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EFFECT OF PRETREATMENT OF BLUE GREEN ALGAL BIOMASS ON BIOADSORPTION OF CHROMIUM AND NICKEL

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Abstract

The presence of heavy metals in aquatic environment is known to cause severe damage to aquatic life. Most of the heavy metals are soluble in water and form aqueous solutions and consequently cannot be separated by ordinary physical and chemical means of separation. Biological methods such as biosorption/ bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods. The biomass is capable of absorbing and adsorbing metal ions from aqueous solution. In this study the effect of pretreatment of Blue Green Algal (BGA) biomasses like *Anabaena variabilis*, *Aulosira* sp, *Nostoc muscorum*, *Oscillatoria* sp and *Westiellopsis* sp. on the Cr (VI) and Ni (II) biosorption capacity were investigated under single and binary metal conditions. For this purpose, the biomasses were subjected to physical treatments such as heat and autoclaving and chemical treatments such as sodium hydroxide and acetic acid. Under single metal condition, all the pretreated biomass increased biosorption of Cr (VI) and Ni (II) in comparison with live biomass (27.90%). The maximum metal removal efficiency was observed under autoclaved biomass (Cr-86.20 %, Ni -85.90 %) followed by acetic acid treatment (Cr-84.60 %, Ni -83.10%). Among the pretreatments the oven dried biomass (Cr-56.90%, Ni -50.90%) and NaOH treated cells (Cr-44.80%, Ni - 47.90%) adsorbed least amount of metal.

Introduction

The biosorption potential under binary metal condition showed the same trend of biosorption under single metal condition. The amount of Cr and Ni biosorbed by blue green algae was dependent on the heavy metal concentration in the medium. To improve the bioadsorption capacity for metal ions by dead biomass, autoclaving and acetic acid treatment are effective methods, but the loss

of biomass after the pretreatment should be taken into consideration while assessing the bioadsorption performance. The aim of this study is to explore the possibility of using native isolates of blue green algal strains to remove heavy metals from aquatic environment.

Key words: Biosorption, Blue green algae, dead biomass, chromium, nickel.

INTRODUCTION

Blue green algae can accumulate heavy metals from their external environment by means of physico-chemical and biological mechanisms. Biosorption is a process that utilizes inexpensive dead biomass to sequester toxic heavy metals and particularly useful for the removal of contaminants from industrial effluents. Biosorbents are prepared from the naturally abundant and/or waste biomass of algae, moss, fungi or bacteria that have been killed while the biomass is pretreated by washing with acids and/or bases before final drying and granulation (Kratchovil and Volesky, 1998).

The use of dried, nonliving or chemically pretreated microorganisms seems to be a preferred alternative to the use of living cells in industrial applications for the removal of heavy metal ions from wastewater. The use of dead cells offers the following advantages over live cells, the metal removal system is not subject to toxicity limitations, there is no requirement for growth media and nutrients, the biosorbed metal ions can be easily desorbed and biomass can be reused and dead biomass-based treatment systems can be subjected to traditional adsorption models in use. As a result, the use of dead fungal biomass has been preferred in numerous studies on biosorption of toxic metal ions from aqueous solutions (Kapoor and Viraraghavan, 1998). The aim of this study was to investigate the effect of physical and chemical pretreatment of different blue green algal biomass on biosorption of Cr (VI) and Ni from aqueous solution.

MATERIALS AND METHODS

Blue green algae culture conditions

The blue green algae isolates *Viz., Anabaena variables, Aulosira* sp. *Nostoc muscorum, Oscillatoria* sp. and *Westiellopsis* sp. were used for this experiment. The method developed by Cabuk *et al*. (2005) was followed for the biosorption experiments. The blue green algae isolates were inoculated in BG-11 broth for mass multiplication and incubated under

fluorescent light (3000 lux) at a temperature of 25±1°C for 18 days. Biomass was then harvested by filtration, washed with generous amounts of deionized water, resuspended and washed again.

Pretreatment of biomass

Thirty grams of wet biomass (blue green algae) was then pretreated in 4 different ways. The treatmental details are, T_1- Live biomass; T_2 - Dried at 60 ^{0}C for 12 h in an incubator; T_3 - Autoclaved for 15 min at 121 ^{0}C at 15 psi ; T_4 - Boiled for 15 min in 500 ml of 0.5 N sodium hydroxide solution ; T_5- Boiled for 15 min in 200 ml of 10% (v/v) acetic acid solution

After each pretreatment with chemicals, the biomass were washed with generous amounts of deionized water and then dried at 60^{0}C for 12 hrs. The sodium hydroxide pretreated biomass was washed with deionized water until the pH of the solution was in a near neutral range (pH 6.8-7.2).

Biosorption protocol

Biosorption experiments were carried out using Cr (VI) and Ni added in the form of $K_2Cr_2O_7$ and $NiCl_2.\ 8H_2O$, the stock solution was prepared in Milli-Q water. The initial Cr (VI) and Ni concentration was adjusted to 5, 10, 15, 20 and 25 ppm. For single metal condition Cr (VI) and Ni salts were added separately into the flask, incase of binary metal state both the metals were added in the same flask to bring the total heavy metal concentration of 5, 10, 15, 20 and 25 ppm. The other procedures are same for single and binary metal conditions. The known amount of dried biomass was introduced to heavy metal solution at pH 5.5. The reaction mixture was agitated at 130 rpm on a rotary shaker. After 24 hrs of contact time the biomass was separated by filtering the reaction mixture and the filtrate was analyzed for metal concentration.

Measurement of heavy metal concentrations

Cr (VI) and Ni concentration in the solution was measured with a Varian Spectra AA 100/200 FAAS. Before measurement, the solutions containing Cr (VI) and Ni were appropriately diluted with deionized water to ensure that the heavy metal concentration in the sample was linearly dependent on the absorbance detected. Biosorption experiments were conducted in duplicate and average values were used in the analysis. The amount of Cr (VI) and Ni

biosorbed per gram of dried biomass was calculated using the following equation:

$$Q = \frac{(C_0 - C_1)}{M} \times V$$

Where,

Q = mg of metal ion biosorbed per gram of biomass

C_0 = Initial metal ion concentration, mg L^{-1}

C_1 = Final metal ion concentration, mg L^{-1}

M = Dry weight of biomass in the reaction mixture, g and

V = Volume of the reaction mixture, ml.

RESULTS AND DISCUSSION

Pretreated blue green algal biomass showed promising results for biosorption of Cr (VI) and Ni from aqueous solution. The findings related to Cr (VI) and Ni biosorption under single metal condition by live and pretreated biomasses are presented in Fig.1-3.

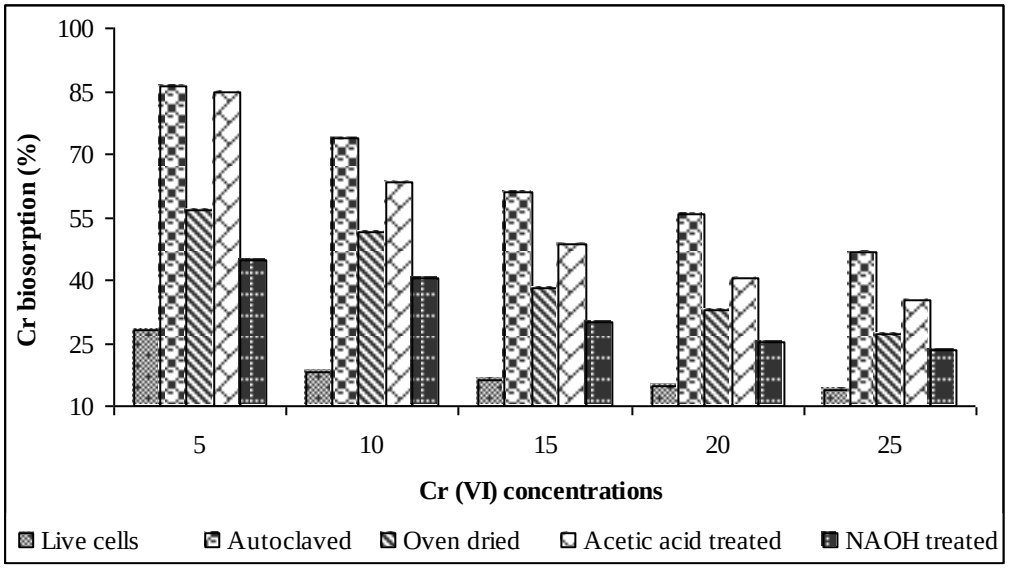

Fig. 1. Cr (VI) biosorption potential of blue green algal consortium under single metal condition

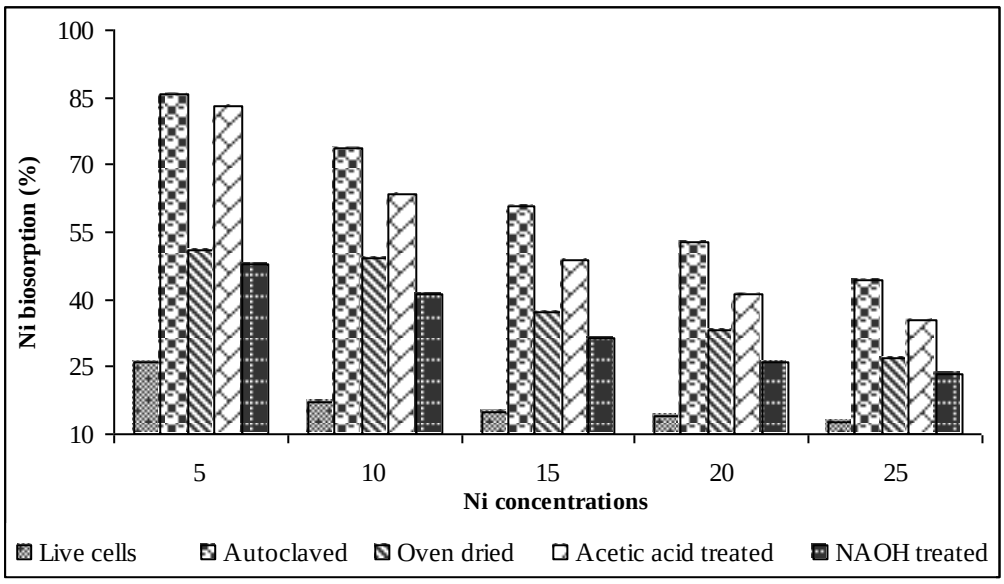

Fig. 2. Ni biosorption potential of blue green algal consortium under single metal condition

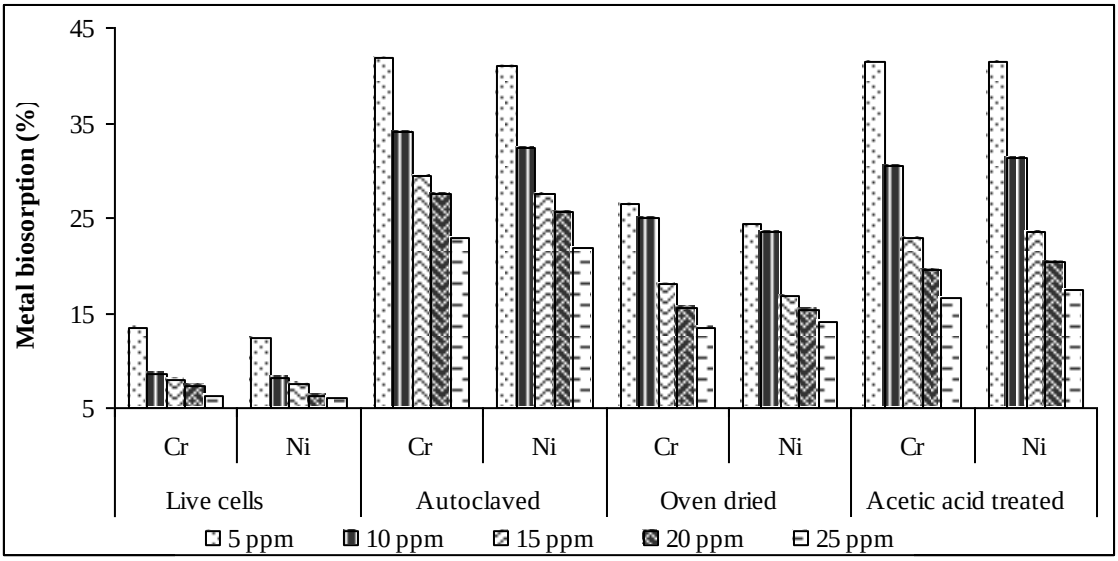

Fig. 3. Cr (VI) and Ni biosorption potential of blue green algal consortium under binary metal condition

Nonviable microbial biomass frequently displays a higher affinity for metal ions compared with viable biomass that might probably due to the absence of competing protons produced during metabolism. It avoids the problem of metal

toxicity for microbial growth and inhibition of metal accumulation by nutrient or excreted metabolites (Fourest and Roux, 1992). Among the pretreatment methods, autoclaved biomass of blue green algal consortium had the highest biosorption of Cr and Ni in both single and binary metal conditions. The sequestraion of metallic species by blue green algal biomasses which constitutes the basis of its biosorbent behavior has mainly been traced to the cell wall. The cell wall is not necessarily the only site where the sequestered metals are located. They may also be found within the cell, associated with various organelles, or may crystallize in the cytoplasm (Volesky, 1990). The drying and then grinding of blue green algal biomass reveals the sites where metal ions could be sequestered and so increase the probability of encountering metal ions.

Initial metal ion concentration plays an important role in determining the adsorption capacity of a biosorbent. Generally, it has been observed that an increase in the initial metal concentration (from 5 to 25 ppm) results in an increase in the metal adsorption capacity of the biosorbent, which culminates in a plateau at very high metal concentration. At lower concentrations, all metal ions present in the solution would interact with the binding sites and thus facilitate higher adsorption. At higher concentrations, more Cr and Ni ions are left unadsorbed in the solution due to the saturation of binding sites. Bai and Abraham (2001) have observed a decrease in percentage adsorption of Cr ions by *Rhizophus nigricans* with an increase in the initial metal concentration from 50 to 400 ppm and the finding is in accordance with our results.

Under single and binary metal conditions the order of biosorption was autoclaved cells > acetic acid treated > oven dried cells > NAOH treated > live cells at all the concentrations of both the metals. Autoclaved cells biosorbed maximum amount of 86.20 % Cr and 85.90 % Ni in single metal conditions where as in binary metals conditions these autoclaved cells biosorbed the highest percentage of 41.90 % Cr and 40.90 % Ni at an initial concentration of 5 ppm. This was corroborated with the findings of Cabuk *et al*. (2005) who reported that the heat and autoclaved pretreatment increased Pb^{2+} biosorption for *Penicillium verrucosum* whereas *Aspergillus versicolor* biomass was negatively affected by these pretreatments. The pretreatment could

release polymers such as polysaccharides that have a high affinity towards certain metal ions. Huang and Huang (1996) reported that if dead biomass is preferred in biosorption of metal ions, it may be ideal to include an autoclaving step in the treatment process because it increased the biosorption capacity of microbial biomass by exposure of latent binding sites after pretreatment. In contrast to this Yan and Viraraghavan, (2000) reported the reduction of bioadsorption capacity of pretreated biomass, in comparison with live biomass may be attributed to the loss of intracellular uptake. The live biomass of *Mucor rouxii* had a high bioadsorption capacity for heavy metals and they might be due to the larger surface area.

When comparing the different methods of pretreatment, the oven dried cells biosorbed lesser amount of Cr (VI) and Ni under both single and binary metal conditions. This might be due to that, the heat treatment could cause a loss of amino functional groups on the blue green algal surface through non enzymatic browning reaction. Amino functional groups are among the functional groups in the composition of polysaccharides which contribute to the binding of heavy metals. These findings are supported by Loaec *et al*. (1997).

The present study showed that, pretreated blue green algal biomasses had high biosorption potential of both the metals in comparison with live cells. An increase in biosorption of Cr (VI) and Ni ions as a result of pretreatment could be due to an exposure of active metal binding sites embedded in the cell wall or chemical modifications of the cell wall components. Huang and Huang (1996) stated that the increase in metal biosorption after pretreating the biomass could be due to the removal of surface impurities and to the exposure of available binding sites for metal biosorption.

All the pretreatment methods (Heat, 0.5N NaOH and 10% acetic acid) resulted in biomass loss in comparison with autoclaved biomass. Especially in the case of NaOH pretreatment, the loss was up to 13.05%. Fourest and Volesky (1996) reported that up to 39% of biomass loss may result from pretreatment of *Sargassum fluitans* using NaOH. The mass loss of biomass during pretreatment may lead to some confusion during the quantitative assessment of the bioadsorption performance. Taking into consideration the biomass loss after pretreatment in this study, it can be found

that enhancement of bioadsorption after pretreatment will be offset to some extent by the loss.

CONCLUSION

The bioadsorption efficiency of blue green algal biomass are greater than that of live cells. The differences in bioadsorption of heavy metals after a specific pretreatment might be attributed to the state of biomass and the nature of metal ions. When non-viable biomass is to be used in the removal of heavy metals, autoclaving is an effective method to improve the bioadsorption capacity. More information on biosorption is required to determine the best combination of metals, biomass types and other conditions. Moreover, further detailed studies should be conducted in order to clarify the causes of enhancement or decrease in adsorption capacity for blue green algal biomasses.

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