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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