\Delta G$  values also decrease in magnitude on increasing the temperature from 283°K through 303°K (Table 2).

Values of Arrhenius constant ( $A^\circ$ ) and the activation energy ( $E_a$ ) were also determined (Table 1) from a linear plot of  $\ln K_2$  versus  $1/T_b$  (Fig. 7) by using equation 11.

**Binding sites of Cd ions on *Spirogyra* spp. surface:** FTIR spectra showed the shift in peaks (Fig. 8a and 8b) of electronegative functional groups, such as hydroxyl, amine, etc. (Table 3).

SEM studies revealed the topographical and elemental appearance of the surface of *Spirogyra* sp. It was observed that Cd (II) loaded algal surface showed altered morphology and surface complexation (Fig. 9 a & b) indicating the binding of Cd (II) ions onto surface; these adsorption sites were specifically located in a patch pattern.

## Discussion

The pH of the solution seemed to have a significant influence on the dissociation site of the surface of algal biomass and the solution chemistry of the heavy metals; for example, hydrolysis, complexation by binding site(s), redox reactions, and precipitation, because every binding site on algal surface has its own specific pKa value. This implies that with the decline of pH (below 4.0), the solution gets protonated and Cd (II) ions have to compete with protons for the electronegative binding sites (Arief *et al.*, 2008). The decreased biosorption at pH ranging from 5.0 to 7.0 may be due to precipitation of solute; hence, decreasing the availability of Cd (II) ions for sorption.

Contact time seems to have influence on uptake of Cd (II) ion; in the first 30 minutes, available binding sites lead to rapid uptake of Cd (II); whereas at later stages (after 30 minutes), decrease in the number of vacant binding sites at algal surface available for Cd (II) ion biosorption, increased the competition, hence slowing down the biosorption.

Effect of biomass concentration onto algal surface could be explained as a consequence of a partial aggregation of biomass at higher biomass concentration, which resulted in a decrease in effective surface area for the biosorption (Gupta & Rastogi, 2008).

Thermodynamic parameters were found to be helpful in understanding the behavior of sorption. Positive values of  $\Delta H$  and  $\Delta S$  and negative values of  $\Delta G$  indicated that adsorption of Cd (II) were spontaneous and feasible under the given conditions (Table 2). This is in agreement with previously performed studies of biosorption of cations by using other biosorbents (Yaqub *et al.*, 2009; Gialamouidis *et al.*, 2010; Vieira *et al.*, 2010; Lawal *et al.*, 2010).



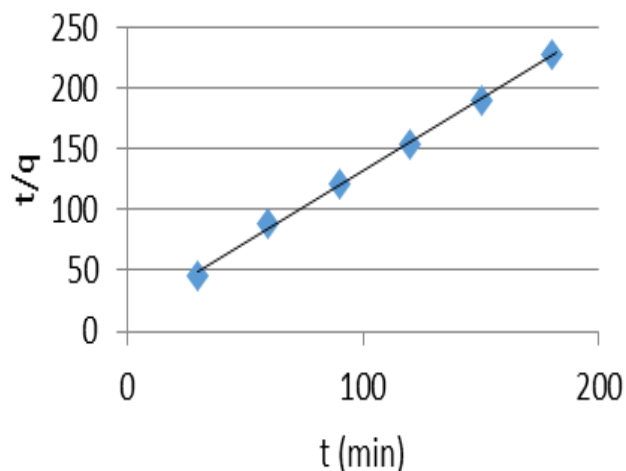


Fig. 6. Linear plot of Pseudo-second order kinetics for sorption of Cd (II) ions onto *Spirogyra* spp.

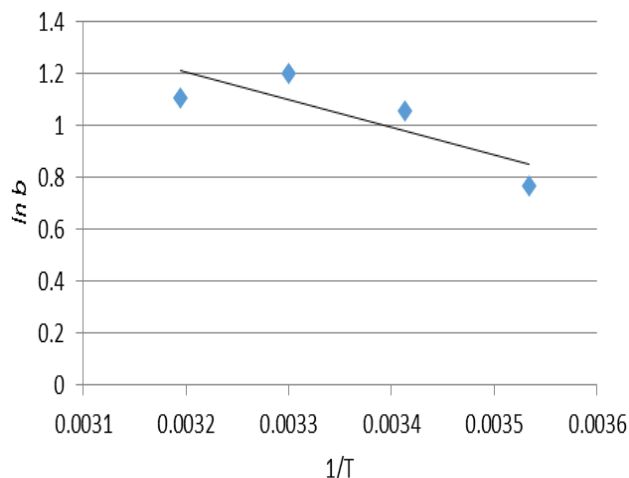


Fig. 7. Thermodynamic profile of sorption of Cd (II) onto *Spirogyra* spp.

**Table 1. Values of constants of various adsorption isotherms.**

Langmuir's constants				Freundlich's constants			Temkin's constants		
$q_{\max}$ ( $\text{mgg}^{-1}$ )	$K_L$ ( $\text{L mg}^{-1}$ )	$R^2$	$k$	$n$	$K_F$	$R^2$	$K_T$	$B$	$R^2$
14.42	0.03	0.9883	0.85	0.39	2.46	0.9957	0.781	0.01	1

**Table 2. Constants of Pseudo-second order kinetics and thermodynamics for the biosorption of Cd (II) ion onto *Spirogyra* spp.**

Pseudo-second kinetics	$q_{eq}$ Cal	$K_2$	$R^2$		
	57.54	0.04	0.9941		
Thermodynamic parameters	$\Delta H^\circ$ ( $\text{KJmol}^{-1}$ )	$\Delta S^\circ$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	$A^\circ$	$E_a$ ( $\text{J mol}^{-1}\text{g}^{-1}$ )	
	2.2	70.7	1.23	38.34	
Free Energy ( $-\Delta G$ ) at varying temperatures	Temperature (Ko)	283	293	303	313
	$-\Delta G$ ( $\text{KJmol}^{-1}$ )	14.89	24.40	24.35	12.07

**Table 3. Shifts in FTIR spectra ( $\text{cm}^{-1}$ ) showing binding sites on *Spirogyra* spp. for Cd (II) ion biosorption.**

Sr. No.	Unloaded samples (control)	Cd (II) ion loaded samples	Probable functional group
1.	3354	3337	-OH -NH
2.	2921	2905	-OH
3.	1650	1634	-CH
4.	1538	1557	-C-H

Shift in peaks of FTIR spectra showing the involvement of electronegative functional groups, such as hydroxyl, amine, etc. (Fig. 8a and 8b), capable of attracting cations (Table 3) confirmed the binding of Cd (II) ions onto these sites. Considering the biochemistry of cell wall, It is quite predictable that all these functional groups are components of organic constitutes, such as aldehyde, ketone, carboxylic acid, alcohols, ethers, esters, etc. These findings further strengthen and establish the involvement of the above mentioned functional groups which is in agreement with the other similar studies (Davis *et al.*, 2003a; Arief *et al.*, 2008).

Appearance of noticeable alterations and surface complexation onto Cd (II) loaded wall of *Spirogyra* spp. as can be seen SEM images (Fig. 9 a & b) confirm the surface sorption; the cell wall was shrink and wrinkled. This sorption was recorded in a patch pattern. These findings are in agreement with the previously reported investigations by using other green algae which have been tested as biosorbent, such as *Saragassum vulgare*, *Chlorella miniata*, yeast cells, etc (Raize *et al.*, 2004; yavuz *et al.*, 2003). In another study using *Spirogyra* spp., SEM graphs of Pb (lead) loading were reported (Gupta & Rastogi, 2008). Several other studies also establish SEM as reliable tool to monitor metal ion loaded cell surface (Zhou *et al.*, 2005; Das *et al.*, 2007).

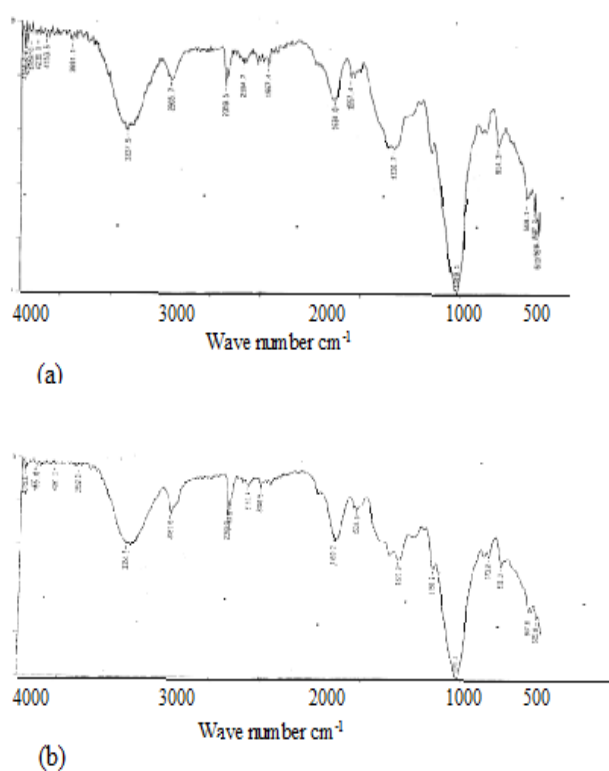


Fig. 8. FTIR spectra of *Spirogyra* spp.  
(a) Control (unloaded/control)  
(b) Cd (II) ions loaded

## Conclusions

All the physicochemical factors studied play significant role in affecting the capacity of biosorbent to adsorb cadmium. Biosorption kinetics was found to follow pseudo-second-order rate expression. Negative values of  $\Delta G$  indicate that biosorption is spontaneous and exothermic in nature while the positive values of  $\Delta S$  and  $\Delta H$  reflect the affinity of the biosorbents for Cd (II) ions. Based on the results of the present study it can be concluded that biomass of *Spirogyra* spp. could be employed as a low-cost and eco-friendly biosorbent as an alternative to traditionally used expensive methods in wastewater treatment.

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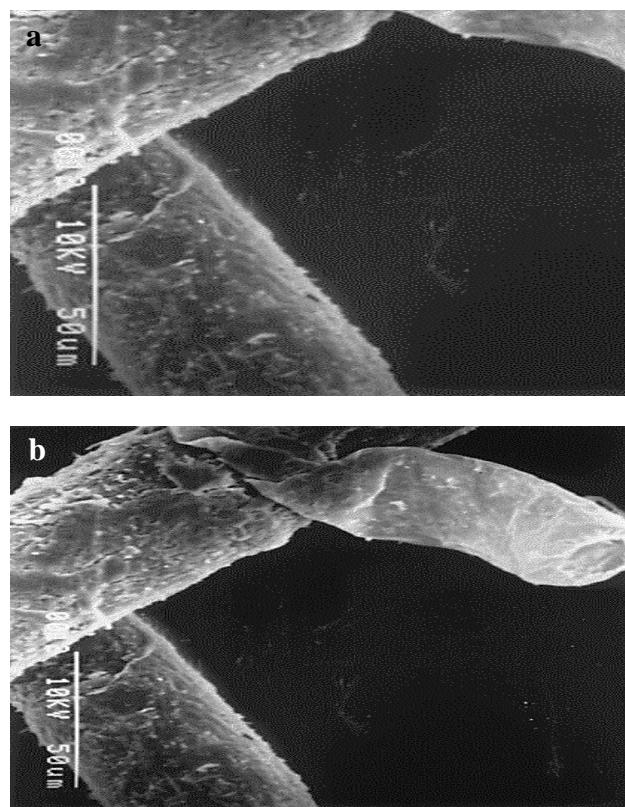


Fig. 9. SEM of *Spirogyra* spp . (a) Control (unloaded);(b) Cd (II) loaded.

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