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Sorption and desorption studies of chromium(VI) from nonviable cyanobacterium *Nostoc muscorum* biomass

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Abstract

This communication presents results pertaining to the sorptive and desorptive studies carried out on chromium(VI) removal onto nonviable freshwater cyanobacterium (*Nostoc muscorum*) biomass. Influence of varying the conditions for removal of chromium(VI), such as the pH of aqueous solution, the dosage of biosorbent, the contact time with the biosorbent, the temperature for the removal of chromium, the effect of light metal ions and the adsorption–desorption studies were investigated. Sorption interaction of chromium on to cyanobacterial species obeyed both the first and the second-order rate equation and the experimental data showed good fit with both the Langmuir and freundlich adsorption isotherm models. The maximum adsorption capacity was 22.92 mg/g at 25 °C and pH 3.0. The adsorption process was endothermic and the values of thermodynamic parameters of the process were calculated. Various properties of the cyanobacterium, as adsorbent, explored in the characterization part were chemical composition of the adsorbent, surface area calculation by BET method and surface functionality by FTIR. Sorption–desorption of chromium into inorganic solutions and distilled water were observed and this indicated the biosorbent could be regenerated using 0.1 M HNO_3 and EDTA with upto 80% recovery. The biosorbents were reused in five biosorption–desorption cycles without a significant loss in biosorption capacity. Thus, this study demonstrated that the cyanobacterial biomass *N. muscorum* could be used as an efficient biosorbent for the treatment of chromium(VI) bearing wastewater.

Keywords: Biosorption; *Nostoc muscorum*; Chromium(VI); Langmuir model; Kinetics; Sorption–desorption

1. Introduction

A manifold enhancement in industrialization in many regions has raised the discharge of industrial wastes, especially those containing heavy metals, into natural water bodies or on land. Their presence in the aquatic ecosystem poses human health risks, and causes harmful effects to living organisms in water and also to the consumers of them. Chromium is one such heavy metal presenting aquatic ecosystem which is widely used in electroplating, leather tanning, metal finishing and chromate preparation. Though chromium exists in nine valence states ranging from −2 to +6, Cr(III) and Cr(VI) are of major environmental significance because of their stability in the natural environment [1]. Cr(VI) is toxic, carcinogenic, and mutagenic to animals as well as humans and is associated with decreased plant growth and changes in plant morphology [2]. In contrast, trivalent chromium [Cr(III)] is relatively less toxic and less mobile. Hence, the discharge of Cr(VI) to surface water is regulated below 0.05 mg/L by the U.S. EPA, and total Cr including Cr(III), Cr(VI) as well as its other forms is regulated below 2 mg/L [3].

Various methods used for the removal of chromium ions include chemical precipitation, reverse osmosis, evaporation, ion exchange and adsorption [4]. These methods have been found to be limited, since they often involve high capital and operational costs and may also be associated with the generation of secondary wastes which present treatment problems. Moreover, these methods are not effective at metal concentrations ranging from 1 to 100 mg/L [5]. The use of microbial biosorbents like bacteria [6] fungi [7], yeast [8], algae [9–11] and cyanobacteria [12] for removal of toxic chromium from waste streams has emerged as an alternative to the existing methods as a result of the search for low cost, innovative methods. Biosorption may occur actively through metabolism or passively through some physical and chemical processes. Biosorption technology based on the utilization of dead biomass offers certain major advantages

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such as lack of toxicity constraints, non-requirement of nutrient supply, and recovery of bound metal species by an appropriate desorption method [13].

Cyanobacteria are suggested to have some added advantages over other microorganisms because of their large surface area, greater mucilage volume with high binding affinity and simple nutrient requirements [14]. Here, we report the metal chromium removal ability of a cyanobacterium *Nostoc muscorum* from aqueous solutions. *N. muscorum* is a cyanobacterium or a blue green alga of filamentous form which occur in ponds, ditches and other pools of water having some gelatinous matter on surface. It is advantageous to carry out biosorption studies on a cyanobacteria *N. muscorum*, as it grows better under low nutrient conditions and generally do not produce any toxic substances as compared to other microbes like bacteria and fungi. Also, they are capable of not only photosynthesis but also nitrogen fixation. Additionally, they can grow under high pH conditions which can prevent contamination by other organisms. Therefore, cyanobacteria can be cultivated under outdoor conditions or in large-scale laboratory cultures at low cost and thus providing a reliable and consistent supply of biomass for such studies and eventual scale-up work. Thus, the utilization of cyanobacteria may be one means of solving problems of hazardous waste in countries of the region.

If the biosorption process is to be used as an alternative in wastewater treatment, the biosorbent regeneration may be crucially important to keep low processing costs and open the possibility to recover the extracted metals from the liquid phase. The desorption process give up metals in a concentrated form, which facilitates disposal and restores biosorbent for effective reuse [15,16]. The desorption mechanism is similar to ion exchange, where metals are eluted from the biosorbent by an appropriate solution to give a small, concentrated volume of metal containing solution. The biomass stripping can be achieved with a relatively inexpensive acid such as HCl, HNO_3 and H_2SO_4 [17–19]. Leaching of metal ions from contaminated soils using EDTA has been performed [20], and the same eluant has been used, as metal chelating agent, in the regeneration of macroalgae and microalgae [21,22].

In our earlier communicated papers we have reported the uptake of Pb(II) by an unknown species of *Nostoc* so, in the same sequence it was considered worthwhile to examine the uptake of another toxic heavy metal Cr(VI) by nonviable cyanobacterium *N. muscorum* biomass. Attempts have been made to understand the kinetics of this sorption process employing pseudo-first- and second-order rate equations. Langmuir and freundlich adsorption isotherms are employed to understand the nature of sorption.

2. Experimental

2.1. Materials/chemicals

All reagents used were of AR grade either from Merck, Germany or SD Fine Chem. Ltd., India and solutions were prepared using milli-Q water. Standard solution of Cr(VI) (1000 mg/L) for atomic adsorption spectrometry was obtained from Merck, Germany. To adjust the pH, 0.1N HCl and 0.1N NaOH solutions were used. The solutions of 0.1 M $NaNO_3$, KNO_3, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $NaNO_3$, NaCl, $Na_2C_2O_4$ and Na_2EDTA were prepared for the effect of light metal ions and anionic ligands.

2.2. Equipment

The pH measurements were made using a pH meter (model cyber scan 510, Singapore). The chromium solutions were analyzed using an atomic adsorption spectrophotometer model Z-7000 (Hitachi, Japan) at a wavelength of 357.9 nm. Carbon content was measured by Elementar CHNS analyzer model Vario EL III (Vario EL, Elementar Analyser systeme GmbH, Hanau, Germany). Infra red spectra of the samples were recorded on a Perkin-Elmer FTIR, Spectrophotometer model −1600 (Perkin-Elmer, USA) and surface analysis of the biosorbent was done by BET method using a quantasorb surface analyzer.

2.3. Biomass

Fresh biomass of cyanobacterium *N. muscorum* was sampled from a pond near Roorkee, India. Before use, the biomass was washed with distilled water to remove dirt and then was kept on a filter paper to reduce the water content. The biomass was then sun dried for 4 days followed by drying in an oven at 70 °C for 24 h. Subsequently it was ground on an igate stone pistol mortar. The biomass was then sieved to select the particles between 150 and 250 mesh sizes for use.

2.4. Batch adsorption studies

The stock solution of Cr(VI) (1000 mg/L) was prepared in milli-Q water with potassium dichromate, $K_2Cr_2O_7$ (Merck, Germany). This was further diluted to get desired concentration for practical use.

To observe the effect of pH of metal ion on its uptake by the cyanobacterium *N. muscorum*, the initial pH values of the Cr(VI) solutions were adjusted to 1.0–4.0 with 0.1 M HCl or 0.1 M NaOH using a pH meter. The adsorption experiments were conducted by constant shaking at 25 °C for 24 h. At the end of adsorption, 1 mL sample was collected and centrifuged at 1500 rpm for 10 min on a centrifuge. The remaining concentration of lead in residual solution was analyzed by taking absorbance on the atomic absorption spectrophotometer. The adsorption capacities at different initial pH were obtained by mass balance calculations. The experiments were repeated three times and average values were reported. Standard deviations were found to be within ±1.5%. Further, the error bars for the figures were so small as to be smaller than the symbols used to plot the graphs and, hence, not shown.

To determine the effect of biosorbent dose, different dose of cyanobacterium was varied and suspended in chromium solutions of fixed initial concentration. The adsorption procedures were the same as described for the effect of pH on adsorption capacity.

To obtain adsorption isotherms the cyanobacterium under study was suspended in chromium solutions (conc. range

10–100 mg/L). The experiments were carried out at three different temperatures, i.e. 25, 35 and 45 °C. The adsorption procedures were same as described for the effect of pH on adsorption capacity.

Kinetic studies of adsorption by cyanobacterium (*N. muscorum*) under study was also carried out at three initial chromium concentrations (25, 50 and 100 mg/L) at 25 °C wherein the extent of adsorption was analyzed at regular time interval.

2.5. Desorption/reuse experiments

For the desorption study, 1.0 g biomass was contacted with 50 mL Cr(VI) solution (100 mg/L). After adsorption experiment, the biomass was collected by filtration on an 0.45 μm Millipore filtration assembly and washed with distilled water for three times, to remove residual Cr(VI) on the surface. Then it was transferred to 50 mL desorbent solutions: deionised water, 0.1 M HCl, HNO_3 and H_2SO_4, 0.2 M $CaCl_2$ and $MgCl_2$, 0.5 M KOH and NaOH, 5% HCHO, 0.1 M EDTA. The mixtures were shaken for overnight, then the filtrates were analyzed to determine the concentration of Cr(VI) after desorption. Desorption ratio was given as

$$\text{desorption ratio} = \frac{\text{amount of metal ions desorbed}}{\text{amount of metal ions adsorbed}}$$

Percent desorption values were obtained by multiplying the above ratio by 100.

2.6. Effect of cations and anions on biosorption

The effect of light metal ions and anionic ligands were studied by using 1 g/L biosorbent and 100 mg/L Cr(VI) solution containing respective cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) and anions (NO_3^-, Cl^-, $C_2O_4^{2-}$ and EDTA). Blank samples without light metals and anionic ligands were used as controls.

2.7. FTIR analysis

Infrared spectra of control (biomass without Cr(VI) treatment) and the biomass mixed with 100 mg/L Cr(VI) at initial pH 3.0 for 2 days was obtained using a Fourier transform infrared spectrometer. A measured amount of biomass was mixed with KBr. The mixture was grounded into fine particles and composed into translucent sample disks by a manual hydraulic press. The disks were then fixed in the FTIR spectrometer for analysis.

3. Results and discussion

3.1. Characterization of the biosorbent

3.1.1. Surface area and composition

The surface area of the cyanobacterium *N. muscorum* was observed to be 1.14 m^2/g by Bruanauer Emmett and Teller method (BET method). The cyanobacterium subjected to elemental analysis showed composition of carbon, nitrogen and sulphur as 15.09, 2.23 and 5.26%, respectively.

Table 1
Surface functional groups observed on cyanobacterial biosorbent *Nostoc muscorum* by FTIR spectroscopy

Pure cyanobacterium *N. muscorum* (cm^{-1})	Cyanobacterium *N. muscorum* with Cr(VI) (cm^{-1})	Bonds indicative
3403	3405	Carboxylic/OH stretch and N–H stretch
2925	2926	Phenolic/carboxylic
1622	1619	C═O stretch, >C═C, >C═N
–	–	Quinine
1429	1426	OH bonds
–	–	─C─O stretching
1125	1127	═C─C═
1060	1062	≡C─N<
874	874	Plane deformation
710	711	
669	669	
602	602	
464	462	C–N–S scissoring

3.1.2. IR spectrum of the biosorbent

FTIR was used to analyze the functional groups in the fresh-dried cyanobacterial biomass. The results of FTIR spectra of the biosorbent *N. muscorum*, in native form and after chromium adsorption, are depicted in Table 1. Interpretations of the spectra were based on the information acquired from the literature [23–26]. There were several functional groups found in the structure of biosorbent such as carboxylic acid, hydroxyl, amine and amido, groups. On comparing fresh-dried and metal-loaden cyanobacterial biomass, it was observed that there was a shift in wave number of dominant peaks associated with the loaded metal which suggested amido, hydroxy, C=O and C–O could combine intensively with Cr(VI). This shift in the wavelength showed that there was a metal binding process taking place on the surface of the cyanobacteria [27]. Some bands in the fingerprint region could be attributed to the phosphate groups.

3.2. Biosorption studies

Biosorption of Cr(VI) by cyanobacterium *N. muscorum* was studied as a function of pH, biosorbent dose, contact time, and temperature. The biosorption data were fitted to different isotherms.

3.2.1. Effect of pH on Cr(VI) biosorption

Hexavalent chromium removal by the cyanobacterium *N. muscorum* at an initial calculated metal ion concentration of 100 mg/L was found to be pH-dependent as shown in Fig. 1. Equilibrium Chromium sorption was favoured by acidic pH range of 2–3 and maximum biosorption by the cyanobacterium (93.02%) was observed at pH 3.0. Increase in pH decreased the biosorption of chromium by the cyanobacterium. Several other studies have also shown dependence of biosorption of metal ions on pH of the solution [6,12]. Maximum metal adsorption at pH

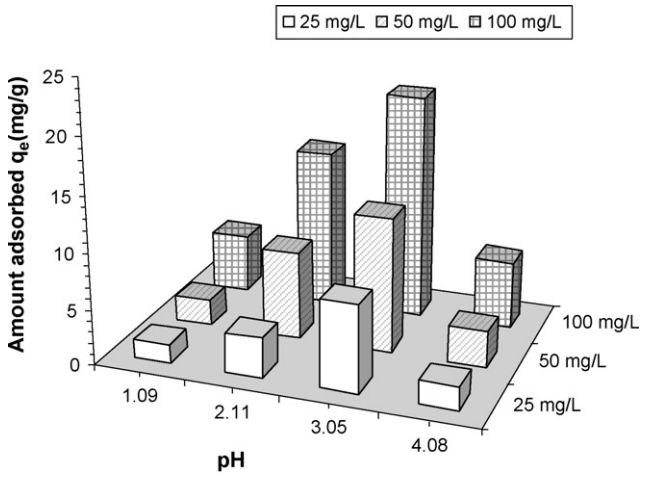

Fig. 1. Effect of pH on biosorption of Cr(VI) ions on cyanobacterial biomass *Nostoc muscorum* from aqueous solutions: temperature 25 °C; concentration of Cr(VI) ions 25, 50 and 100 mg/L; algal dose 1.0 g/L (average value of three tests, error <1.5%).

2–3 seems to be due to a net positive charge on cyanobacterial surface at low pH. Cr(VI), which may exist as $HCrO^{4-}$, $Cr_2O_7^{2-}$, etc. in solution at optimum sorption pH [28] has a tendency to bind to the protonated active sites of the biosorbent. But as pH of the solution increases, algal cell wall becomes more and more negatively charged due to functional groups, which repulse the negatively charged chromate ions thereby affecting Cr(VI) biosorption on the algal surface. However, 50–55% removal of Cr(VI) takes place even above pH 3.0, which indicates involvement of some other metal binding mechanism such as physical adsorption or ion-exchange mechanism at higher pH [29].

3.2.2. Effect of biosorbent dose

To determine the effect of biosorbent dose, different amounts (0.2–1.6 g/L) of biosorbent (*N. muscorum*) was suspended in 10 mL chromium solution in which the concentration of chromium was 100 mg/L under optimized conditions of pH and contact time. The effect of adsorbent dose on the amount of chromium(VI) adsorbed in mg/g and extent of removal of chromium for the test cyanobacteria is shown in Fig. 2. The amount of adsorbent significantly influenced the extent of chromium(VI) adsorption. The extent of Cr(VI) removal was found to be 5.6% for 0.2 g/L of biomass *N. muscorum*. It greatly increased to 64.5% for 1.0 g/L of biosorbent, respectively. However, it has been observed that there was only a slow change in the extent of Cr(VI) adsorption for the cyanobacterium, when the biosorbent dose was over 1.0 g/L. Furthermore, higher adsorbent dose result in lower adsorption capacity ($q_e = 3$ mg/g at 1.6 g/L dose for *N. muscorum*) value at a fixed Cr(VI) concentration (100 mg/L), as shown in Fig. 2. At low dose, all types of sites are entirely exposed and the adsorption on the surface is saturated faster, showing a higher q_e value. But at higher adsorbent dose, the availability of higher energy sites decrease with a larger fraction of lower energy sites occupied, resulting in a lower q_e value. Thus, an optimum dose of 1.0 g/L is selected for all the further studies.

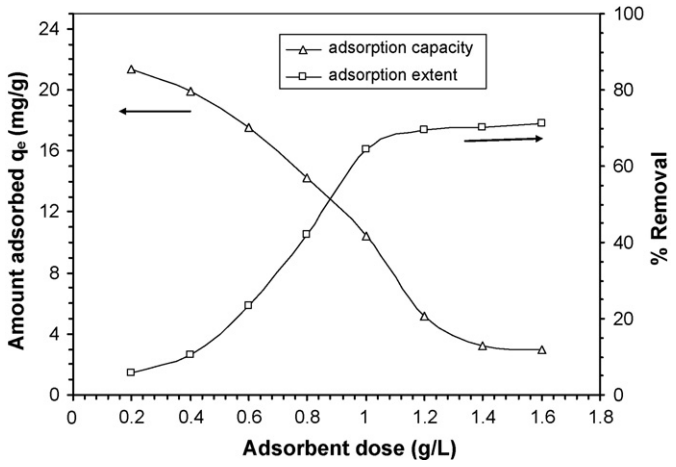

Fig. 2. Effect of adsorbent dose on the biosorption of Cr(VI) ions on cyanobacterial *N. muscorum* from aqueous solutions: temperature 25 °C; initial concentration Cr(VI) ions 100 mg/L (average value of three tests, error <1.5%).

3.2.3. Effect of contact time/biosorption rate

Chromium biosorption rate was obtained by following the decrease of the concentration of Cr(VI) ions within the adsorption medium with time (Fig. 3). The figure shows the comparative data of the effect of contact time on the extent of biosorption of Cr(VI) on the biomass at 25, 50 and 100 mg/L initial Cr(VI) concentration. It has been observed that the Cr(VI) adsorption rate is high at the beginning of adsorption and saturation levels were completely reached at about 120 min for chromium ions for *N. muscorum*. After this equilibrium period, the amount of biosorbed Cr(VI) ions on the cyanobacterial preparations did not significantly changed with time. Note that there are several parameters, which determine the biosorption rate such as stirring rate of the aqueous phase, structural properties of the biosorbent. The data obtained from this experiment was further used successfully to evaluate the kinetics of the adsorption process.

3.2.4. Effect of temperature

The effect of temperature on the Cr(VI) biosorption experiment have been investigated at three different temperatures (25,

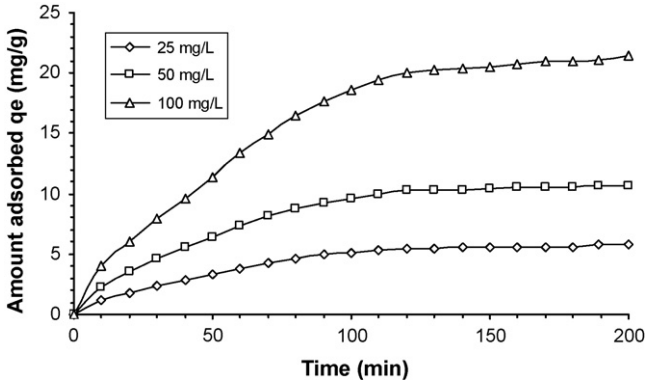

Fig. 3. Effect of contact time on the biosorption of Cr(VI) ions on cyanobacterial biomass *N. muscorum* from aqueous solutions: temperature 25 °C; initial concentration Cr(VI) ions 25, 50 and 100 mg/L; algal dose 1.0 g/L (average value of three tests, error <1.5%).

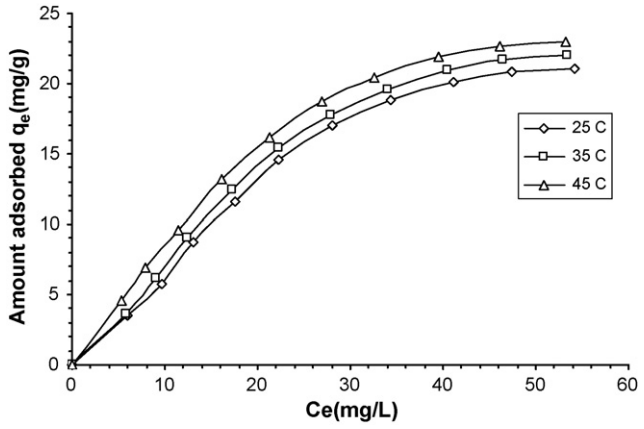

Fig. 4. Adsorption isotherms at three different temperatures for cyanobacterial biomass *N. muscorum* (average value of three tests, error <1.5%).

35 and 45 °C) for the biomass and is given in Fig. 4. The temperature of the adsorption medium could be important for energy dependent mechanisms in metal biosorption by microbial cells. For an increase in temperature from 25 to 45 °C, an increase in the adsorption of *N. muscorum* was observed (21.07 mg/g at 25 °C to 23.0 mg/g at 45 °C at 100 mg/L initial chromium concentration). The increase in adsorption with increasing temperature indicated endothermic nature of the adsorption process. Similar endothermic nature of the adsorption process has been reported for other adsorbent systems [30,31]. The increase in sorption with temperature may be attributed to either increase in the number of active surface sites available for sorption on the adsorbent or due to the decrease in the boundary layer thickness surrounding the sorbent, so that the mass transfer resistance of adsorbate in the boundary layer decreased [32].

3.3. Adsorption isotherms

To understand the biosorption mechanism and surface characteristics of the cyanobacterium, the mathematical models developed by Langmuir and Freundlich have been applied to the data.

Langmuir isotherm, which assumes that there are finite numbers of binding sites distributed homogeneously over the surface of the adsorbent, can be represented as

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (1)$$

where C_e is equilibrium concentration (mg/L), q_e the amount of Cr(VI) adsorbed at equilibrium (mg/g) and Q_0 (mg/g) and b (L/mg) are Langmuir constants showing the adsorption capacity and energy of adsorption, respectively. Langmuir isotherm (figure not shown) showed linear plots $1/q_e$ versus $1/C_e$ for three different temperatures. Values of Langmuir constants (Q_0 and b) were calculated from the slope and intercept of the plots. Adsorption capacity ($Q_0 = 22.92$ mg/g) and correlation coefficients values obtained were very high which strongly support the fact that the chromium–cyanobacterium biomass biosorption data closely follow the Langmuir model of sorption.

Freundlich isotherm was also applied to study the adsorption behavior as it is widely used in environmental engineering practice. This assumes heterogeneous surface of the adsorbent and linearized form of the model is as follows:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (2)$$

where K_F is Freundlich constant indicating adsorbent capacity (mg/g dry weight) and n is Freundlich exponent known as adsorbent intensity. Linear plot of $\log q_e$ versus $\log C_e$ shows the applicability of this isotherm and the values of K_F and n along with R^2 calculated from the plots are given in Table 2. The high values of K_F and n show high feasibility of Cr(VI) adsorption on the biomass surface from metal containing waste water.

High values of regression coefficients between the sorbate and sorbent systems for both Langmuir and Freundlich models (>0.952) indicated the applicability of this cyanobacterial system for Cr(VI) removal in both monolayer biosorption and heterogeneous surface conditions, but the values of R^2 for Langmuir adsorption isotherms are greater than that of Freundlich isotherms showing its higher applicability. When compared with several other algal systems the present cyanobacterial strain was found to show comparable hexavalent chromium biosorption (22.92 mg/g). Green algae like *Chlamydomonas reinharditii*, *Spirogyra* sp., *Chlorella vulgaris*, *Synechocystis* sp., and *C. crispata* have been reported to show maximum Cr(VI) uptake of 18.0, 15.0, 34.0, 39.0 and 40.0 mg/g, respectively [9,30,33,34].

3.4. Thermodynamic study

The free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for adsorption process by the cyanobacterium was calculated using following equations:

$$\Delta G^\circ = -RT\ln(b) \quad (3)$$

$$\ln\left(\frac{b_2}{b_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (4)$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \quad (5)$$

Table 2
Langmuir and Freundlich isotherms constants for the biosorption of Cr(VI) on cyanobacterial biomass (*N. muscorum*) at different temperatures and pH 3.0

Biomass	Temperature (°C)	Langmuir constant			Freundlich constant		
		b (L mg^{-1})	Q_0 (mg g^{-1})	R^2	n	K_F (mg g^{-1})	R^2
N. muscorum	25	0.020	22.92	0.988	1.214	8.069	0.953
	35	0.021	26.73	0.986	1.234	8.446	0.952
	45	0.023	29.49	0.994	1.414	8.755	0.962

Table 3
Thermodynamic parameters for the biosorption of Cr(VI) on cyanobacterial biomass (*N. muscorum*) at different temperatures

Biomass	Temperature (°C)	ΔG° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔH°[a] (kJ mol^{-1})
N. muscorum	25	−19.013	0.078	
	35	−20.746	0.079	3.013
	45	−21.624	0.079	

[a] Measured between 25 and 45 °C.

Table 4
Comparison between adsorption rate constants, q_e estimated and coefficient of correlation associated to the Lagergren pseudo-first- and second-order adsorption for the cyanobacterium *N. muscorum* (pH 3.0)

Biomass	Initial conc. (mg L^{-1})	$q_{e\,exp.}$ (mg g^{-1})	First-order model			Second-order model		
			k_1 ($\times 10^{-3}$ min^{-1})	$q_{e\,cal.}$ (mg g^{-1})	R^2	K_2 ($\times 10^{-3}$ g mg^{-1} min^{-1})	$q_{e\,cal.}$ (mg g^{-1})	R^2
N. muscorum	25	5.5	18.194	6.02	0.990	2.125	7.770	0.987
	50	10.3	21.648	11.25	0.981	1.319	14.065	0.989
	100	20.2	19.345	22.05	0.973	0.446	30.395	0.980

The values of these parameters are summarized in Table 3. For the test biomass studied, the enthalpy change ΔH° is positive (endothermic) due to increase in adsorption on successive increase in temperature. Further, negative ΔG° values indicate spontaneous nature of the adsorption process and positive value of ΔS° reveals the increased randomness at the solid–solution interface during the fixation of the chromium ion on the active sites of the biosorbent.

3.5. Biosorption kinetics modelling

One of the major characteristics to define the efficiency of sorption is its kinetics. Different biosorbents conform to different models. Here in our investigations, the Lagergren first-order and pseudo-second-order models were used to test adsorption kinetics data to investigate the mechanism of biosorption. The Lagergren rate equation is the most widely used model for the sorption of a solute from a liquid solution and the first-order, rate expression of Lagergren is given as [35]

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,ads}}{2.303} t \quad (6)$$

where q_e and q_t (mg/g) are the amounts of chromium adsorbed on the cyanobacterial biomass at equilibrium and time t, in mg/g, and $k_{1,ads}$ (min^{-1}) is the rate constant of first-order adsorption. The slope and intercept of the plot of $\log(q_e - q_t)$ versus t (figure not given) for *N. muscorum* biomass was used to determine the values of q_e and $k_{1,ads}$ as shown in Table 4.

The pseudo-second-order kinetic model [36] in its integrated and linearized form has been used and is given as

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{1}{q_e} t \quad (7)$$

where $k_{2,ads}$ (g mg/min^{-1}) is the rate constant of second-order adsorption. The plot t/q versus t (Fig. 5) for the biosorbent studied, gave a straight line shows, second-order kinetics is applicable and q_e and $k_{2,ads}$ (Table 4) were determined from the slope and intercept of the plot, respectively. It is important to notice that for the application of this model the experimental estimation of q_e is not necessary.

Table 4 lists the results of rate constant studies for different initial chromium concentrations by the Lagergren first-order and pseudo-second-order models for the biomass studied. From the table it is suggested that both first-order and second-order models are suitable to describe the adsorption kinetics of Cr(VI) by the biomass from the values of correlation coefficient R^2 (>0.973) for both the models, but the values of adsorption capacity as determined by first-order model are more close to the calculated experimental. Therefore, it has been concluded that both first-order and pseudo-second-order adsorption models are suitable to describe the adsorption kinetics of Cr(VI) by the biomass *N. muscorum*.

3.6. Effect of various desorbents and sorption–desorption process

In order to design and optimize a biosorption process for industrial application, it is extremely important to elucidate metal sorption and desorption behaviour of biomass. Metal

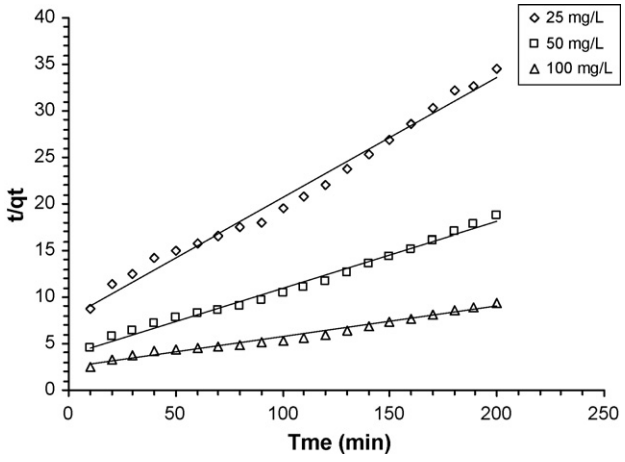

Fig. 5. Second-order kinetic modelling of Cr(VI) ions biosorption on cyanobacterial biomass *N. muscorum*.

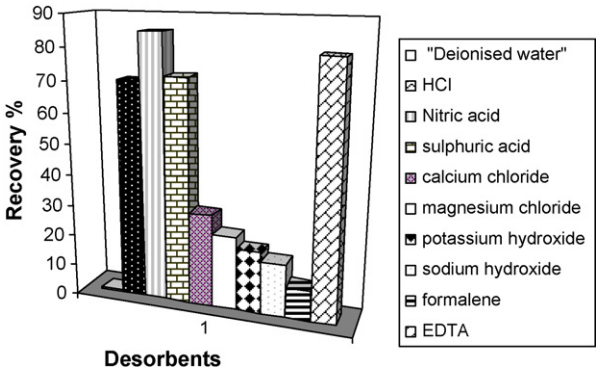

Fig. 6. Chromium(VI) recovery by different desorbents.

sorbed on the biomass can be desorbed by a suitable eluant or desorbing solution, and thus biomass can be used in multiple sorption–desorption cycles. In the present investigation, 10 different desorbing agents deionised water, 0.1 M HCl, HNO_3 and H_2SO_4, 0.2 M $CaCl_2$ and $MgCl_2$, 0.5 M KOH and NaOH, 5% HCHO, 0.1 M EDTA have been scrutinized for Cr(VI) metal desorption ability from the cyanobacterial biomass. Fig. 6 shows the percentage of Cr(VI) released after treatment with different desorbents. It was observed that EDTA and HNO_3 were most efficient among all the desorbents studied while desorption with deionised water was almost negligible. Earlier Chojnacka et al. [37] have studied the desorption of Cr, Cd and Cu from *Spirulina* sp. using 0.1 M EDTA, 0.1 M HNO_3 and deionised water. They found that the most efficient desorbent was nitric acid (0.1 M) which removed almost all the metal ions (98%) bound with the biomass whereas 0.1 M EDTA desorption efficiency ranged between 53 and 63%.

In the present study, in order to show the reusability of the biosorbent *N. muscorum*, adsorption–desorption cycle of Cr(VI) was repeated five times. Cr(VI) ions adsorbed onto biosorbent was eluted with 0.1 mol/L EDTA. More than 90% of the adsorbed Cr(VI) ions was desorbed from the biosorbents. The adsorption capacities of the biosorbent did not noticeably change (only a maximum 10–15% change was observed with the tested biosorbent) during the repeated adsorption–desorption operations (Fig. 7). These results showed that the test biosorbent could be repeatedly used in Cr(VI) ion adsorption studies without significant losses in its initial adsorption capacity.

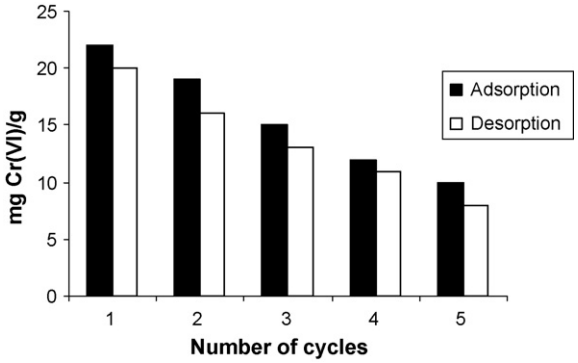

Fig. 7. Adsorption–desorption cycles for *N. muscorum* cyanobacterial biomass.

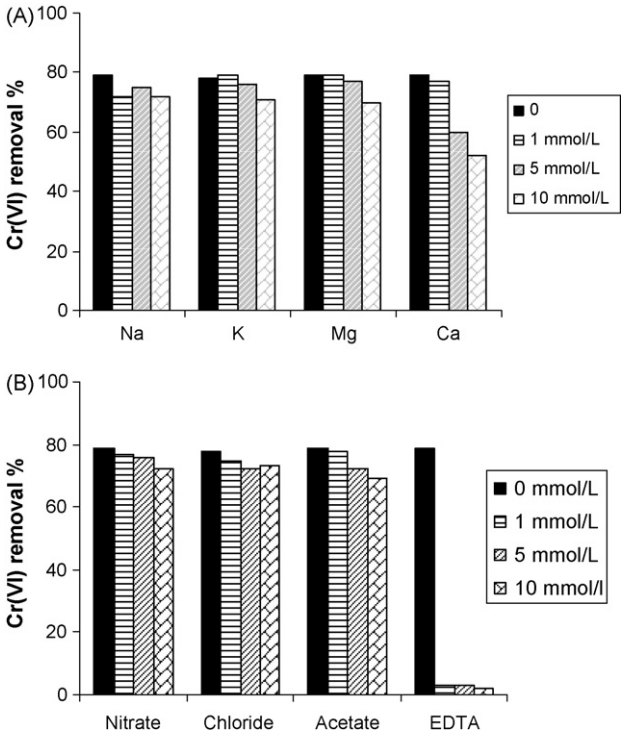

Fig. 8. The effect of (A) cations and (B) anions on the uptake of Cr(VI) ions from aqueous solutions by *N. muscorum* biomass.

3.7. Effects of light metal ions on biosorption

Actual industrial wastewaters contain different kinds of impurities, which may significantly affect metal biosorption. Among such impurities, cations such as Na^+, K^+, Mg^{2+} and Ca^{2+}, and anions like sodium salts of chloride, nitrate, acetate and EDTA, may be present which may interfere with the uptake of heavy metal ions by biomass. So, in the present investigation, the effect of different concentrations (0, i.e. control, 1, 5 and 10 mmol/L) of these cations and anions on chromium uptake by the cyanobacterium *N. muscorum* was studied and the results are shown in Fig. 8(A) and (B). It was evident that the effect of Na^+, K^+ and Mg^{2+} on adsorption of Cr(VI) was very small (max. 8–10%). In contrast, Cr(VI) removal percentage dropped with increasing concentration of Ca^{2+}. The presence of Ca^{2+} at 10 mmol/L caused removal percentage to drop by 30%. The effect of Ca^{2+} on uptake is due to the competition with Cr(VI) for the binding sites. The presence of chloride, nitrate and acetate did not greatly affect the Cr(VI) removal (Fig. 8B). Acetate, at 10 mmol/L, caused the removal efficiency to drop by 8%. It was obvious that EDTA affected the adsorption remarkably. At the presence of 1 mmol/L EDTA, Cr(VI) removal efficiency dropped by 78%. As EDTA increased to 10 mmol/L, the removal efficiency reduced nearly to zero. This is because Cr(VI) can combine with EDTA strongly instead of biomass.

Hence, *N. muscorum* has immense potential for removal and recovery of heavy metals from industrial effluents and is an ideal candidate for developing a cheap and effective biosorbent.

4. Conclusions

The results of this study indicated that the biomass of *N. muscorum* was suitable for the development of efficient biosorbent for the removal and recovery of Cr(VI) from wastewater. The adsorption process was fast enough, as maximum removal took place within 120 min of contact time. The maximum Cr(VI) biosorption capacity for *N. muscorum* has been found to be 22.92 mg/g at a dose of 1.0 g/L with initial Cr(VI) concentration of 100 mg/L and optimum pH of 3.0. The equilibrium data fitted in both the Langmuir and Freundlich adsorption isotherms for the cyanobacterial biomass. Analysis of data shows that the process involves both first- and second-order kinetics and thermodynamic treatment of equilibrium data shows endothermic nature of the adsorption process. IR spectrum analysis suggested amino or carboxyl groups could combine intensively with Cr(VI). The test biosorbent was reused in five biosorption and desorption cycles with negligible decrease in their biosorption capacities. Thus, the biomass of *N. muscorum* has the potential to be used as an ecofriendly and economic biosorbent material for the removal of chromium from wastewater.

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