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Biosorption of chromium Cr (IV) by indigenously isolated Non-living biomass of *Nostoc* sp.

Pandav Parag Vishwanath[1], Javalkote Vivek Shiwshankar[1] and Patil Liladhar Shivram[2]

[1]Department of Biotechnology, School of Life Sciences, North Maharashtra University, P.O. Box No. 80, Umavinagar,

Jalgaon- 425001, (MS), India.

[2]TVS's Loksevak Madhukarrao Chaudhari College of Pharmacy Nehru Vidyanagar, Faizpur, Dist-Jalgaon 425503 India

Author for correspondence: Email: parag.alga@gmail.com

Abstract

Biosorption is cost-effective and well documented process for the removal and recovery of heavy metal ion from aqueous solutions. The microalgae have been reported to have biosorption capacities for heavy metals. Removal of toxic metal Cr (IV) from aqueous solution by dried biomass of *Nostoc* sp. (collected from indigenous site) was investigated. Batch biosorption experiments were carried out to describe the effects of parameters (biomass dosage, initial metal concentration, pH and contact time) were studied. The kinetics of biosorption was described with Langmuir and Freundlich model isotherm. The adsorption of Cr (IV) supported Langmuir isotherm model for adsorption with their R^2 value 0.965. The adsorption was strongly pH dependent as maximum Cr (IV) biosorption occurred at pH 3. The maximum biosorption capacity of Cr (IV) metal ions was 10.54 mg/g at biomass dosage 1 g/L, pH 3 and contact time 120 min. This study demonstrated that *Nostoc* sp. constitute a promising, efficient, cheap, environmental friendly and biodegradable sorbent biomaterial for removing the heavy metal pollution in the environment.

Keywords: Biosorption, *Nostoc*, Chromium, Langmuir isotherm, Freundlich isotherm.

Introduction

Recently, environmental pollution due to heavy metals is a serious worldwide problem. The heavy metals are release from industrial waste. Presence of heavy metals in aquatic ecosystem poses human health risks, and cause harmful effects to aquatic organisms and also to the consumers of them. The effort have been made to remove such heavy metals from the environment by using conventional technologies such as ion exchange or limit precipitation, reverse osmosis, evaporation and adsorption (Selvaraj K., 2003) are expensive and insufficient for removal of heavy metal ions and also leads to create of toxic sluge which then adds on technoeconomic possibility of treatment process (Volesky B., 1994; Ahluwalia S.S. and Goyal D., 2007). Chromium exists in several oxidation states, from which Cr (IV) is highly mobile and toxic. It is widely used in industries for commercial process (Sathvara *et al*., 2007).

Biosorption proved to be an alternative method which is effective, economic as well as environment friendly. It is well accepted process used as a wastewater treatment and various microalgae adsorbents were investigated in the literature (Gaur J., 2009; Abuzer et al., 2010; Kumar D. and Gaur N.P, 2011) due to their small size have a high surface area to volume ration and therefore provide large contact area for metal binding (Zhou J.L. 1998 and Zouboulis A.I., 2004). For instance, the metal-binding capacities of several biological materials have been identified to be very high, including marine algae, fungi and yeasts (Chen, 2005).

Biosorption technology based on the utilization of dead biomass offers definite advantages. Cyanobacteria are the largest and most diverse group of prokaryotes oxygenic photosynthetic. They are found from fresh and marine to terrestrial environments (Chinnasamy *et al*., 2007). They are suggested to have advantages because of their large surface area, greater mucilage volume with high binding affinity and simple nutrient requirements (Roy *et al*., 1993).

The present work is to investigate, the removal of chromium metal of indigenous cyanobacterium non-living biomass of *Nostoc* sp from aqueous solution. *Nostoc* is a blue green filamentous alga found in ponds, ditches and other pools where gelatinous matter is present.

Our earlier communicated papers we have reported the tolerance of Cr (IV) indigenous *Nostoc* sp. The present work aims to examine the non-living biomass of indigenous *Nostoc* sp. was characterized for its Cr (IV) removal potential from aqueous solution and the experimental parameters affecting the biosorption process such as pH, biomass dosage, initial metal ion concentration and contact time was investigated for metal sorption process along with equilibrium sorption kinetics.

Material and method

Biomass preparation and culture medium

In this experiment *Nostoc* sp. was used and tested for its adsorption capacity. Sample of the *Nostoc* sp. was collected from indigenous terrestrial site, which was isolated thoroughly pure using standard isolation and culturing procedures (Mostafa *et al*., 2006; Torrecilla *et al*., 2004). Identification of pure culture was carried on the basis of criteria given in literature (Prescott, 1970; Anagnostidis K. and Komarek J, 1988) and purified *Nostoc* sp. was cultivated (Yavuz *et al*., 2006). Medium was sterilized by autoclaving at 121ºC for 20 min. After 21 days cultivation period cells were harvested by centrifugation and rinsed thoroughly with distilled water in order to remove debris. The harvested biomass was kept on a filter paper to diminish the water content. The biomass was oven dried at 60ºC for 24 h, then ground with mortar and pestle to a gritty consistency and sieved to a particle size smaller then 1mm. The biomass was stored in airtight polyethylene bottles and keeps in dry cabinet for experiments.

Reagents and equipments

A stock solution of 1000 mg/L of Cr (IV) metal was obtained by (Hi media) dissolving in distilled water. Working solutions of various concentrations range from 10 mg/L to 100 mg/L were prepared by diluting the stock solution with distilled water. The solution pH was adjusted using 0.1 M NaOH and 0.1 M HNO_3 at beginning of the experiment. The Erlenmeyer flasks (250 mL) were shaken at 120 rpm in rotary shaker.

The Cr (IV) metal concentrations in solution were determined using flame atomic absorption spectrophotometer (Thermo, USA) with deuterium background corrector. All measurements were carried out in an air/acetylene flame.

Batch biosorption experiment

Batch mode of adsorption studies were carried out in Erlenmeyer flasks to investigate the effect of different parameters such as adsorbent dose, adsorbate concentration, optimum pH and contact time. Solution containing adsorbate and adsorbent was taken in 250 mL capacity Erlenmeyer flasks and agitated at 120 rpm in a shaker. The contents of the flask were filtered through whatman filter paper No.1 and the filtrate was analyzed for metal concentration by using flame AAS.

Determination of adsorbent dosage

In order to investigate the optimum adsorbent dosage for Cr (IV) metal biosorption i.e., the amount of biomasses on the adsorption was studied at different dosage ranging from 0.1 to 2 g were added to different flask containing 100 mg/L Cr (IV) metal solution. Flasks were agitated at room temperature (25±2ºC) for 2 h at 120 rpm in shaker. The sample were analysed by AAS and the metal adsorption (q) and the percentage of biosorption were calculated according to the following equation:

$$q = (C_i - C_f)\, V / M$$

$R\ (\%) = (C_i - C_f)/\ C_i \times 100$

Where, q is metal adsorption (mg/g), V is volume of initial ion metal solution (L), M is dry mass (g) and C_i and C_f are initial and final metal ion concentrations (mg/L), respectively.

Determination of metal concentration

For the determination of rate of metal biosorption by biomasses from 100 ml at different concentrations (10, 20, 40, 60, 80 and 100 mg/L) on Erlenmeyer flask 250 mL, the supernatant was analyzed for residual Cr (IV) metal at different concentrations. The pH-5±0.01 and adsorbent dosage 1±0.01 g was kept constant and agitated at room temperature (25±2ºC) at 120 rpm in shaker. The sample were analysed by AAS and percentage of biosorption was calculated as mentioned above.

Determination of pH

The pH for Cr (IV) metal biosorption was investigated by adding 1 g of *Nostoc* sp. biomass to 100 mg/L Cr (IV) metal solution adjusted to various pH values (1-6) using 0.1 M NaOH and 0.1 M $HNO_{3.}$ Flasks were agitated at room temperature (25±2ºC) for 2 h at 120 rpm in shaker. The sample were analysed by AAS and percentage of biosorption was calculated as mentioned above.

Determination of contact time

A quantity of 1 g biomass was added to 50 ml Cr (IV) metal solution adjusted to pH-5. Flasks were agitated at 120 rpm and room temperature (25±2ºC) in shaker. Samples were taken at t = 5, 10, 15, 30, 60, 90, 120, 150, 180 and 200 min and the sample were analysed by AAS.

Results and discussion

Effect of biomass dosage

The effect of biomass dosage on the biosorption of Cr (IV) metal ion was studied using different biomass dosage in the range 0.1 to 2 g/L (Fig.1.).

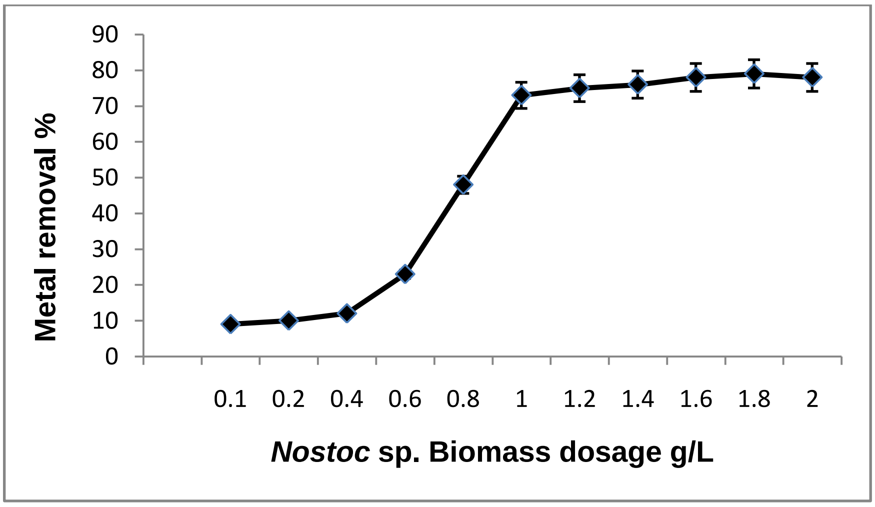

Fig. 1. Effect of biomass dosage on biosorption of Cr (IV) by *Nostoc* sp. (biomass dose= 0.1 – 2 g, pH= 3 metal concentration = 100 mg/L, agitation speed = 120 rpm)

Results showed that biosorption efficiency was highly dependent on the increase in biomass dosage. The maximum biosorption (79%) of Cr (IV) metal ion was attained by increasing biomass dosage 0.1 to 2 g/L from 100 mg/L of Cr (IV) metal containing solution. This can be expected because the maximum dose of biosorbent in the solution, the greater availability of exchangeable sites for the ions. This could be accredited to a partial aggregation of biomass which reduces effective surface area for the biosorption. Therefore, the maximum biomass dosage was selected as 1 g/L for further experiments.

Determination of metal concentration

The effect of metal concentration on the biosorption studies carried out for Cr (IV) metal ion using different Cr (IV) concentration ranges from 10 to 100 mg/L by 1 g of *Nostoc* sp. biomass exhibited effective role of initial metal ion concentration on metal removal. Results showed that biosorption efficiency was consistently decreased in metal biosorption by increasing external Cr (IV) metal concentrations (Fig. 2.).

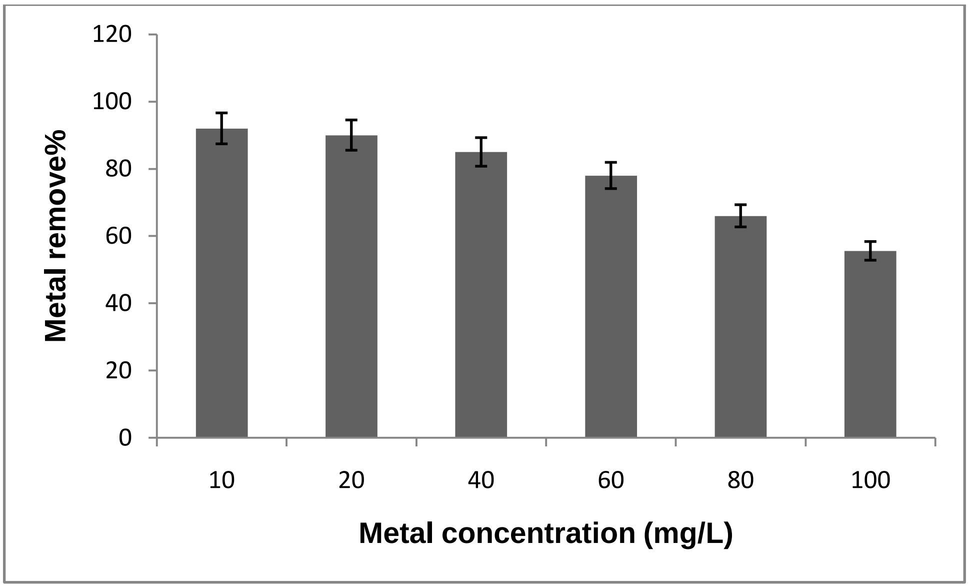

Fig. 2. Effect of initial metal concentration of Cr (IV) on biosorption by *Nostoc* sp. (biomass dose= 1g, pH= 3 metal concentration = 10, 20, 40, 60, 80 and 100 mg/L, agitation speed = 120 rpm)

36.42% decrease Cr (IV) biosorption efficiency was observed by increasing external zinc metal concentration from 10 to 100 mg/L with maximum 92% biosorption from solution containing 100 mg/L solution.

Effect of solution pH

pH is the important parameter affecting the biosorption of metal ions is acidity of solution by *Nostoc.* The pH solution affects the cell wall metal binding sites and metal ion chemistry in water. Various authors (Anjana K. *et al* 2007; Kiran B. 2007 and Razaei H., 2011) have shown that solution pH greatly influences metal biosorption by algal biomass. Therefore to examine the effect of pH on the biosorption efficiency, the experiment were carried out at different pH values ranges from 1 to 6 at 100 mg/L as shown in (Fig. 3.).

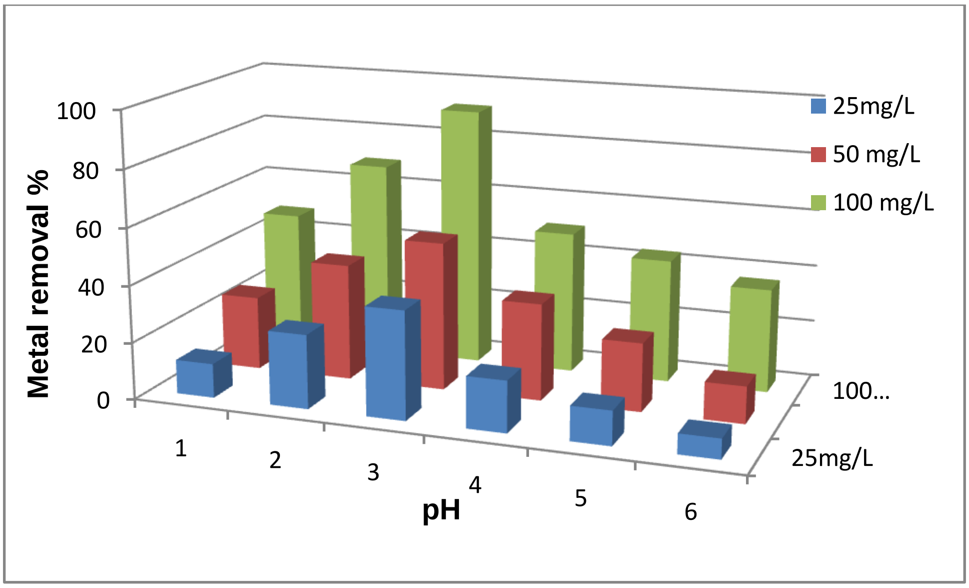

Fig. 3. Effect of pH on biosorption of Cr (IV) by *Nostoc* sp. (biomass dose= 1g, pH=1, 2, 3, 4, 5 and 6 metal concentration = 25, 50, 100 mg/L, agitation speed = 120 rpm)

Equilibrium Chromium sorption was favoured by acidic pH ranges 2-3. The biosorption capacity increases up to pH 3 where the maximum biosorption efficiency was obtained (91.6 %). Increase in pH decreased the biosorption of chromium by blue green algae. At higher pH values, the biosorption of metal ion were significantly decreased (36.4 %). Therefore all further biosorption experiments were carried out at pH 3.

Effects of contact time

The contact time rapid metal biosorption profile was also evaluated as one of the most important factors affecting the biosorption efficiency. It was obtained by following the decrease of the metal concentration of Cr (IV) ions within the adsorption medium with time (Fig. 4.).

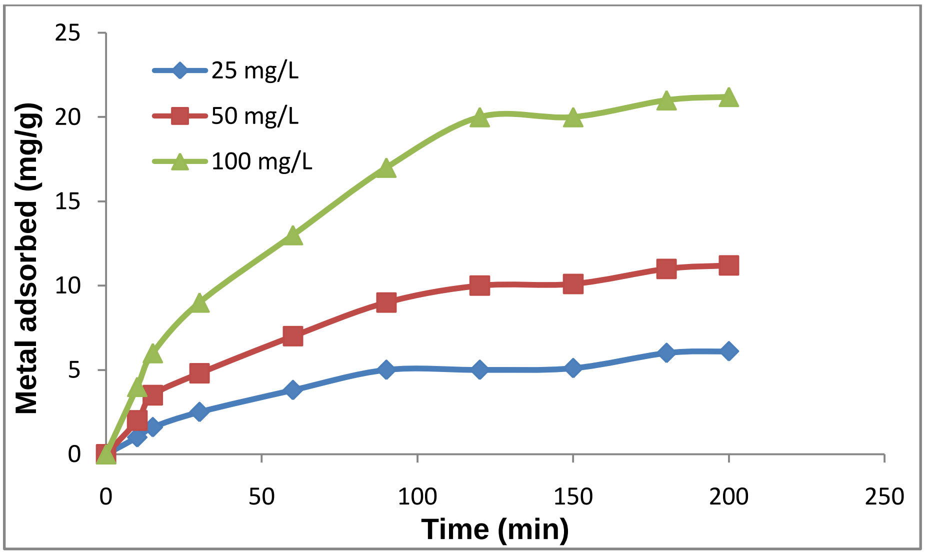

Fig. 4. Effect of contact time on biosorption of Cr (IV) by *Nostoc* sp. (biomass dose= 1g, pH=3, metal concentration = 25, 50, 100 mg/L, agitation speed = 120 rpm)

The figure showed the biosorption efficiency of Cr (IV) metal ions by *Nostoc* biomass as a function of contact time. It also shows the comparative data of the effect of contact time on extent of biosorption of Cr (IV) on biomass at 25, 50 and 100 mg/L initial metal concentration. The biosorption efficiency significantly enhanced by increasing the contact time up to 120 min and above that it was more or less constant. It exhibited rapid biosorption in first 120 min (90.0%) of Cr (IV) from metal solution. Therefore, the optimum contact time was selected as 120 min for further experiments.

Biosorption equilibrium isotherm model

Biosorption equilibrium isotherm was established between absorbed Cr (IV) metal ions and the metal ions in the solution after 120 min with maximum biosorption efficiency with 90% (Fig. 3.). Increase in metal biosorption efficiency from 100 mg/L metal solution for Cr (IV) was observed on increasing biomass dosage (Fig. 1.).

A biosorption equilibrium isotherm studies were performed in the solution with Cr (IV) metal concentration ranging from (10 to 100 mg/L) at optimum pH values for ions (pH = 3). After agitating the flask in the shaker (120 rpm, 25ºC) for 2h the flask containing mixture of biomass and ion, the amount of the residual ions in the filtrate solution was analyzed. In this study, Langmuir isotherm model was selected to fit experimental data. This model assumes that the sorpt ion process takes place at a specific sorption surface. Langmuir isotherm model can be defined following equation:

$$q = q_{max} C_f b / 1 + C_f b \qquad (3)$$

After arrange we have;

$$C_f/q = 1/ q_{max} b + C_f / q_{max}$$

Where q is the equilibrium metal ion concentration on the adsorbent (mg/g), C_f equilibrium metal ion concentration in the solution (mg/L), q_{max} is monolayer biosorption capacity of the adsorbent (mg/g) and b is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption. q_{max} and b can be determined from the linear plot of C_f / q versus C_f (Fig. 5.).

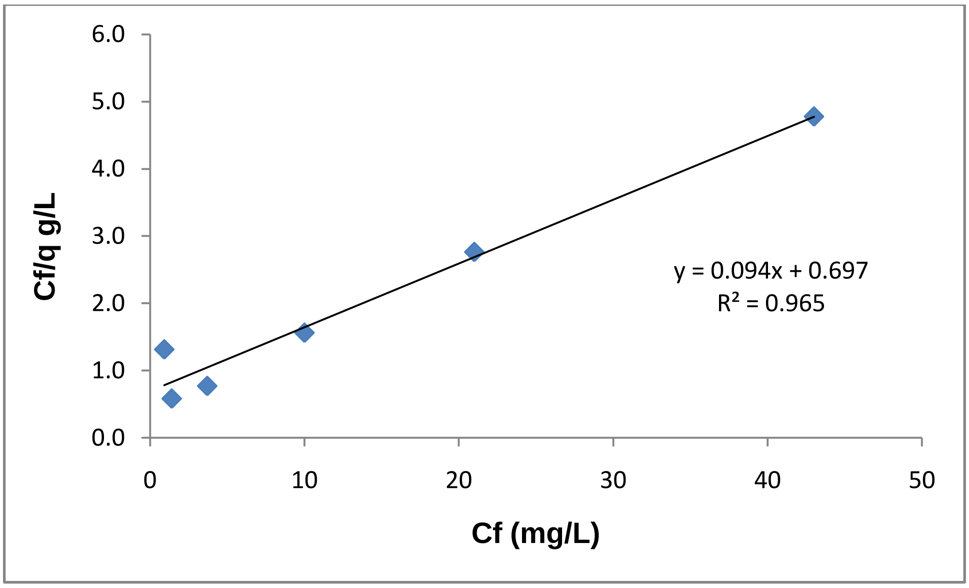

Fig. 5. Langmuir adsorption isotherm models for Cr (IV) by *Nostoc* sp. (q_{max}=10.54 mg/g, b=0.135 L/mg)

The empirical Freundlich equation based on sorption on a heterogeneous surface is given by following equation:

$$q = kC_f^{(1/n)} \qquad (4)$$

Where k and n are constant characteristic of system and indicator of adsorption capacity and adsorption intensity, respectively. Equation can be linearized in logarithmic form and Freundlich constant can be determined (Fig. 6.).

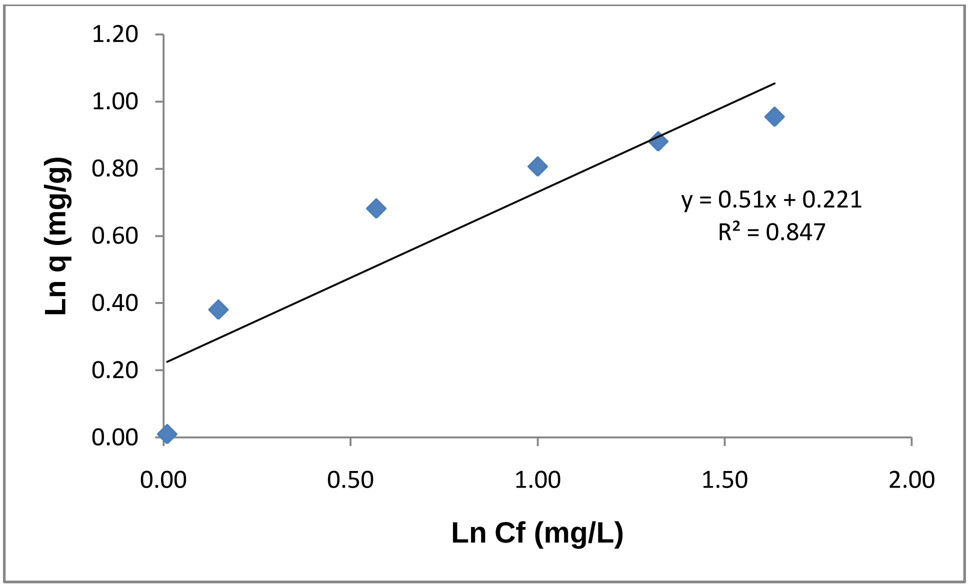

Fig. 6. Freundlich adsorption isotherm models for Cr (IV) by *Nostoc* sp. (n=1.96, k=0.37)

The equilibrium experimental results of Cr (IV) ions have been fitted in the Langmuir and Freundlich isotherm models (Fig. 5.) and (Fig. 6.) indicates the linear relationship between the amounts (mg) of Cr (IV) metal ions sorbed per unit mass (g) of *Nostoc* sp. against the concentration of Cr (IV) metal ions remaining in solution (mg/L) (Table.1.) describes summaries of linear regression data for Langmuir and Freundlich isotherms for Cr (IV) biosorption using *Nostoc* sp. biomass.

Table. 1. Parameters of isotherm models for chromium Cr (IV):

Biomass	Langmuir parameter			Freundlich parameter		
	q_{max} (mg/g)	b (L/mg)	R^2	$k_f(mg^{1-n}/g\ l^n)$	n	R^2
Nostoc sp.	10.54	0.135	0.965	0.37	1.96	0.847

Langmuir and Freundlich constant b and k were obtained from the linear equations of both models b= 0.135 (L/mg), k= 0.37 ($mg^{1-n}/g\ l^n$) and n= 1.96 given in (Table.1.). The correlation coefficient (R^2) was 0.965 and 0.847 for Cr (IV) metal biosorption Langmuir and Freundlich respectively. The (R^2) value indicated that the equilibrium data better fitted to the Langmuir isotherm model. As shown from (Table.1.) the maximum biosorption capacities (q_{max}) was 10.54 mg/g by 1 g/L of *Nostoc* sp. biomass. Therefore, it can be noteworthy that the *Nostoc* sp. has considerable potential for the adsorbent of Cr (IV) metal ions from aqueous solution.

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Conclusions

This study focused on the biosorption of Cr (IV) metal ions onto non-living biomass of indigenously isolated *Nostoc* sp from aqueous solution. The operating parameters such as biomass dosage, initial metal ion concentration, pH of solution and contact time affected the biosorption efficiency of Cr (IV) metal ions. The biomass of *Nostoc* demonstrated a high capacity of metal biosorption. According to this investigation, non-living biomass of *Nostoc* can be used as an alternative and effective biomass for the removal of heavy metal ions from industrial effluents due to being natural, renewable, high biosorption capacity, cost-effective and environmental friendly.

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