THE UPTAKE OF Cr(III) IN THE PRESENCE OF Mn(II) DURING GROWTH OF *Arthrobacter* SPECIES

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Abstract

The uptake of Cr(III) by *Arthrobacter* species (*Arthrobacter globiformis* 151B and *Arthrobacter oxidas* 61) were studied without and in the presence of Mn(II) ions during growth of *Arthrobacter* species using simultaneous application dialysis and atomic absorption analysis. It was shown, that when added Cr(III) concentration is increased, the interaction of Cr(III) with *Arthrobacter* species are increased too and approximately it is equal to 10^{13} atom Cr per *Arthrobacter* species. It was shown, that biosorption characteristics did not change in the presence of Mn(II) ions during growth of *Arthrobacter* species. This means, that Mn(II) did not significantly affect the biosorption of Cr (III) ion-*Arthrobacter* species, i.e. Mn(II) essentially did not displace Cr(III) from bacteria.

Introduction

Nanotechnology has been identified as a technology that could play an important role in resolving many of the problems related to water purification and water quality [1]. Bioremediation is an ecologically sound natural process where natural strains of bacteria breakdown organic wastes most effectively. The field of nanotechnology is an immensely developing field as a result of its wide-ranging applications in different areas of science and technology [2]. Synthesis of nanoparticles using microbes is a new and emerging in nanotechnology science. Nanoparticles are metal particles. Research on synthesis of nanoparticles is the current area of interest. Nanoparticles are biosynthesized when the microorganisms grab target ions from their environment and then turn the metal ions into the element metal through enzymes generated by the cell activities. The modes by which the microorganisms remove metal ions from solution are: extracellular accumulation/ precipitation, cell surface sorption or complexation.

Gram-positive Arthrobacter species bacteria can reduce Cr(VI) to Cr(III) under aerobic growth and there is a large interest in Cr-reducing bacteria. The exact mechanism by which microorganisms take up the metal is relatively unclear. The inhibitive effect of FeS on Cr(III) oxidation by biogenic Mn-oxidas that were produced in the culture of a known species of Mn(II) oxidizers, *Pseudomonas putida*. In soils containing manganese oxides, the immobilized form of chromium Cr(III) could potentially be reoxidized [3, 4]. Equilibrium data, commonly known as adsorption isotherms, provide information on metal binding capacity of the adsorbent [5]. In the literature, there are some reports evaluating biosorption of chromium(III) *Spirulina platensis* [6], *Chlorella miniata* [7]).

In the present work, chromium(III) uptake by *Arthrobacter* species without and in the presence of Mn(II) during growth of *Arthrobacter* species were studied using simultaneous application dialysis and atomic absorption analysis.

Materials and methods

Organisms, culture techniques, cell dry weight measurement, metal analysis methods, data analysis are the same as have been described previously [8].

Results and discussions

Cr(III) uptake by cells of *Arthrobacter globiformis 151B* and *Arthrobacter oxidas* 61B and in the presence of Mn(II) ions and without it during growth of *Arthrobacter* species were studied as a function of metal concentration. The linearized adsorption isotherms of Cr–bacterium and in the presene Mn during growth bacterium species at room temperature are shown in **Figures 1** and **2** by fitting experimental points. The adsorption yields determined for each *Arthrobacter* were compared in table 1. The data in **Table 1** are not show a significant difference between the binding constants for Cr(III)–*Arthrobater oxidas* and Cr(III)–*Arthrobater globiformis*. (Biosorption constants for *Arthrobacter oxidas* and *Arthrobacter globiformis* are: $2.60 \cdot 10^{-3}$ and $2.02 \cdot 10^{-3}$, respectively). Insignificant decrease in bioavailability has been observed experimentally for Cr(III)–*Arthrobacter globiformis* as compared with *Arthrobacter oxidas*. As seen from **Table 1** for both *Arthrobacter* species n (1.37 and 1.23) values are not significantly different and their sorption intensity indicator are generally small. It was shown also, that when added Cr(III) concentration is increased, the interaction of Cr(III) with *Arthrobacter* species are increased too and approximately it is equal to 10^{13} atom Cr per *Arthrobacter* species.

Uptake of metals by microorganisms is substantially influenced by the following parameters: nature of biosorbent, age of culture and origins of biomass, the nature of interactions of metals with functional groups native to the biomass cell wall, concentration of biosorbent, properties of metals and their concentrations, pH, temperature and presence of other cations. pH strongly influenced protonation of metal binding sites exposed by cell surface. If pH increased, more ligands such as carboxyl, phosphate, imidazole and amino group would become deprotonated and thus available of positively charged metal cations. *Pyrobaculum islandicum*, an anaerobic hyperthermophilic microorganism, was reported to reduce many heavy metals including U(VI), Tc(VII), Cr(VI), Co(III), and Mn(IV) with hydrogen as the electron donor [9].

The role of presence Mn(II) cations in biosorption Cr(III)–*Arthrobacter* species were discussed by us. Biosorption characteristics K and n for *Arthrobater oxidas* in the presence of Mn(II) are $2.43 \cdot 10^{-3}$ (K) and 1.41 (n), respectively, for *Arthrobacter globiformis* in the presence of Mn(II) $1.94 \cdot 10^{-3}$ (K) and 1.47 (n), respectively. The correlations between experimental data and the theoretical equation were extremely good, with R above 0.93 (**Table 1**) for all the cases. The higher correlation coefficient shows that the Freundlich model is very suitable for describing the biosorption equilibrium of Chromium by the *Arthrobacter* species in the studied concentration range.

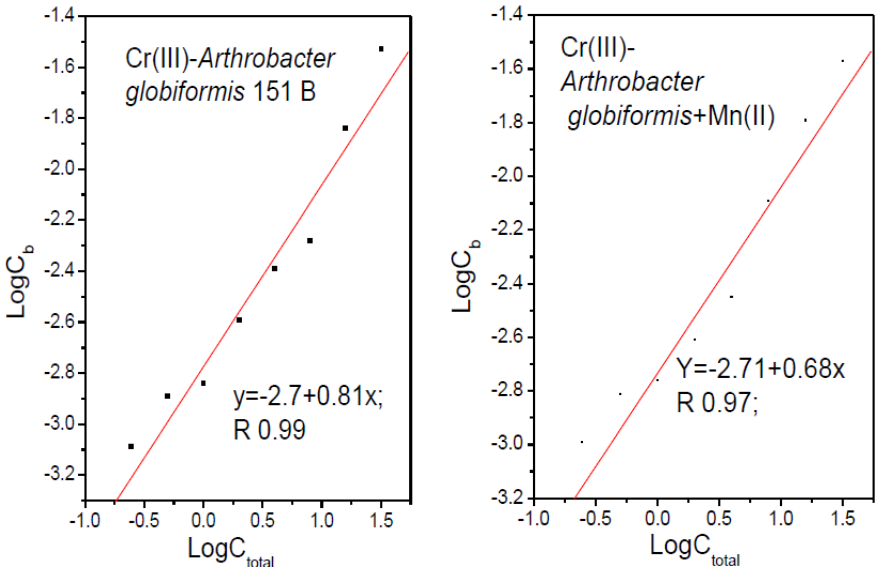

Figure 1. The linearized Freundlich adsorption isotherms of Cr(III) ion–*Arthrobacter globiformis* without and in the presene of Mn(II) ions during growth of baterium. (C_b is the binding metal concentration (mg / g) and C_{total} is initial Cr concentration (mg / l).

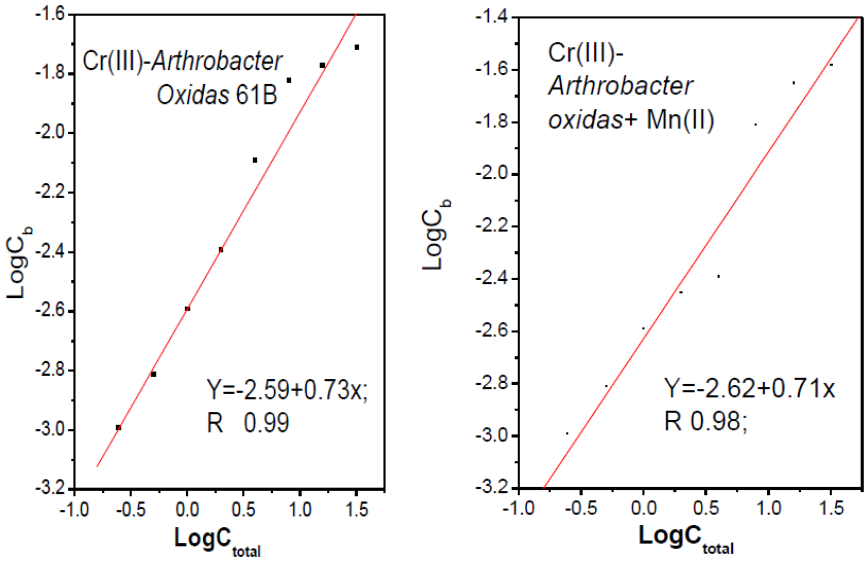

Figure 2. The linearized Freundlich adsorption isotherms of Cr(III) ion-*Arthrobacter oxidas* without and in the presence of Mn(II) ions during growth of baterium. (The parameters are the same as in **Figure 1**).

Table 1. Biosorption characteristics for Cr(III)–*Arthrobacter* species in the presence of Mn(II) during growth of bacterium and without it at 23 °C.

	Cr(III)		
Biosorption characteristics (K and n)	$K \cdot 10^{-3}$	n	R^2
Arthrobater oxidas	2.60	1.37	0.98
Arthrobacter globiformis	2.02	1.23	0.98
Arthrobater oxidas + Mn(II)	2.43	1.41	0.96
Arthrobacter globiformis + Mn(II)	1.94	1.47	0.94

It is seen, that biosorption characteristics did not change in the presence of Mn(II) ions. This means, that Mn(II) did not significantly affect the biosorption of Cr(III) ion–*Arthrobacter* species, i.e. Mn(II) essentially did not displace Cr(III) from bacteria. This fact leads us to speculate that primary binding site for Cr(III) is different than the binding site for Mn(II). The distorted octahedral coordination sphere proposed for Cr(III) and strong tendency to coordinate donor atoms equatorially may be responsible for the specific interaction with *Arthrobacter* species.

Comparative Cr(VI)–*Arthrobater species* [8] and Cr(III)–*Arthrobacter* species shown, that Cr(III) was more effectively adsorbed by both bacterium than Cr(VI). The adsorption capacity is the same for both the Chromium-*Arthrobacter* systems. The biosorption constants for Cr(III) is higher than for Cr(VI) 5.65 – 5.88 fold for both species. Cr(VI) is one of the more stable oxidation states, the others being chromium(II), chromium (III). Cr (VI) can be reduced to Cr(III) by the biomass through two different mechanisms [10]. The first mechanism, Cr(VI) is directly reduced to Cr(III) in the aqueous phase by contact with the electron–donor groups of the biomass. The second mechanism consists of three steps. The binding of anionic Cr(VI) ion species to the positively charged groups present on the biomass surface, the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups and the release of the Cr(III) ions into the aqueous phase due to electronic repulsion between the positively charged groups and the Cr(III) ions. The "uptake–reduction" model for chromium (VI) carcinogenicity is, that tetrahedral chromate is actively transported across the cell membrane via mechanisms in place for analogous such as sulfate, SO_4^{2-}. Chromium (III) is not actively transported across the cell membrane to lack of transport mechanisms for these octahedral complexes. Comparative our results for Cr(VI) [8] and present work shown, that Cr(VI) may be adsorbed to bacterium a much lower degree than Cr(III).

Uptake of metal ions by bacterium may be associated not only to physico-chemical interactions between the metal and the cell wall, but also with other mechanisms, such as the microprecipitation of the metal [11] or the metal penetration through the cell wall [12].

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