Short Communication

Biosorption of arsenic and cadmium from aqueous solutions

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The biosorption of cadmium and arsenic from aqueous solutions onto the unmodified compact biomass of microscopic filamentous fungus *Aspergillus clavatus* DESM. was studied in the concentration range of $0.25 - 100$ mg.l^{-1}. The experimental biosorption results for arsenic and cadmium followed well the Freundlich equilibrium sorption model.

Key words: Biosorption, arsenic, cadmium, microscopic filamentous fungi.

INTRODUCTION

Microscopic filamentous fungi as a part of microbial communities influence transformation and distribution of metal (loid)s in the environment. Interactions between microorganisms and ions of different metal (loid)s can be divided in two basic categories; transformations, that lead to the mobilization of heavy metals (bioleaching, biological methylation and reduction), and transformations that immobilize metal(loid)s, such as biosorption, or different types of microbial precipitation, or binding of metalloids to macromolecules (Gadd, 2000; Slaninka et al., 2006; Šimonovičová and Franková, 2001).

Nowadays, environmental biotechnologies use these interactions to decrease concentration of potentially toxic chemicals in wastewaters or industrial substrates. The most frequent biotechnology is biosorption. The biosorption is passive non-metabolic process of binding various chemicals on biomass (Volesky, 1990), including physicco-chemical interactions, adsorption and ion exchange (Gadd and White, 1993). In case of biosorption, ion exchange is the most important mechanism, that is realized by interaction between ions of metal (loid)s and active groups on cell wall biopolymers. The biomass represents polyelectrolyte with amino, carboxyl, phosphate, phenol and sulphydril active groups (Naja et al., 2005).

Biosorption by the biomass of microscopic filamentous fungi represents economically and technically relevant technology for bioremediation of wastewaters contaminated with metal (loid)s (Pümpel and Scinner, 1993). In this paper was studied potential of microscopic filamentous fungus *Aspergillus clavatus* to sorb ions of cadmium and arsenic from aqueous solutions.

MATERIALS AND METHODS

Preparation of biomass

As a sorbent was used biomass of microscopic filamentous fungus *A. clavatus* DESM. isolated from a locality Pezinok – Kolársky vrch (Slovakia), highly contaminated with metal(loid)s. The biomass used in experiment was prepared by static cultivation. 50 mL of Sabouraud medium (SAB – Himedia, Mumbai, India) were inoculated with 5 mL of spore suspension of microscopic filamentous fungus *A. clavatus*. The biomass was cultivated for two weeks under laboratory conditions. Prepared biomass was 5 to 6 cm in diameter and 0.5 cm in height. The biomass was then isolated from the SAB medium by filtration and centrifugated for 10 min to remove the rest of the medium (3000 rpm; MPW-340, Mechanika Precyzyjna, Poland). The biomass was than dried and subsequently the weight for each sample was adjusted to 1.11 g.

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Table 1. Amount of immobilized arsenic for aqueous solution by microscopic filamentous fungus *Aspergillus clavatus* (n = 3).

Amount of cadmium in 50 ml of solution before sorption (mg)	Amount of arsenic in 50 ml of solution after sorption (mg)	Amount of immobilized arsenic by biomass (mg)	Arsenic immobilized by biomass (%)
0.0125	0.0108	0.0017	13.6
0.025	0.0214	0.0036	14.4
0.05	0.0456	0.0044	8.80
0.125	0.1147	0.0103	8.24
0.25	0.2207	0.0293	11.7
0.5	0.4547	0.0453	9.06
1.25	1.1434	0.1066	8.53
2.5	2.3567	0.1433	5.73
5.0	4.5400	0.4600	9.20

Table 2. Amount of immobilized cadmium for aqueous solution by microscopic filamentous fungus *Aspergillus clavatus* (n = 3).

Amount of cadmium in 50 ml of solution before sorption (mg)	Amount of cadmium in 50 ml of solution after sorption (mg)	Amount of immobilized cadmium by biomass (mg)	Cadmium immobilized by biomass (%)
0.025	0.0137	0.0113	45.2
0.05	0.0253	0.0247	49.4
0.125	0.0838	0.0412	33.0
0.25	0.1986	0.0514	20.6
0.5	0.4544	0.0456	9.12

Biosorption of arsenic and cadmium from aqueous solutions

Aqueous solutions (50 mL) with desired concentration of arsenic (0.25, 0.5, 1, 2.5, 5, 10, 25, 50 or 100 mg.L^{-1} As) or cadmium (0.5, 1, 2.5, 5 or 10 mg.L^{-1} Cd) were prepared from stock solutions of pentavalent arsenic oxyanion (AsO$_4^{-3}$) or bivalent cadmium ion (Cd(NO$_3$)$_2$) stabilized in 0.5 M HNO$_3$ (Merck, Germany). All experiments were replicated in three runs. The biomass was in direct contact with prepared aqueous solution for one hour. Each system was shaking for 1 h on shaker (120 rpm, Unimax 2010, Heidolph, Germany). After an hour's sorption, compact biomass was mechanically isolated from solution and washed with 20 ml of deionized water. Subsequently the total arsenic and cadmium content in aqueous solution was measured as described below (Bujdoš et al., 2000).

Analytical method

The arsenic standard was prepared by a dilution of stock solutions of As 1.000 g.L^{-1} (Merck, Germany, H$_3$AsO$_4$ in 0.5 mol.L^{-1} HNO$_3$) and of Cd 1.000 g.L^{-1} (Merck, Germany, H$_3$AsO$_4$ in 0.5 mol.L^{-1} HNO$_3$). The total concentration of arsenic in aqueous solution was analyzed by using hydride generation atomic absorption spectrometry (HG AAS), using the Perkin-Elmer Atomic Absorption Spectrometer model 1100 (USA) equipped with a hydride generator LabTech HG-2 (Czech Republic). Cadmium was analyzed by using flame atomic absorption spectrometry (FAAS), using the Perkin-Elmer Atomic Absorption Spectrometer model 1100 (USA).

RESULTS AND DISCUSSION

In this paper was determined the ability of fungal *A. clavatus* strain to biosorb (immobilize) oxyanions of arsenic (0.25 – 100 mg.L^{-1}) and bivalent ion of cadmium (0.5 - 10 mg.L^{-1} Cd) from aqueous solutions. Amounts of biosorbed arsenic and cadmium onto fungal biomass are shown in Tables 1 and 2. The results has shown that arsenic oxyanions and cadmium behave differently by the low concentrations of metal (loid)s in aqueous solution. Sorption of arsenic onto unmodified biomass of *A. clavatus* in concentration range from 0.5 to 5 mg.L^{-1} is low (around 10 % from original amount of arsenic in solution), while the biosorption of cadmium is nearly three times higher. Lower sorption of arsenic by biomass, which is in solution presented as negative charged oxyanion, may relate with repulse electrostatic interactions between negatively charged surface of biomass and AsO$_4^{3-}$.

Experimental results from biosorption are usually quantitative evaluated by using adsorption isotherm models, which show dependency of sorbed amount of certain chemical compound in sorbent S_{eq} (concentration of metal (loid) in biomass of microscopic filamentous fungus) and concentration of this chemical compound in aqueous solution C_{eq} (equilibrium concentration of metal (loid) in aqueous solution after biosorption).

Quantitative evaluation of biosorption using equilibrium adsorption models is important for constructing and optimizing parameters of adsorption system for removal of toxic metal (loid)s from waters. Biosorption of arsenic and cadmium were evaluated in this paper using standard adsorption model, Freundlich isotherm, which expects heterogeneous distribution of energy of adsorption sites on sorbent. Freundlich adsorption isotherm has form:

Table 3. Freundlich constants for biosorption of cadmium and arsenic onto biomass of Aspergillus clavatus strain from aqueous solutions.

Metal	$\log K_F$ $(mg.g^{-1})/(mg.ml^{-1})^N$	N	R^2
Cadmium Cd^{2+}	-0.685 (-1.09 – -0.282)	0.435 (0.289 – 0.580)	0.762
Arsenic AsO_4^{3-}	0.413 (0.253 – 0.574)	0.890 (0.826 – 0.955)	0.970
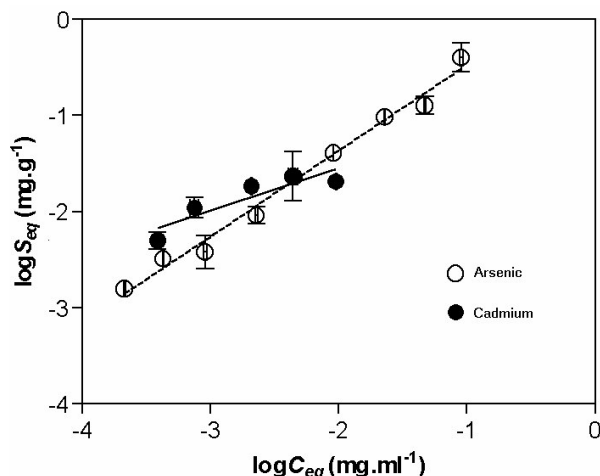
Figure 1. Application of Freundlich model to arsenic and cadmium biosorption onto biomass of fungal *Aspergillus clavatus* strain.

$$S_{eq} = K_F C_{eq}^N \qquad (1)$$

and its linear form is:

$$\log S_{eq} = \log K_F + N \log C_{eq} \qquad (2)$$

where S_{eq} is adsorbed amount of metal(loid) onto bio-mass $(mg.g^{-1})$, C_{eq} is equlibrium concetration of metal (loid) in aqueous solution $(mg.ml^{-1})$, K_F and N are Freundlich constants.

For determination of Freundlich constants its linear form (2) was used and their values along with determination coefficients for biosorption of arsenic and cadmium are shown in Table 3.

The experimental biosorption results for arsenic and cadmium followed well the Freundlich equilibrium sorption model in the concentration range of 0.25 – 100 mg.l^{-1} (Figure 1), and dependency of S_{eq} and C_{eq} were statistically significant ($P < 0,001$ for As and $P < 0,05$ for Cd). Adsorption isotherm for biosorption of arsenic is relatively linear because Freundlich exponent N is around 1 (Table 3). This shows that there were not all of the active sites occupied in certain concentration range, while the absorption capacity of biomass did not change. The ability of biomass to sorb arsenic without respect to initial concentration of arsenic in aqueous solution also support relative constant of immobilized arsenic by biomass, which are shown in Table 1. On the other hand, adsorption isotherm of cadmium is significantly nonlinear and has convex

form ($N < 1$), which refers to lower affinity of cadmium to biomass in higher initial concentration of cadmium in aqueous solution. This means that sorption capacity of biomass for cadmium ions is limited in this concentration range (Table 2).

Conclusion

Application of biosorption for removal of potentially toxic metal (loid)s from contaminated waters is a problem that is mostly studied under laboratory conditions. But we can plan real technologies useable for *in situ* bioremediation only when all of the parameters of this technology are verified mathematically to guarantee economical advent-age of this technology in comparison with conventional chemical methods. This is why laboratory experiments represent important step before the construction of large-scale bioreactor. In this paper the biosorption of cadmium and arsenic from aqueous solutions onto the unmodified compact biomass of microscopic filamentous fungus *A. clavatus* DESM. was studied in the concentration range of 0.25 – 100 mg.l^{-1}. Mathematical model (Freundlich isotherm) from experimental results suggests potential of biomass of microscopic filamentous fungi for removing of toxic metal (loid)s from contaminated waters.

ACKNOWLEDGEMENTS

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