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Biosorption of electroplating heavy metals by some basidiomycetes

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Abstract

Three species of Basidiomycetous fungi namely *Schizophyllum commune* Fries*, Ganoderma lucidum* (Curt. Fr.) P. Karst and *Pleurotus ostreatus* (Jacq.) Quélet was investigated for removing heavy metal ions viz., Cu(II), Cr(VI), Ni(II) and Zn(II) from electroplating industrial effluents. Biosorption assays indicated that the test fungi possess great ability for removal of heavy metal ions. *S. commune* exhibited the maximum biosorption efficacy followed by *G. lucidum* and *P. ostreatus,* respectively through predilection of metal ions follow the order of: Ni(II) > Cu(II) > Cr(VI) > Zn(II).

Keywords: Biosorption, Basdiomycetes, Heavy metal, *Pleurotus ostreatus Schizophyllum commune.*

Introduction

Industrial wastewater pollution is one of the most debatable dilemma especially in countries like Pakistan, India and South Africa where potable water is in short supply. Industrial wastewater is heavily loaded with different types of inorganic and organic pollutants, which are discharged through aquatic routes either in water soluble or insoluble forms (Dahiya *et al*., 2007). In this regard, occurrence of heavy metals in the aquatic system has become a global phenomenon due to their carcinogenic and mutagenic nature (Mahiva *et al*., 2008). Electroplating sector in Pakistan is contributing its major part in deteriorating the country environment at massive scale with the accumulation of heavy metals in aqueous environment. The chemically polluted water has seriously damaged the ecology of surface and ground water, which eventually impart serious consequences on agriculture due to contamination of crops grown in a polluted area (Mufti *et al*., 1997). This serious kind of heavy metal pollution is now felt more than ever because of currently severe water crises in Pakistan.

In recent years, the research for the removal of toxic metal has focused on new technologies rather than conventional methods such as ion exchange, chemical precipitation, membrane processes and solvent extraction, which are expensive and inefficient (Yan and Viraraghavan, 2001; Veit *et al*., 2005). The potential use of microorganisms in treatment of hazardous materials and metals from their aqueous environments by biosorption is considered as a preferred method. The term 'biosorption' has been used to describe the passive nonmetabolically mediated process of metal ion binding by living or dead biomass (Markandey and Markandey, 2002; Volesky and Naja, 2005). Biomaterials like fungi have been proven more efficient and economical for removal of toxic metals from dilute aqueous solutions because of thier filamentous morphology and high percentage of cell walls (Lacina *et al*., 2003). Moreover large quantity of fungal biomass is available from the antibiotic and food industries. Ultimately the biosorption results not only in metal removal but provides an eco-friendly environment. The ability of the basidiomycetes to adsorb and accumulate metals together with excellent mechanical properties of fungal mycelia provides an opportunity to utilize such candidates in selective sorption of industrial heavy metal ions from polluted waters (Iqbal and Edyvean, 2004; Bayramoglu *et al*., 2005; Pogaku and Kulkarni, 2006; Razmovski and Siban, 2008).

The present study aims to investigate the potential of three basidiomycetes viz., *S. commune, G. lucidum* and *P. ostreatus* for adsorbing heavy metal ions from electroplating industrial effluents.

Materials and Methods

Sampling

Effluents samples were collected from outlet pipes of electroplating industry, Shahdrah. To ensure accuracy and precision, triplicate effluents samples were drawn from the sampling point. The samples were given proper treatment for storage at

4 °C by acidification with 1.5 mL conc. HNO_3 per liter of the samples to pH < 2 (Tayim and AlYazouri, 2005).

Procurement, growth and maintenance of test fungal strain

The pure cultures of test fungal species viz., *G. lucidum* (FCBP 316) and *P. ostreatus* (FCBP 317) were obtained from First Fungal Culture Bank of Pakistan, Institute of Mycology and Plant Pathology, Punjab University. While, that of *S. commune* was acquired from Pakistan Council of Scientific and Industrial Research (PCSIR) Laboratories, Lahore. These pure cultures were maintained on 2% MEA, for utilization in biosorption studies.

Biomass production of test fungal species

Mycelial biomass of the each test fungal species was grown in 2% malt extract (ME) both in 250 mL conical flasks by taking active inocula from preserved stock culture. Inoculated flasks were incubated for 15 days under controlled temperature of 25±1 °C in stationary phase. After the incubation period, the biomass of each candidate fungus was separated from culture broth by filtration and subjected to successive washings with double distilled deionized water. The biomass was dried in oven at 60 °C for 24 hours and homogenized in a blender to break the cell aggregates into smaller fragments of 0.5-1 mm diameter (mesh size 150 μm). The dried biomass was preserved in airtight jar to be used in biosorption test series.

Batch biosorption experiments

Batch experiments were performed by taking 0.2 g of oven dried biomass of test fungus in 250 mL flask containing 100 mL of Cu(II): 23.56, Ni(II): 54.83, Zn(II): 42.87 and Cr(VI): 93.54 mg L^{-1} solution at 150 rpm and 25 °C for 12 hours. After each experiment, the mixture was filtered through Whatman filter paper No.1 and the residual metal ions concentration was determined using Atomic absorption spectrophotometer (Model, Varian AA 1275 series).

Biosorption data evaluation

All the experiments were run in triplicates and controls were also run on same pattern without addition of biomass. The amount of metallic ions biosorbed per g of biomass (q) and the efficiency of biosorption (E) were calculated using following equations.

$$q = \left(\frac{C_i - C_f}{m}\right)V \qquad E = \left(\frac{C_i - C_f}{C_i}\right) * 100$$

,

Where, C_i = initial concentration of the metallic ions (mg L^{-1}); C_f = final concentration of metallic ions (mg L^{-1}); m = dried mass of the biosorbent in the reaction mixture (g); V = volume of the reaction mixture (mL). All the data were subjected to analysis of variance (ANOVA).

Results and Discussion

Physicochemical Analysis of Electroplating Industrial Effluents

The data recorded on the physico-chemical characterization of the main polluting heavy metal ions and other parameters viz., pH, temperature, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Dissolve Solids (TDS) levels found in the Electroplating effluents, Shahdrah, Lahore are presented in Table. 1. The concentration of various heavy metal ions i.e., Cu(II), Cr(VI), Ni(II) and Zn(II) in electroplating effluents was found to be many times higher than the levels permitted by the environmental legislation of NEQS and WHO. The wastewater had pinching odour, acidic in nature with pH ranging from 4.50 to 5.00 and of dark yellow colouration. The BOD (70 mg L^{-1}) and TDS (770 mg L^{-1}) levels were within the desirable limits. However, the level of COD (2800 mg L^{-1}) was higher than that of tolerance limits. The biological analysis indicated the absence of biological flora in all samples.

Batch Biosorption Assays

Analysis of variance clearly depict that the effect of test fungi viz., *S. commune, G. lucidum* and *P. ostreatus* was highly significant ($P \leq 0.001$) in their biosorption potential of four heavy metal ions i.e., Cu(II), Ni(II), Zn(II) and Cr(VI) in the reaction mixture. Similarly, high F-value in this factorial design also displayed a significant difference in absorption capacity of all the four metallic species by the test fungal species. The interactive effect of fungi x metal ions also exhibited a highly significant level (Table 2).

Although all the test species exhibited significant biosorption capacity for all the metal ions in the electroplating effluents, a considerable species specific variation was also evident in the extent of metal ions uptake. In general, the test species displayed maximum biosorption capacity for Ni(II) (22.70-52.74 mg g^{-1}) and minimum for Zn(II) (4.14-7.12 mg g^{-1}). The remaining metallic ions i.e., Cu(II) and Cr(VI) were also adsorbed in considerable amounts, but the removal of former (13.63-15.42 mg g^{-1}) was comparatively greater than the later (11.67-15.72 mg g^{-1}). There was however, considerable difference in biosorption capability of the test fungal species. *S. commune* showed its maximum biosorption capacity for all heavy metal ions, followed by *G. lucidum* and *P. ostreatus*, respectively. However, the superior biosorption potential of *P. ostreatus* (35.51 mg g^{-1}) over *G. lucidum* (22.70 mg g^{-1}) was dominant in case of Ni(II) ion. In general, biosorption capacity of the test fungi for metal ions was observed to follow the sequence in following mode: Ni(II) > Cu(II) > Cr(VI) > Zn(II) (Fig. 1A).

Table 1: Physico-chemical characterization of electroplating effluents, Shahdrah, Lahore.

Sr.#	Parameters	Electroplating Effluents Current status	NEQS Acceptable limits	WHO Acceptable limits
1.	Copper(II), mg L^{-1}	± 23.56	1.00	2.0
2.	Chromium(III),mg L^{-1}	-	1.00	0.10
3.	Chromium(VI),mg L^{-1}	± 93.50	1.00	0.05
4.	Nickel(II), mg L^{-1}	± 54.83	1.00	0.07
5.	Zinc(II), mg L^{-1}	± 42.87	5.00	2.00
6.	pH Value	± 4.5-5.0	6.0-10	No guideline
7.	Temperature (°C)	± 25-26	40	No guideline
8.	Biochemical Oxygen Demand (BOD) at 20°C, mg L^{-1}	± 70	80	No guideline
9.	Chemical Oxygen Demand (COD), mg L^{-1}	± 2800	150	No guideline
10.	Total Dissolved Solids (TDS) mg L^{-1}	± 770	3500	No guideline

±: indicate standard error mean of three replicates

- NEQS (1999) : National Environmental Quality Standards for liquid Industrial effluents
- WHO(2006) : World Health Organization guidelines for drinking water quality

Table 2: Analysis of variance (ANOVA) for biosorption capacity (q) of the test fungi for Cu(II), Ni(II) Zn(II) and Cr(VI) ions.

Sources of variation	df	SS	MS	F values
Treatments	11	6234	567	72.23***
Fungi (F)	2	477	239	30.41***
Metal (M)	3	4814	1605	205***
F × M	6	943	157	20.03***
Error	24	189	7.85	
Total	35	17751		

***: significant difference at $P \leq 0.001$

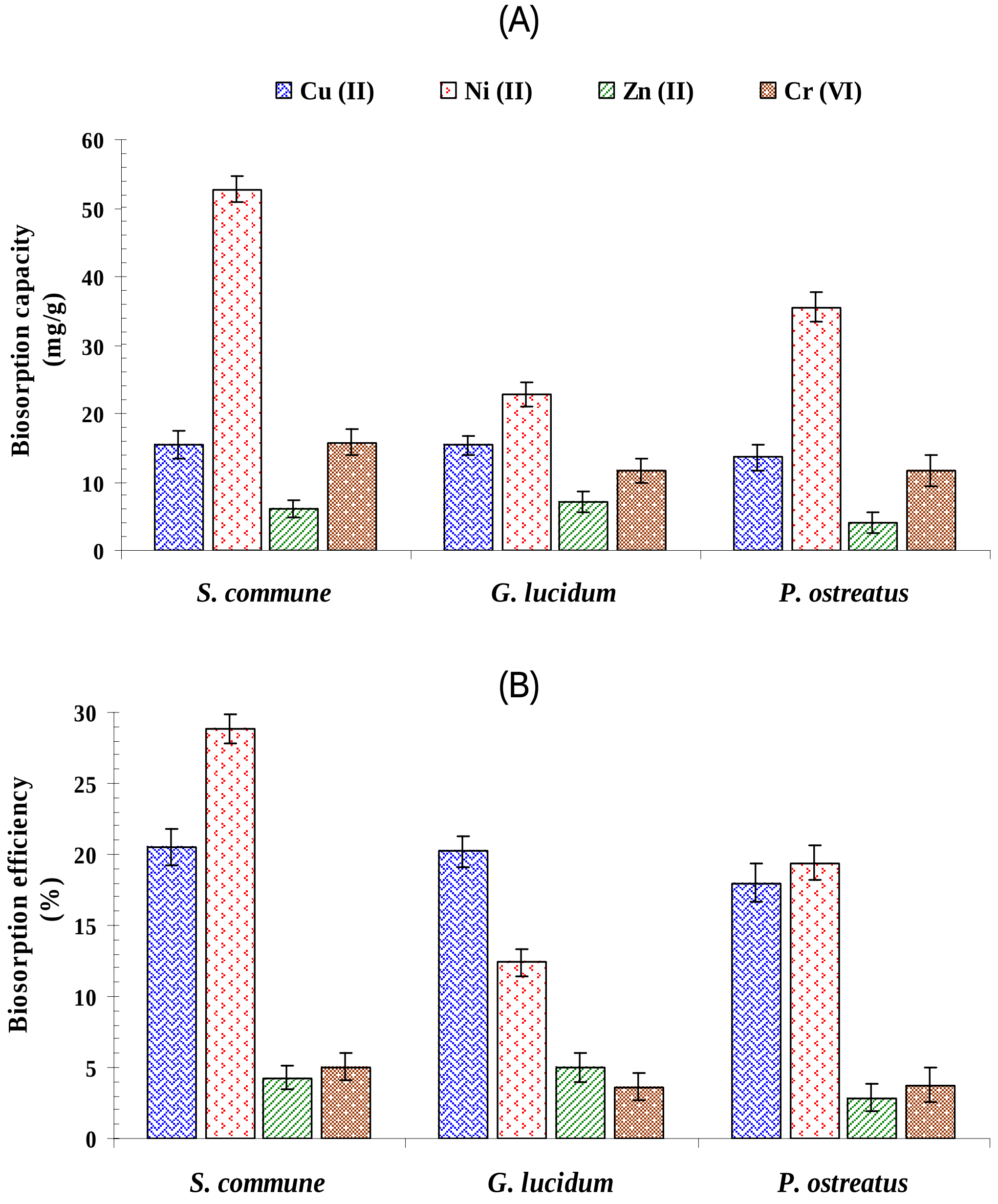

Fig. 1 A & B: Biosorption capacity (A) and efficiency (B) of the test fungal species for metal ions from electroplating industrial effluents
Initial concentration of Cu(II): 23.56, Ni(II): 54.83, Zn(II): 42.87 and Cr(VI): 93.50 mg L^{-1} ions in the reaction mixture. Biosorption conditions: biosorbent concentration, 0.03 g 100 mL^{-1}; pH, 5.0 (the solution pH was not controlled during the experiment); 150 rpm and 25°C for 12 hours. Vertical bars show standard error of means of three replicates.

Biosorption efficiency (%) of the test species revealed among three test fungi, *S. commune* showed maximum biosorption efficiency for Ni(II) (28.87%) followed by Cu(II) (20.51%), Cr(VI) (5.05%) and Zn(II) (4.26%) ions. Similar preference for metal ions in terms of maximum biosorption efficiency was observed in *P. ostreatus* for Ni(II) (19.42%), Cu(II) (18.00%), Cr(VI) (3.74%) and Zn(II) (2.88%). However, in case of *G. lucidum* the maximum sorption efficiency was noticed for Cu(II) (20.21%) followed by Ni(II) (12.40%), Zn(II) (4.98%) and Cr(VI) (3.65%) ions. Therefore, sorption efficiency of *S. commune* and *P. ostreatus*, for metal ions represented selectivity order of: Ni(II) > Cu(II) > Cr(VI) > Zn(II), while *G. lucidum* exhibited its preference in order of: Cu(II) > Ni(II) > Zn(II) > Cr(VI) (Fig. 1B).

The present study was intended to evaluate the biosorption potential of three

Basidiomycetous members viz., *S. commune*, *G. lucidum* and *P. ostreatus* in removing heavy metal ions from the effluents of electroplating in Pakistan. The test fungal species in the experiment showed variable adsorption capacity for metal ions which is in line with earlier findings in several investigations (Arica *et al*., 2003; Veit *et al*., 2005; Bayramoglu *et al*., 2005). The species specific variability has also been attributed to differential innate properties of the biosorbents e.g., functional group and surface area, depending on the fungal division, genera and species (Veit *et al*., 2005). Others have also interpreted it as inherent capacity of a biosorbent for several types of metal ions, while carrying specific affinity for particular metal (Volesky and Holan, 1995).

The biosorption potential assays presently revealed the selectivity order viz., Ni(II) > Cu(II) ≥ Cr(VI) > Zn(II) by the test fungi. This indicates their variability in metal ions binding affinities for the same or different functional groups (amino, carboxylate, phosphate, sulphahydral, phosphate and thiol) on cell walls. Since in solution all the metal ions are in competition with each other for the available binding sites, a metal that has a higher affinity for particular functional group would bind in greater concentration. Earlier workers have also observed that fungal biosorbents carry high affinity for Cu(II) and Ni(II) as compared to other metal ions (Holan and Volesky, 1995; Kapoor and Viraraghavan, 1998, Bayramoglu *et al*., 2003). Similar other reports have also highlighted the preferential sorption of Cu(II) ion by fungi (Kapoor *et al*., 1999) and declared it as attractive scope of readily absorbed metal ion in treatment of industrial wastewater in comparison to Cr(VI) and Zn(II), being poorly adsorbed metal ions. This could be further explained in terms of the partial oxidation and deprotonation of the carboxylate and phosphate groups in the outer membrane of fungi by the CrO_4^{2-}, thereby increasing the net negatively charged functional groups resulting in enhanced biosorption of Ni(II) and Cu(II) ions to the biomass (He and Tebo, 1998). The low uptake of Cr(VI) and Zn(II) probably arises due to antagonistic effect of Ni(II) and Cu(II) ions in biosorption mixture. This may also be related to differential electrode potential of various metal ions, resulting in different biosorption affinities (White *et al*., 1979). Similar concept of stronger chemical and physical affinity for metal ion at greater electronegative bonds and ionic radii has been suggested in other studies (Tsezos and Volesky, 1981; Weast, 1988). The order of selectivity recorded in present investigation, however was not in conformity with Irving-Williams series of stability (1948) i.e., Cu(II)>Zn(II)> Ni(II)> Cr(VI) and previous findings of Yetis *et al*. (1998); Kovacevic *et al*. (2000) and Mihova and Godjevargova (2001). This might be explained by the fact that presently an excessive complex interaction was involved among several factors such as, different charge/mass ratios, availability of varied functional groups on the fungal cell walls and a variety of cations competing for the same binding sites.

Conclusion

Results obtained from the current investigation conclude that the test fungi displayed tremendous removal potential for Cu(II) and Ni(II) in relation to Cr(VI) and Zn(II) ions from effluents of electroplating. However, *S. commune* exhibited the superior biosorption potency for heavy metals among the candidates.

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