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Nostoc Linckia as Biosorbent of Chromium and Nickel from Electroplating Industry Wastewaters

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Abstract: The present study relates to the use of cyanobacterium *Nostoc linkia* for removal of chromium and nickel from wastewater of galvanic industry. To determine concentrations of Cr and Ni in wastewater samples atomic absorption spectrometry was used. The samples of dried nostoc biomass after exposure to wastewater were subject to nondestructive instrumental neutron activation analysis. During 30 min of the contact of biomass with wastewater 84% of chromium was removed from the wastewaters. Beside chromium after 30 min nostoc biomass accumulates the amount of iron and zinc that exceeds their concentrations in the control biomass samples by a factor of 6 and 8, respectively. Nickel content in biomass after interaction with Cr-containing wastewater increases sixty fold and copper-sixteen fold. During the same time of biomass-Ni-containing wastewater interaction, 50% of nickel were accumulated. The method of Fourier transform infrared spectroscopy was applied to identify functional groups responsible for metal binding.

Key words: Biosorption, chromium, nickel, neutron activation analysis, FT-IR spectroscopy, cyanobacterium, *Nostoc linckia.*

1. Introduction

Cyanobacteria are autotrophic organisms with property of performing oxygenic plant-like photosynthesis [1, 2]. The ecology, morphology, physiology and biochemistry of cyanobacteria are extremely diverse [3]. Representatives of the group have been found in fresh and marine waters, terrestrial and several types of extreme environments [2, 4]. Cyanobacteria including *Nostoc*, *Arthrospira* (*Spirulina*) and *Aphanizomenon* species have been used for food for thousands of years [5].

Owing to their large surface area, greater mucilage volume, high binding affinity and simple nutrient requirements [6, 7] cyanobacteria, as well as several species of microalgae have been regarded as good candidates for various biotechnological applications [2].

One of the most important applications of cyanobacteria is their use in the environmental studies on wastewater purification. Cyanobacteria play an important role in the treatment of wastewater containing heavy metals in concentrations below 100 mg/L, because traditional techniques at this concentration are costly and no profitable [8]. There are three main processes of metal biological removal from solution: biosorption of metal ions onto the surface of a microorganism, intracellular uptake of metal ions and chemical transformation of metal ions by microorganisms [8]. For economic reasons, biosorption has been reported as more rapid and

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efficient mechanism. Heavy metal accumulation by cyanobacteria and microalgae [7, 9-11], including *Nostoc linkia* [12], *Nostoc punctiforme* [3, 13], *Nostoc muscorum* [14] is well documented. Wastewater usually have complex organic and inorganic composition, containing a variety of heavy metals, such as cadmium, copper, chromium, nickel, lead and zinc, which significantly contribute to the increase of these toxic substances in the aquatic environments [15].

Chromium and nickel are released into the environment by a large number of processes such as: mining, refining, electroplating industries, leather tanning, wood preservation, stainless steel, alloy and catalyst production [7, 16, 17]. Chromium, a vital heavy metal pollutant in the aquatic environment exists mostly in hexavalent [Cr (VI)] and trivalent [Cr (III)] forms [18]. Hexavalent chromium is highly soluble in water and carcinogenic to human. Nickel is an essential microelement for human and animals due to its importance in the metabolic pathways. Though, it is an essential micronutrient and/or cofactor, nickel is one of the heavy metal toxicants at higher concentration and is a well-known human carcinogen [16, 19].

Due to their toxic effects on living systems, US Environment Protection Agency (EPA) has set the maximum contaminant concentration level for Cr (VI) in domestic water supplies at 0.05 mg/L [20]. Nickel permitted level in human consumption water is under 0.04 mg/L [21].

The scope of the present work was to study nickel and chromium uptake by cyanobacteria *Nostoc linckia* from chemically complex wastewater effluents with the goal of water recycling. To study the metal content in biomass multi-element neutron activation analysis (NAA) was applied. Atomic adsorption spectrometry (AAS) was used for determination of Cr and Ni concentrations in supernatant solutions (wastewaters). Functional groups responsible for metal binding were determined by Fourier transform infrared spectroscopy (FT-IR).

2. Experiments

2.1 Wastewaters

Two types of wastewaters were obtained from electroplating units of the Scientific Production Association "Atom" (Dubna, Russia): the first one containing chromium of approximately 9.4 mg/L and the other containing nickel of approximately 14.1 mg/L along with other metal ions at various concentrations.

2.2 Biomass

The culture of *Nostoc linckia CNM-CB-03* was grown on mineral medium Gromov-6 stirring daily, continuous illumination (a light intensity of 2,000-3,000 Lx), at a temperature of 25-30 °C and the optimum pH of 6.0-7.0. The nostoc biomass after cultivation was separated from the nutritive medium by centrifugation.

2.3 Biosorption Experiment

In the present study two types of experiments were performed: with chromium- and nickel-containing wastewaters. The conditions of the experiment for both types of wastewater were the same.

25 mL of nostoc biomass (C = 6.5 g/L) was inoculated into a series of 250 mL conical flasks containing either 100 mL of wastewater on a rotary shaker set at 100 rpm. Samples were removed at different time intervals (5, 15 and 30 min), centrifuged and dried.

After metal sorption, biosorbents were recovered and dried at 105 °C. The resulting samples were packed in polyethylene bags and aluminum cups for neutron activation analysis. Chromium and nickel content in the supernatant (wastewaters) solutions was determined by atomic absorption spectrometry.

To observe the effect of pH of nickel uptake a series of model solutions with pH 1.9, 4.5 and 5.5 were prepared.

2.4 Atomic Absorption Spectrometry (AAS)

Chromium and nickel remaining concentration in residual solutions were determined on AAC-spectrometer at a resonance line of 357.9 nm for chromium and 232.0 nm for nickel, respectively using an air-acetylene flame. The strength of the current was 7 mA. Before, the investigation the solutions of determined metals of concentration 1 g/L were diluted and series of standards were prepared.

2.5 Neutron Activation Analysis (NAA)

To determine the elemental content of *Nostoc linckia* biomass, neutron activation analysis (NAA) at the pulsed fast reactor IBR-2 (FLNP JINR, Dubna) was used. The analytical scheme used has been described in detail elsewhere [22] and only a brief account is given here. To determine short lived isotopes, samples were irradiated for 3 min and measured for 15 min. In case of long lived isotopes, samples were irradiated for 4 days, repacked and measured, using high purity germanium detectors, twice, after 4-5 days and 20-23 days of decay.

The chromium content in the samples was determined by γ-line with the energy of 320.1 keV of isotope ^{51}Cr and nickel by γ-line with the energy of 810.7 keV of isotope ^{58}Co through fast neutron reaction ^{58}Ni (n, p)^{58} Co.

Element contents were determined on the basis of certified reference materials: 1566b (NIST, Oyster Tissue), 433 (IAEA, Marine Sediment), 690CC (ERM, Calcareous Soil), 1633c (NIST, Coal fly ash), 1632c (NIST, Trace elements in coal).

The NAA data processing and determination of element concentrations were performed using the software developed in FLNP JINR [23].

2.6 Fourier Transform Infrared Spectrophotometer (FT-IR) Analysis

FT-IR spectroscopy was used to confirm the presence of the functional groups in samples of *Nostoc linckia* and to observe the chemical modification after heavy metal adsorption. Infrared spectra were recorded in the 4,000-600 cm^{-1} region using a Perkin Elmer Spectrum 100 FT-IR spectrometer.

3. Results and Discussion

Biosorption of heavy metals by microorganisms depends on many factors as: biological properties of microorganisms, properties of metal ions, pH, contact time, the presence of other ions in the solution, initial concentration of metal ions.

Preliminary experiments on nickel biosorption by nostoc biomass showed that at the pH value 1.7 the destruction of main biomass components takes place and not biosorption occurs (Fig. 1).

Biosorption capacity of *Nostoc linckia* increased with pH range from 1.9 to 4.5 and its values coincide for the pH 4.5 and 5.5. The same data were obtained for chromium model solutions. Therefore, the pH of both types of wastewater was adjusted to the value 4.8. Dixit and Singh [24] showed that for *Nostoc muscorum* the optimum pH value for surface binding of Pb and Cd were at pH 5 and pH 6, respectively. Maximum biosorption of chromium (VI) by *Nostoc muscorum* was observed at pH 3.0 [7]. The same pH value was reported for Cr (IV) biosorption by dried biomass of *Nostoc* sp. [10].

An important step in the study of metals biosorption is determination of the optimal time required for nostoc biomass to bind the maximum amount of nickel and chromium ions. The saturation of the nickel and

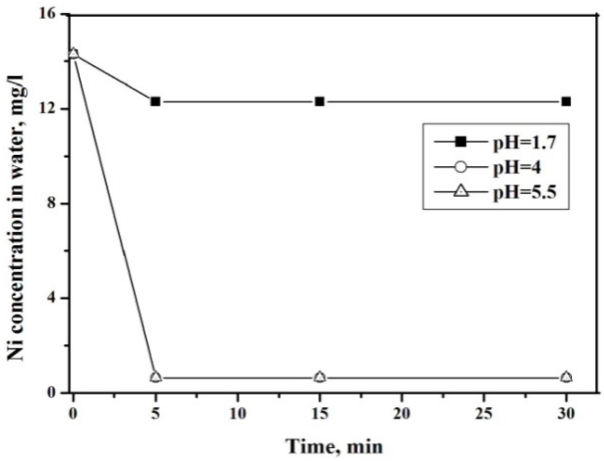

Fig. 1 Effect of the pH on the nickel biosorption process by *Nostoc linckia* (the lines for pH 4.5 and pH 5.5 coincide).

chromium removal capacity of nostoc was achieved within the first 15 min in the wastewaters and it does not change further (Figs. 2 and 3). Rapid uptake of nickel and chromium ions in the first 15 min might be attributed to freely available binding sites on the cyanobacteria cell wall, after it achieved the equilibrium due to their saturation. The initial concentration of nickel in biomass was 14 µg/g. After one hour of interaction its content in biomass increases 50-fold. AAS data (Fig. 2) support this fact: 50% of nickel were removed from wastewater.

Data obtained by AAS showed that the cyanobacteria could reduce metal concentrations to very low residual level, within 30 min 84% of chromium was removed from wastewater (Fig. 3). The content of chromium in biomass before addition of wastewater was 6 ppm. The amount of chromium in the biomass after 30 min of interaction was 87 times higher than in the native biomass.

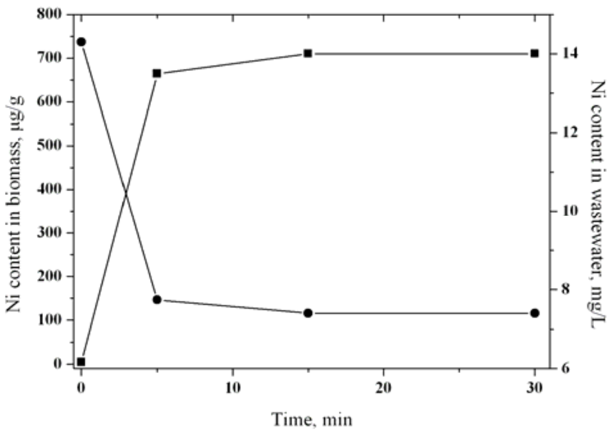

Fig. 2 Nickel content in *Nostoc linckia* biomass and in the wastewater *versus* the contact time.

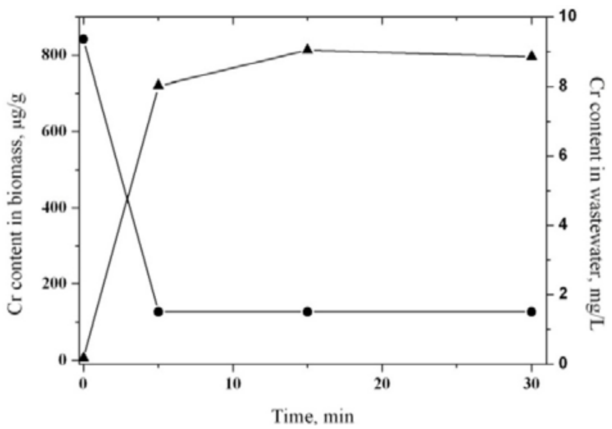

Fig. 3 Chromium content in *Nostoc linckia* biomass and in the wastewater *versus* the contact time.

Chromium was more efficiently removed from wastewater than nickel. Firstly, it can be explained by its lower concentration in wastewater. Secondly, it is known that Ni^{2+} in water generates very stable aqueous complexes and thus it probably became poorly exchangeable with the protons bound to the active sites of the biosorbent. Micheletti et al., studying metal removal by nine cyanobacteria showed that their affinity decreased in the order Cu > Cr > Ni [15].

Industrial wastewaters contain different kinds of impurities, which may significantly affect metal biosorption. The results of present study (Table 1) indicated that biomass of *Nostoc linckia* can be used for complex purification of wastewaters.

In case of wastewater containing chromium, a large variety of elements were adsorbed: Fe, Ni, Cu, Zn, Co, and Ba. Data for Fe, Ni, and Zn are presented in Table 1. The results obtained show that after 30 min nostoc biomass accumulates the amount of iron and zinc that exceeds their concentrations in the control biomass samples by a factor of 6 and 8, respectively. Nickel content in biomass after interaction with Cr-containing wastewater increases sixty fold and copper-sixteen fold. No significant changes in content of listed elements were observed after interaction of biomass with wastewater containing nickel. It can be explained by differences in wastewaters composition.

The binding mechanism of sorbate onto biosorbent in biosorption mechanism is a complex process. Metal removal from wastewater may involve the following pathways: bioaccumulation, volatilization, microprecipitation, displacing of either bound metal cation (ion exchange). During the biosorption process, protons and/or light metal cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) which are naturally bound with functional groups located on the surface of biomass (are exchanged with metal cations present in wastewaters [25, 26]. Data obtained for K and Br (Cr-loaded biomass) and Mg, K, Br and Na (Ni-loaded biomass) (Table 1) support this

Table 1 Change of metal concentrations in *Nostoc linckia* biomass as a function of contact time with wastewater.

Element (µg/g)	Experimental time			
	Control	5 min	15 min	30 min
Wastewater containing chromium				
Fe	159 ± 11	990 ± 69	967 ± 67	937 ± 65
Ni	50 ± 4.5	260 ± 23	300 ± 27	303 ± 27
Zn	9.3 ± 0.8	70 ± 6.3	80 ± 7.2	82 ± 7.3
K	21,300 ± 2,532	3,733 ± 447	3,500 ± 420	2,906 ± 348
Br	1.6 ± 0.1	0.7 ± 0.08	0.7 ± 0.08	0.6 ± 0.07
Wastewater containing nickel				
Mg	1,787 ± 107	1,103 ± 66	1,140 ± 68	1,136 ± 68
Br	1.6 ± 0.1	0.8 ± 0.09	0.8 ± 0.09	0.8 ± 0.09
K	21,300 ± 2,532	3,623 ± 507	3,700 ± 518	3,226 ± 451
Na	1,833 ± 73	17,000 ± 680	16,667 ± 667	17,300 ± 692

fact. The loss of electrolytes (K^+) and increase of extracellular ion-sodium content could be attributed to the disturbance of the permeability of cell wall. In addition to this, heavy metals are also known to induce formative changes and inhibit the vital metabolic processes [27]. The content of manganese and bromine declined markedly with increasing concentrations of chromium and nickel in biomass.

The composition of the cell wall is of great importance to the biosorption process.

The cell wall of biomass is composed mainly of polysaccharides, proteins and lipids, and contains a number of functional groups: hydroxyl (OH), phosphoryl (PO_3O_2), amine (NH_2), carboxyl (COOH), sulphydryl (SH) [18] able to bind metal ions [25, 28]. Extracellular secreted polysaccharides (exopolysaccharides) of nostoc have been identified as having a high biosorption capacity for metal ions [29].

To explore the biosorption mechanisms, it is essential to identify the sorbent functional groups that are involved in the biosorption process [25]. FTIR spectra for control sample and for samples containing chromium and nickel were recorded to determine functional groups responsible for metal binding (Spectra not shown).

IR spectra showed the presence of functional groups as: OH, NH_2, NH-CH_2, CH=CH, NHC(O) amid and their participation in the adsorption process for Cr-loaded biomass. Essential decrease of the intensity of the adsorption bands in the spectrum of Ni-loaded biomass for NH_2, CH=CH, OH and N-CH_2 indicates their involvement in the adsorption process.

4. Conclusions

The possibility of using cyanobacterium *Nostoc linckia* for nickel (II) and chromium Cr (VI) removal from wastewaters was experimentally supported. Besides chromium, the high content of Fe, Ni, Cu, Zn, Co, and Ba were accumulated in the biomass from wastewater, containing chromium. The maximum uptake for nickel and chromium occurred after 15 min of biomass-wastewaters interaction. A decrease in Br, K and Mg concentrations indicates the destruction of biomass in the process of metal accumulation. FTIR spectra revealed that metal removal takes place through binding to OH, NH_2, CH=CH, and NHC(O) amid groups. Biosorption is a cheap and environmentally friendly method of electroplating industry wastewaters purification.

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