



Full Length Article

Removal of Ni(II) Ions from Substrate using Filamentous Fungi

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ABSTRACT

Ni(II) uptake capacity of eight fungal species viz., *Aspergillus niger*, *A. terreus*, *A. flavus*, *Rhizopus arrhizus*, *Cunninghamella echinulata*, *Alternaria alternata* and *Trichoderma harzianum* was evaluated through batch biosorption assays. Biosorption experiments were conducted with 0.1 g of fungal biomass in 250 mL flask filled with 100 mL metal solution using constant shaking at 150 rpm. The maximum adsorption capacity was recorded for *T. harzianum* (11.77 mg/g) followed by *R. arrhizus* (9.28 mg/g), *A. terreus* (7.86 mg/g), *A. niger* (7.69 mg/g), *A. flavus* (7.5 mg/g), *A. alternata* (7.37 mg/g) and *C. echinulata* (4.69 mg/g). Experimental data of Ni(II) adsorption on fungal biomass is appropriately described by Langmuir and Freundlich adsorption isotherms within concentration range of 25–100 mg L⁻¹. © 2012 Friends Science Publishers

Key Words: Biosorption; Fungi; Heavy metal; Ni(II); Isotherms

INTRODUCTION

Nickel (Ni) is well-known toxic heavy metal mainly added at noxious concentration (20–200 mg/L) into the environment through electroplating sector (Revathi, 2005). Other essential sources of Ni are silver refineries, storage battery industries and zinc base casting (Sitting, 1976). The permissible limits of Ni in drinking water and industrial effluent are 0.01 mg/L and 2 mg/L, respectively (Sharma *et al.*, 1992). Exceeding level of Ni in soil resulted in phytotoxicity in plants (Brune & Dietz, 1995), low concentration < 0.5 mg per kg of dry weight of plant exhibited stimulatory effect on growth of various crops (Mishra & Kar, 1974). It has been reported that Ni(II) above permissible level (0.07 mg/L) is responsible for headache, vomiting, chest pain, rapid respiration, cyanosis, bone dermatitis and lungs cancer etc. (Kadirvelu, 1998).

Biological approach like biosorption may provide attractive solution for treatment of metal bearing effluents through utilization of fungi as an efficient and economical adsorbent (Krim *et al.*, 2006). Some fungi are recognized as hyper-accumulators of heavy metals (Purvis & Halls, 1996) due to their filamentous morphology, robust nature and high percentage of cell wall material. The fungal hyphal wall was found to be a primary site of metal ions accumulation owing to presence of the acet-amido group of chitin, amino and phosphate groups in nucleic acids, amino, amido, sulfhydryl and carboxyl groups in proteins and hydroxyls in polysaccharides (Veglio & Beolchini, 1997).

The study was intended to assess biosorption capability of seven filamentous fungi for removal of Ni(II) ions within concentration range of 25–100 mg/L along with assessment of experimental data in accordance with the Langmuir and Freundlich adsorption isotherms.

MATERIALS AND METHODS

The pure cultures of test fungal species were acquired from First Fungal Culture Bank of Pakistan, Institute of Agricultural Sciences, University of the Punjab, Pakistan. Mycelial biomass of each test fungal species was prepared on 2% malt extract. Fresh biomass after 7th day of incubation was dried in an oven at 60°C, ground to size of less than 100 μm and was utilized in batch experiments.

The stock solutions of Ni metal ions (1000 mg L⁻¹) were prepared from its nitrate salts of analytical grade by dissolving the exact quantity of salt in double distilled deionized water. Further concentrations were prepared by diluting stock solution with double distilled deionized water. Biosorption experiments were performed by suspending 0.1 g of biosorbent in 100 mL of metal solution in 250 mL flask stirred at 150 rpm at pH 4.5 for 3 h. Different sets of experiments were carried out to appraise the maximum metal accumulating capacity of the biosorbents at different initial concentration of metal ions ranging between 25–100 mg L⁻¹. After desired contact time, the mixture was filtered through Whatmann No.1 filter paper and the residual metal ion concentrations were determined using Atomic absorption spectrophotometer (AAS).

The amount of metallic ion biosorbed per gram of biomass (q) and the efficiency of biosorption (E) were calculated using following equations:

$$q = \left(\frac{C_i - C_f}{m} \right) V \text{ and } E = \left(\frac{C_i - C_f}{C_i} \right) \times 100$$

C_i and C_f, initial and final concentration of the metallic ion (mg/L); m = dried mass of the biosorbent in the reaction mixture (g) and V = volume of reaction mixture (L).

The data of influence of initial concentrations of metal ions on biosorption capacity of the fungi was calculated by using equilibrium isotherms i.e., Langmuir (1916) and Freundlich (1906) adsorption isotherm models.

Langmuir model: $q_{eq} = q_{max}bC_{eq}/1 + bC_{eq}$

Freundlich model $q_e = K_F(C_e)^{1/n}$

q_{eq} = metallic ions adsorbed per unit of weight of adsorbents at equilibrium (mg/g); q_{max} = maximum adsorption capacity of metal (forming monolayer) per unit weight of the adsorbent (mg/g); b = constant related to the affinity of binding sites for metal ions (L/mg); C_{eq} = equilibrium concentration (mg/L); K_F (L/g) and n = Freundlich characteristic constants. All experimental data were acquired in triplicate and average values were used to compare data.

RESULTS AND DISCUSSION

Assessment of metal removal potential of fungal species:

Among seven fungal species, *Rhizopus arrhizus* and *Trichoderma harzianum* showed the maximum (2–10 mg/g), while *Cunninghamella echinulata* exhibited the minimum (1–4 mg/g) biosorption capacity within applied concentrations range of 25 to 100 mg/L of Ni(II) ions. Remaining four candidates namely *Aspergillus niger*, *A. terreus*, *A. flavus* and *Alternaria alternata* exhibited parallel biosorption capacity @ ~1.5–8.5 mg/g between concentration series of 25–100 mg/L, respectively (Table I). The difference in the removal ability of candidate fungi could be attributed to the larger surface area of *R. arrhizus* and *T. harzianum* biomass for adsorption, as mycelium of these fungi grow in the form of suspended growth, while *Aspergillus* spp. generally form pellets with a lower surface area (Ahmad *et al.*, 2005). Least biosorption potency obtained in case of *C. echinulata* possibly might be due to the sensitivity of fungus cell wall to the medium composition and growth conditions as reported by Brady *et al.* (1999).

In the current study, concentration range of 25–100 mg/L apparently exhibited significant elevation in uptake capacity and reduction in efficiency of the fungal adsorbents (Table I). The mechanism of metal uptake is mainly reliant on the initial concentration of metal. At low concentration, metals are adsorbed by specific sites, while with rising metal concentrations the specific sites are saturated and

the exchange sites are filled (Lehman & Harter, 1984).

Isotherm studies: The interaction of solute with adsorbent is described through isotherm assessments. The appropriateness of the isotherm equation on the adsorption data was compared by comparing the value of coefficients of determination, R^2 (Table II). Two distinctive types for adsorption are generally pointed out by adsorption isotherms (1) reversible (composed of both physisorption and weak chemisorption) (2) irreversible (strongly chemisorbed) (Al-Anber, 2007).

In chemisorption, the chemi-adsorbed material form a cover over the adsorbent surface, and the molecules are not considered free to move from one surface site to another (Kong, 2009). It is an irreversible type of adsorption on account of coverage of adsorbent surface by the monomolecular layer. Therefore, desorption becomes difficult due to change in the chemical nature of adsorbent(s) (Al-Anber, 2007; Al-Anber & Z. Al-Anber, 2008). *Physisorption*, involves weak intermolecular forces (Van der Waals forces) that do not cause a considerable alteration in electronic orbital patterns of the species. Multilayer adsorption would result due to establishment of equilibrium between the adsorbate and the fluid phase and adsorbed molecule is free to move rather fixing on the specific site on the adsorbent. Physical adsorption is generally reversible carried capability of desorption of adsorbed material. In addition, the adsorbed material may condense and form several superimposed layers on the surface of the adsorbent (Kong, 2009).

Langmuir adsorption isotherm: Coefficients of determination ($R^2 > 0.98$) of Langmuir model indicates suitability of this model for describing the adsorption of Ni(II) onto fungal biomass. In the light of Langmuir isotherm it could be suggested a monolayer coverage of Ni(II) ions onto mycoadsorbents biomass through both chemisorption and physical adsorption (Table II). It means that both physisorption and chemisorption may occur on the surface at the same time, a layer of molecules may be physically adsorbed on a top of an underlying chemisorbed layer (Denizli *et al.*, 2000). Low values of b revealed favorable and a reversible type of adsorption.

Freundlich adsorption isotherm: The coefficient of determination ($R^2 > 0.97$) of Freundlich adsorption revealed that the adsorption process is multi layered; with a non uniform distribution of heat of adsorption (Table II). It

Table I: Evaluation of biosorption potency of test fungal biomass for Ni(II) ion at different initial concentration of Ni(II) ions. Biomass quantity, 0.1g 100/mL: pH, 4.5 at 150 rpm for 3 h

Biosorbents	25 mg/L		50 mg/L		75 mg/L		100 mg/L	
	q (mg/g)	(%)	q (mg/g)	(%)	q (mg/g)	(%)	q(mg/g)	(%)
<i>R. arrhizus</i>	1.5	6	3.57	7.14	6.75	9	9.61	9.51
<i>T. harzianum</i>	1.6	6.4	3.56	7.12	6.73	8.97	9.66	9.56
<i>A. niger</i>	1.4	5.6	3.55	7.1	6.76	9.01	9.61	8.5
<i>A. terreus</i>	1.25	5	3.74	7.48	5	6.66	7.5	7.5
<i>A. flavus</i>	1.24	4.96	3.73	7.46	4.99	6.65	7.49	7.49
<i>A. alternata</i>	1.39	5.56	3.54	7.08	6.75	8.8	9.6	8.5
<i>C. echinulata</i>	0.7	2.8	2.21	4.42	3.12	4.16	4	4

Table II: Isotherm model parameters for Ni(II) adsorption onto fungi biomasses

Isotherm parameters	Biosorbents	q _{max} (mg/g)	b (L/mg)	R ²
Langumir	<i>R. arrhizus</i>	11.77	1.41	0.99
	<i>T. harzianum</i>	9.28	1.95	0.99
	<i>A. niger</i>	7.69	2.82	0.99
	<i>A. terreus</i>	7.86	2.73	0.97
	<i>A. flavus</i>	7.5	2.64	0.97
	<i>A. alternata</i>	7.37	2.71	0.99
	<i>C. echinulata</i>	4	0.26	0.98
Freundlich	<i>R. arrhizus</i>	0.022	0.77	0.98
	<i>T. harzianum</i>	0.014	0.68	0.99
	<i>A. niger</i>	0.018	0.72	0.99
	<i>A. terreus</i>	0.022	0.74	0.99
	<i>A. flavus</i>	0.022	0.78	0.98
	<i>A. alternata</i>	0.013	0.68	0.99
	<i>C. echinulata</i>	0.137	1.09	0.97

characterizes an initial surface adsorption followed by a condensation effect resulting from strong adsorbate-adsorbate interaction. The magnitude of $1/n$ quantifies the favorability of adsorption and the extent of heterogeneity on the fungal surface (Ozcan *et al.*, 2004). The high $1/n$ value of *C. echinulata* (1.09) in relation to remaining fungal species (>1) indicates the preferential sorption of Ni(II) ions by other fungal species. Value of K_F in the range 1–10 is required for beneficial adsorption. The K_F value of all test fungal species fall between 0.013–0.022 confirmed their greater desorption capacity and express easy separation of metal ions from aqueous medium (Bayramoglu *et al.*, 2003).

CONCLUSION

T. harzianum (11.77 mg/g) followed by *R. arrhizus* (9.28 mg/g), *A. terreus* (7.86 mg/g), *A. niger* (7.69 mg/g), *A. flavus* (7.5 mg/g), *A. alternata* (7.37 mg/g) and *C. echinulata* (4.69 mg/g) had the ability to sequester Ni(II) from aqueous solution within concentration range of 25–100 mg L⁻¹. The Langumir and Freundlich isotherms provided the best for sorption of Ni(II) onto fungal biomass.

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