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Uptake efficiency, equilibrium kinetics and thermodynamics of Zn^{2+} biosorption by a *Nostoc* sp. isolated from Shahlang coal mine in Meghalaya, India

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Abstract — Cyanobacteria are fast becoming popular organisms for bioremediation research. A *Nostoc* sp. isolated from coal mining area was undertaken for Zn sorption analysis. The percent sorption increased with increase in biomass (1 to 3 µg/mL) and contact time (30 min to 24 h). Metal biosorption was rapid in the initial phase (within 2 h) on the cyanobacterial biomass after that it remained constant up to 24 h. Maximum percent sorption of ~ 65 % was seen at pH 8 from a 10 ppm Zn supplemented medium. A comparative FTIR analysis of control and Zn treated cells established signature regions of various functional groups that were involved in metal binding. Langmuir isotherm was best fitted model with a R^2 value of 0.986 as against that of Freundlich R^2 value of 0.857 for 2 h. The organism's maximum sorption capacity (Q_{max}) was 4.3 mg of Zn taken up per gram of *Nostoc* biomass. Thermodynamic studies for Zn biosorption produced negative values for ΔG indicating the process to be spontaneous. Further, ΔH i.e. the change in enthalpy with a value of 7.626 kJ/mol and ΔS, the entropy change with a value of 0.034 kJ/mol/K signified the process to be endothermic and thermodynamically favourable.

Index Terms— *Nostoc* sp., Zn biosorption, Langmuir and Freundlich isotherms, Maximum sorption capacity, Thermodynamic studies, Van't Hoff plot, Free energy change.

1 INTRODUCTION

Water is defined as a colourless, transparent, odourless, liquid which forms the seas, lakes, rivers, and rain and is the basis of the fluids of living organisms. In recent times, various forms of waterbodies are being polluted in leaps and bounce to such an extent that there is scarcity of potable water in the midst of plenty. Meghalaya, one of the North-Eastern states of India holding the rank of being the wettest place on earth has seen pollution of its waterbodies in recent times by various contaminants including heavy metals due to extensive coal and limestone mining. Mine waters typically contain dissolved heavy metals such as iron, zinc, copper, aluminium and manganese etc. [1], [2]. Persistence of heavy metal contaminants in the environment is a serious concern due to their toxicity and non-degradable nature, with potential for bioaccumulation along the food web leading to various metabolic disorders and diseases including cancer, liver and kidney dysfunction among others. However many metal ions are essential for proper functioning of biological processes. Among these, zinc is crucial as DNA-binding Zn fingers [3], [4] and it is important for other physiological functions in the living tissues where it regulates many biochemical processes in higher organisms [5]. Zn also plays crucial role in plants and microbes [6], [7]. In cyanobacteria, the organism of interest in the study, Zn is essential for proper functioning of carbonic anhydrase in carboxysomes [8], [9] and its deficiency leads to reduced membrane integrity and synthesis of nucleotides, cytochromes, auxins, chlorophylls and carbohydrates [10]. However, Zn overdose is hazardous to living organisms. In humans it damages pancreas, causes cerebral edema, anemia, stomach cramps, nausea and impaired absorption of iron and copper [11], [12], [13]. In plants and microbes, Zn has been shown to inhibit photosynthetic activity in the green alga *Chlorella pyrenoidosa* [14], respiratory electron transport systems in bacteria and in mitochondria [15], [16], [17], [18] and induce alterations in the photosystem II mediated photochemistry of the cyanobacterium *Spirulina platensis* [19].

Microbes have many negatively charged functional groups on their cell surfaces by virtue of which they bind positively charged ions. Although, this helps them to concentrate essential nutrients they also bind to nonessential and harmful positively charged ions indiscriminately whenever these contaminants are in high concentration in their vicinity. This binding process is termed as biosorption. In recent times the process of biosorption has been intensely studied for its potential in removing environmental pollutants including heavy metals from wastewater by both living and dead microorganisms.Typical biosorbents can be derived from three sources as follows (1) non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell, etc. (2) algal biomass [20], [21], [22] (3) microbial biomass, e.g. bacteria, fungi and yeast. Different forms of inexpensive, non-living plant material such as potato peels [23], sawdust [24], black gram husk [25], eggshell [26], seed shells [27], coffee husks [28], sugar-beet pectin gels [29], citrus peels [30], Ca-alginate beads [31] etc., have been widely studied as potential biosorbents for heavy metals. A wide range of microbial biomass types have also been investigated in biosorption studies due to their fast growth. These include archaea, bacteria [32], [33], [34], [35], [36] and cyanobacteria [37], [38], [39], [40]. Among these, cyanobacteria are commonly found in wetlands, rivers, spring, ponds, as well as on rocks and soil surfaces in hot and cold desert [41], [42]. They play a major role in the carbon, nitrogen and oxygen dynamics of many aquatic environments [43]. Cyanobacteria have cell walls similar to gram-negative bacteria. Thus, in cyanobacterial cell wall biosorptive component is peptidoglycan, with some species also producing sheaths as well as copious mucilaginous polysaccharide (extracellular polymeric substances, EPS). Three main mechanisms for the binding of metals to bacterial cell walls are known: (i) ion exchange reactions with peptidoglycan and teichoic acid, (ii) precipitation through nucleation reactions, and (iii) complexation with nitrogen and oxygen ligands. The cell wall and exopolymer sheaths of cyanobacteria contain negatively charged functional groups such as carbonyl, phosphoryl, hydroxyl and amines by virtue of which they bind to various positively charged metal ions [44], [45]. This property of cyanobacteria therefore is being researched in order to project cyanobacteria as potential bioremediators of heavy metals from wastewater. Owing to their minimal nutritional requirement and their rapid growth that increases biomass quantity yielding high surface area for metal binding, cyanobacteria are fast becoming popular organisms for bioremediation research in recent times.

In this study a cyanobacterium *Nostoc* sp. isolated from the coal mine of Shahlang, West Khasi Hills, India has been used for Zn biosorption study. Its biosorption potential towards Cr has already been studied [46]. That this organism was isolated from a contaminated water sample from a mining area showed its resilience and tolerance to various heavy metal contaminants. Pre-exposure to such contaminants may have endowed the organism with adaptive strategies to combat high metal concentrations in its vicinity and therefore presents an intriguing case study towards heavy metal removal from contaminated water. In the present study, Zn uptake efficiency of the organism, equilibrium modelling and thermodynamics of the Zn-cyanobacterial interaction has been evaluated in order to understand the dynamics of Zn removal by the organism.

2 MATERIALS AND METHODS

2.1 Growth and maintenance of *Nostoc* sp.

The *Nostoc* sp. used in our study was isolated from a coal mine and identified by comparing partial sequencing of 16S rRNA gene with similar sequences deposited in GenBank (NCBI) database using BLAST. The accession number KX814344 was generated for this organism during our course of earlier study. The organism was grown in BG-11_0 medium (Macronutrients (g/l): $K_2HPO_4.3H_2O$ (40); $MgSO_4.7H_2O$ (75); $CaCl_2.2H_2O$ (36); Citric acid (6); Ferric ammonium citrate (6); Na_2CO_3 (20) EDTA (disodium salt) (1); Micronutrients (g/l): H_3BO_3 (2.86); $MnCl_2.4H_2O$ (1.81); $ZnSO_4.4H_2O$ (0.22); $Na_2MoO_4.2H_2O$ (0.39); $CuSO_4.5H_2O$ (0.079); $Co(NO_3)_2.6H_2O$ (0.0494)) and maintained at 30 ± 2˚C in a culture room under continuous light with a photon fluence rate of 50 μmol/ m^2/ s. Chlorophyll '*a*' content is one of the parameters that is used to evaluate cyanobacterial growth [47]. The growth of the *Nostoc* sp. Under study was measured in terms of increase in chlorophyll '*a*' concentration [46]. Three mL cyanobacterial culture was centrifuged at 2500 rpm for 3 min. Supernatant was discarded and equal volume of 100% methanol was added to the pellet. The tubes were vortexed and kept in boiling water bath for the extraction of chlorophyll 'a' following which the tubes were centrifuged at 2500 rpm for 3 min. The absorbance of the supernatant was read in a spectrophotometer at 663 nm. Chlorophyll 'a' concentration was calculated by using the formula:

Chlorophyll *a* (μg/mL)= Absorbance at 663 nm × 12.63 (Eq.1)

2.2 Metal treatment

2.2.1 Preparation of heavy metal stock solution

All chemicals and reagents used in the study were of analytical grade obtained from Sisco Research Laboratories (SRL), HiMedia India Ltd. and Merck India Ltd. Zinc sulphate ($ZnSO_4.7H_2O$) was used as the source of Zn for all experiments. Working solutions were prepared using a 100 ppm metal stock solution made in double distilled deionized water and stored at 4°C. The concentration was calculated for the metal ion and not for the whole salt.

2.3 Factors regulating metal sorption

2.3.1 Effects of biomass, pH and contact time on Zn sorption

10 ppm of Zn was added to the test samples. Each culture tube contained cyanobacterial biomass of different concentrations (i.e. 1, 2 and 3 μg m/L) and inoculated in medium of different pH (i.e. pH 6, 7 and 8) and the temperature was maintained at 30°C. The intervals of contact time allowed were 30 min, 2 h and 24 h respectively. After the incubating period, the samples were centrifuged and the supernatant were given for Atomic Absorption Spectrophotometric (AAS) analysis.

2.3.2 Effects of temperature and metal concentration

In order to check the capacity of the biosorbent to sorb the metal ion, the % Zn removal was studied by varying the metal concentrations (1, 5, 10 and 15 ppm of Zn^{2+}). Cyanobacterial biomass (3 μg/mL) and pH 8 were kept constant as best sorption was seen under these conditions from the previous study. Three sets of experiments were conducted in triplicate: 1, 5, 10 and 15 ppm of Zn^{2+} was added to different test tubes maintained at 20, 25 and 30°C respectively. These were kept on horizontal shaker (50 rpm) for 30 mins, 2 h and 24 h to study the effect of temperature and contact time. After the incubation period the amount of residual metal ions was estimated in the supernatant using AAS. This value was subtracted from the initial amount of supplemented metal ions in the test medium to arrive at the amount of metal ion removed. The percent removal of Zn was calculated using the Eq. 2.

$$\% \text{ Zn removal} = \frac{C_I - C_F}{C_I} \times 100 \qquad \text{Eq. 2}$$

Where, C_I is initial Zn concentration present in the medium; C_F is residual Zn concentration in the supernatant.

2.4 Fourier Transform Infra-Red (FTIR) spectroscopic

analysis

FTIR technique was used to determine the functional groups present on the cyanobacterium cell surface which bind the Zn ions. For FTIR spectroscopic analysis, 5 mL of control and Zn treated cultures (for 24 h) were transferred onto petri-plates and dried in oven at 40°C. Dried samples were mixed with desiccated spectroscopic-grade potassium bromide (KBr), 1:10 (w/w) to make pellets. FTIR analysis was carried out using Perkin Elmer, 400 FT-IR/FT-FIR spectrometer; MODEL: SP400 operating in the range of 4000-450 cm^{-1}.

2.5 Equilibrium isotherm studies

The popular Langmuir and Freundlich adsorption isotherms [48], [49] were employed for isotherm modelling of Zn removal based on the reports on metal biosorption studies by other researchers [50], [51], [52], [53]. For analysing Zn sorption, media containing Zn concentrations (1, 5, 8, 10, 12 and 15 ppm) were taken along with fixed biomass concentration of 3 µg/mL in the experimental setup. The amount of metal uptake by the *Nostoc* sp. biomass was expressed as q (mg of metal ion taken up per g of the biosorbent) and this was calculated using the following. Eq. 3 below:

$$q = \frac{(C_I - C_F).V}{w} \qquad \text{(Eq. 3)}$$

Where,
q = metal uptake (mg metal per g biomass)
C_I = initial metal concentration (mg metal per L solution)
C_F = final metal concentration (mg metal per L solution)
v = volume of solution (L)
w = biomass weight (g) of biosorbent.

Langmuir equation assumes that (1) there are no interaction among the adsorbed species (2) there are finite numbers of energetically uniform sites on the adsorbent and (3) adsorbate forms a monolayer on the adsorbent surface beyond which no further adsorption takes place. The Langmuir's isotherm is mathematically expressed as

$$q_F = \frac{Q_{max}.K_L.C_F}{1+K_L.C_F} \qquad \text{(Eq. 4)}$$

The Eq. 5 can be linearized as

$$\frac{C_F}{q_F} = \frac{1}{Q_{max}K_L} + \frac{1}{Q_{max}}C_F \qquad \text{(Eq. 5)}$$

Where,
q_F = metal adsorbed per g of biosorbent at equilibrium
C_F = equilibrium concentration of metal ion
Q_{max} = maximum adsorption capacity for metal ion per unit weight of the biosorbent
K_L = equilibrium adsorption constant related to the binding affinity

From the Langmuir equation, a dimensionless equilibrium parameter known as separation factor can also be obtained which predicts the nature of interaction of the biomass with the metal ions. The separation factor (R_L), is calculated by the following equation

$$R_L = \frac{1}{(1+K_L\ C_I)} \qquad \text{(Eq. 6)}$$

The calculated value of $R_L > 1$ indicates unfavorable interaction; $R_L = 1$ shows linear interaction; $R_L < 1$ indicates favorable interaction and $R_L = 0$ means the interaction is irreversible [54]. On the other hand, Freundlich's isotherm describes adsorption characteristics of a heterogeneous surface with the assumption that enthalpy of adsorption is independent of the amount adsorbed. It is mathematically expressed as

$$q_F = K_F C_F^{\ 1/n} \qquad \text{(Eq. 7)}$$

Where K_F and n are the Freundlich constants indicating sorption capacity and intensity, respectively and can be calculated from the linearized logarithmic form of the Eq. 7 as given below:

$$log q_F = log K_F + \frac{1}{n} log C_F \qquad \text{(Eq. 8)}$$

2.6 Evaluation of thermodynamic parameters of Zn sorption

From a thermodynamic perspective, in the adsorbent-adsorbate system in metal removal process, evaluation of both energy and entropy factors must be considered in order to determine if the process will occur spontaneously [54]. In our study, for evaluation of thermodynamic parameters, the Zn uptake by the organism was calculated from the Van't Hoff plot which was obtained by plotting ln K *vs* 1/T and ΔG was calculated using the following equation;

$$\Delta G = -RT ln K \text{ or } \Delta G = -2.303\, RT log K \qquad \text{(Eq. 9)}$$

The thermodynamic parameters for the bioremoval of Zn at 20°C (293K), 25°C (298K) and 30°C (303K) were calculated from following Eq. 10 below.

$$\Delta G = \Delta H - T\Delta S \qquad \text{(Eq. 10)}$$

Where, ΔG (kJ/mol) is the change in Gibbs free energy,
ΔH (kJ/mol) is the change in enthalpy,
ΔS (kJ/mol/K) is the change in entropy,
K (L/g) is an equilibrium constant, R is the universal gas constant (8.314×10^{-3} kJ/mol/K) and T(K) is the absolute temperature [54].

3 RESULTS AND DISCUSSION

3.1 Effects of biomass, pH, metal concentration, contact time and temperature on Zn sorption

Many factors can affect biosorption. Actual biosorption of metal ions showed dependence on amount of biosorbent available, pH of the medium, contact time allowed for interaction, temperature and concentration of metal ions present [54]. The effects of three parameters pH, contact time and biomass have been presented in the Fig. 1.

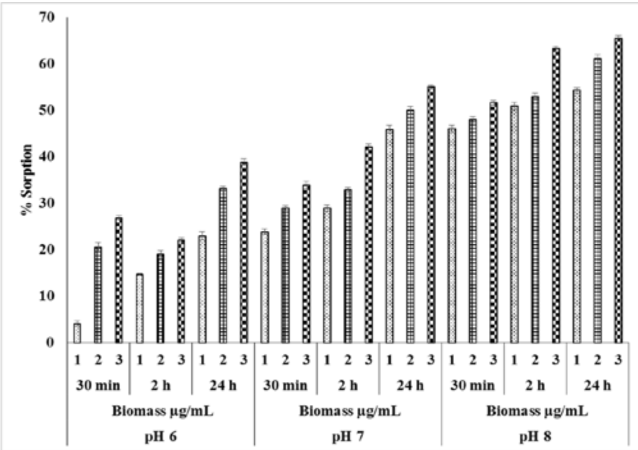

Fig. 1 Effect of biomass concentration, pH and contact time on the % Zn sorption from a fixed metal concentration (10 ppm).

Three pH studied were chosen keeping in mind the range of pH in which the organism could survive and proliferate. Our previous study with the organism had established that beyond 3 µg/mL concentration of biomass leads to clumping of cells within the confinement of experimental tubes. Therefore 1, 2 and 3 µg/mL cultures were taken for the study. Percent sorption increased with increase in biomass from 1 to 3 µg/mL as well as with increase in contact time. Maximum percent sorption was seen at pH 8. However, at pH 8, the maximum percent sorption of ~ 65 % was already achieved by 2 h of contact time which remained constant thereafter. Having established that pH 8 and 3 µg/mL biomass is ideal for optimum biosorption, effect of temperature and varying metal concentration was studied keeping the pH and biomass at 8 and 3 µg/mL respectively. As seen from the Fig. 2 the best biosorption was at 30°C with maximum sorption of ~65% was reached within 2 h from a solution containing 10 ppm Zn. Therefore for all further experiments the temperature was set at 30°C, pH at 8, biomass concentration at 3 µg/mL and metal concentration was fixed at 10 ppm.

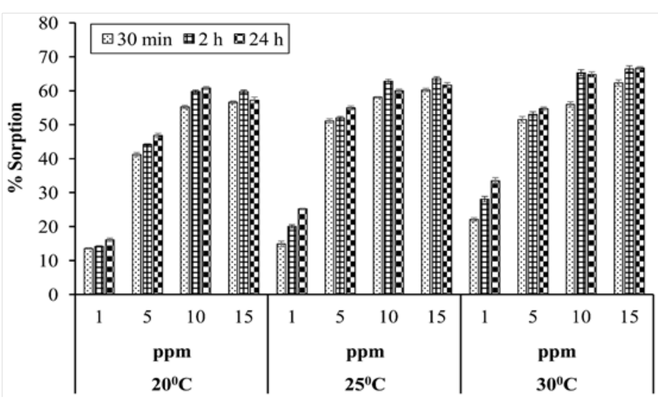

Fig. 2 Effect of temperature and metal concentration on the % Zn sorption at pH 8 and biomass concentration of 3 µg/mL.

Various other researchers have worked on Zn removal efficiency in different organisms. A comparison drawn among these organisms is presented in Table 1. The *Nostoc* sp. used in our study had recorded a very competitive Zn removal percentage among the other organisms reported.

Table 1 A comparison of % Zn removal by different organisms

Organism	Zn Removal %	Authors
Pseudomonas veronii 2E	50%	Vullo *et al*. 2008 [56]
Nostoc muscorum *Anabaena subcylindrica*	73.2% 51.53%	Mane and Bhosle, 2012 [57]
S. neglecta *P. oedogonia* *C. calliceima* *H. reticulatum*	83% 58% 63% 34%	Singh *et al*. 2007 [58]
Nostoc sp.	73%	Diengdoh *et al*. [59]
Nostoc sp.	65%	Current study

3.2 FTIR spectrum

A comparative FTIR analysis presented in the Fig. 3 showed changes in the peak patterns of Zn treated cells in comparison to the control cells, inferring binding of metal ions. Table 2 highlights the functional groups of the cyanobacterial cell surface that were involved in metal binding. A shift in the region of 1050-1645 cm^{-1} indicated contribution of C-O groups. Involvement of carboxylic group was evident from the vibrational shift from 1690-1630 cm^{-1}. Shift in frequency from 2950-2850 cm^{-1} specified alkyl stretch. Shift towards higher frequency between 3550-3200 cm^{-1}region indicated involvement of O-H groups.

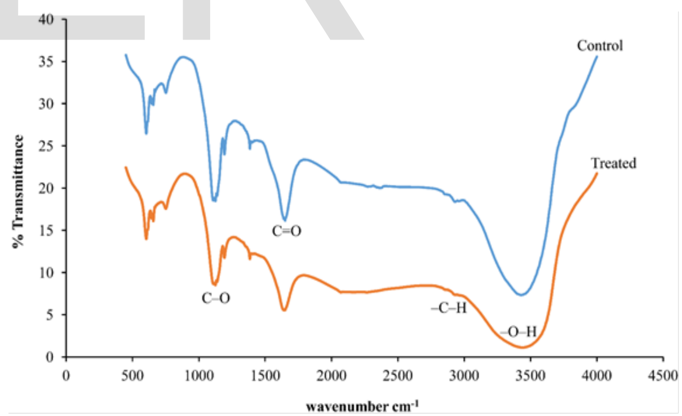

Fig. 3 FTIR spectra of control and Zn treated *Nostoc* sp. cells after 24 h incubation.

Table 2 Comparative table showing shift in peaks as seen in the FTIR spectra [60]

Observed peaks in		Absorption location Wavenumber (cm^{-1})	Corresponding Functional group
Control (cm^{-1})	Treated (cm^{-1})		
1124	1122	1050-1645	C-O
1651	1624	1690-1630	C=O(amide stretch)
2926	2920	2950-2850	C-H (alkyl stretch)
3467	3450	3550-3200	O-H(alcohol/phenol stretch)

3.3 Evaluation of sorption performance

In order to analyse sorption performance for Zn removal, experimental data recorded were fitted into Langmuir and Freundlich isotherm models (Fig. 4a and Fig. 4b). The temperature for the isotherm study was maintained at 30°C. The various Langmuir and Freundlich isotherm parameters are listed in Table 3. Langmuir isotherm was best fitting with a R^2 value of 0.986 as against that of Freundlich R^2 value of 0.857 for 2 h. The 2 h contact period was considered for the equilibrium isotherm study as this length of contact time was enough for maximum biosorption (Fig. 1).

3.4 Evaluation of thermodynamic parameters

The feasibility of spontaneity of interaction between the cyanobacterial biomass and the Zn ions were evaluated by studying various thermodynamic parameters of the interaction. A Van't Hoff plot drawn between ln *K* and *1/T* resulted in a highly linear plot for Zn sorption by the cyanobacterium (Fig. 5).

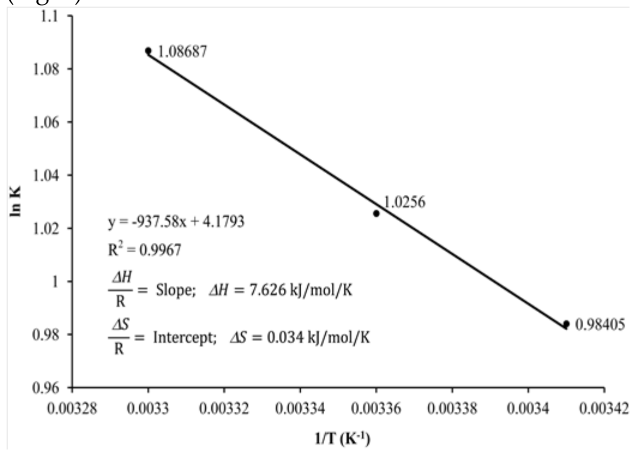

Fig. 5 Van't Hoff plot of *1/T* vs ln *K* for the absorption of Zn (10 ppm). The slope and intercept of the plot yielded the thermodynamic parameters *ΔH* and *ΔS*.

Table 3 Langmuir and Freundlich adsorption isotherm parameters of Zn-treated *Nostoc* sp. KX814344

Temperature	Langmuir Isotherm								Freundlich Isotherm		
	Time	Q_{max} (mg/g)	K_L (L/mg)	R^2	R_L values for the studied concentration range						
					5 ppm	10 ppm	15 ppm	20 ppm	*n* (g/L)	K_F (mg/g)	R^2
30°C	2 h	4.314	0.46	0.986	0.3	0.17	0.12	0.1	1.94	2.041	0.857

The organism's maximum sorption capacity, Q_{max} was calculated to be 4.3 mg of Zn taken up per gram of the *Nostoc* sp. biomass within this period. The calculated value obtained for *n* (1.93 g/ L) indicated favourable sorption for Zn by this cyanobacterial biomass that corroborates earlier findings by Lai and Goldberg [32], [55]. The separation factor (R_L) that predicts the nature of interaction of the biomass with the metal ions, calculated for each concentration in the range studied, was found to be <1 indicating favourable interaction (Table 3).

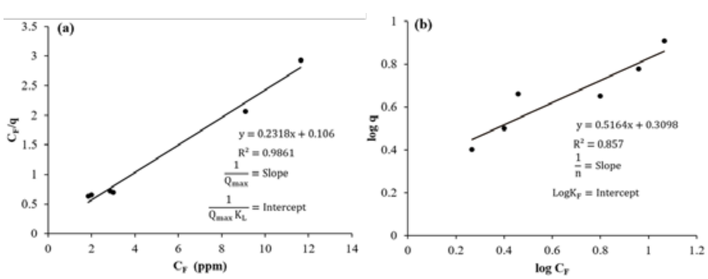

Fig. 4(a) Langmuir isotherm plot (b) Freundlich isotherm plot

Table 4 The Gibbs free energy change (*ΔG*) for Zn sorption by *Nostoc* sp. (GenBank Accession No.KX814344)

ΔH (kJ/mol)	*ΔS* (kJ/mol/K)	Gibbs Free Energy (*ΔG=ΔH-TΔS*) (kJ/mol)		
		293 K	298 K	303 K
7.626	0.034	-2.336	-2.506	-2.676

All values for *ΔG* calculated (Table 4) for the three temperatures studied produced negative values indicating the process of Zn biosorption to be spontaneous. As seen from the graph, ln *K* values increased from 0.098 to1.03 to1.09 as temperature was raised from 293K to 298K to 303K respectively identifying the affinity of the *Nostoc* sp. for Zn ions as a function of temperature. The intercept and the slope of the plot provided the *ΔH* i.e. the change in enthalpy with a value of 7.626 kJ/mol and *ΔS*, the entropy change with a value of 0.034 kJ/mol/K respectively. The positive *ΔH* value indicated the process to be endothermic and positive *ΔS* value that signified increase in randomness indicated the thermodynamically favourable nature of Zn sorption. In totality Langmuir and Freundlich isotherm modelling as well as thermodynamic studies showed that Zn sorption on the *Nostoc* sp. cells was a favourable and spontaneous process.

4. CONCLUSION

Research over the years have established that many factors influence biosorption potential of various organisms. Of different physico-chemical factors, pH is possibly the most important. Metal biosorption has frequently been shown to be strongly pH dependent in almost all systems reported, including bacteria, cyanobacteria, algae, and fungi [57]. However other factors also contribute towards the removal efficiency. The temperature, surface area to metal ion ratio, contact time also play important role in determining sorption competence of an organism. The charge and the ionic radii of the metal ions and the various cell surface functional groups eventually decide the total binding capacity. As pointed out earlier using live biomass is advantageous to dead biomass as if the conditions are kept optimal for the organism's growth there is possibility of newer cell surface being generated by the dividing cells for continuous binding of metal ions. Cyanobacteria being both photosynthetic and nitrogen-fixing require minimal nutrient input for their growth and therefore are economically viable to be considered for bioremediation of various pollutants including heavy metal ions from wastewater. This study provided evidence that the process of biosorption of Zn is energy independent, spontaneous and relatively quick which further establishes the potential of using this organism in bioremediation of heavy metals. Moreover, the use of a locally isolated cyanobacterium for the purpose of this study involving heavy metal removal may be regarded as a stepping stone towards use of such readily available indigenous strains of cyanobacteria as a continuously renewable source of biomass in bioreactor systems employed for bioremediation of heavy metal contaminated waters.

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