Pak. J. Bot., **42(3): 2105-2118, 2010.**

BIOSORPTION OF HEAVY METALS USING A DEAD MACRO FUNGUS *SCHIZOPHYLLUM COMMUNE* FRIES: EVALUATION OF EQUILIBRIUM AND KINETIC MODELS

AMNA JAVAID*, RUKHSANA BAJWA AND ARSHAD JAVAID

Institute of Mycology and Plant Pathology,
University of the Punjab, Lahore, Pakistan

Abstract

Biomass of a wood rotting fungus viz., *Schizophyllum commune* Fries was utilized for the treatment of electroplating wastewater that contained Cu(II), Ni(II), Zn(II) and Cr(VI) ions. Preliminary batch assays were conducted with synthetic pure metal-bearing solutions. Results obtained showed that among various parameters studied, solution pH between a range of 2.0-6.0 induced negligible uptake at pH < 3.5 and exhibited maximum at around 4.5-5.5 for Ni(II), Cu(II) and Zn(II) ions, while for Cr(VI) ion the highest was evidenced at pH 2.0-2.5. The kinetics of all metal ions was fast and biosorption equilibrium was established in 1 hour with appropriateness of pseudo-second-order. A temperature change in the range of 15–45 °C did not affect the biosorption capacity of the candidate fungus. The biosorption of metal ion increased on elevating initial metal ions concentrations (20-100 mg L^{-1}) in the medium. The maximum biosorption capacity of fungus biomass was 9.0, 21.27, 4.83, 18.54 mg g^{-1} for Ni(II), Cu(II) and Zn(II) and Cr(VI), respectively. The experimental data was best adjusted by Langmuir, Freundlich and modified Langmuir models. Biosorption assays conducted with actual electroplating effluents under pre-optimized conditions revealed efficiency of 72.01, 53.16, 7.08 and 19.87% for Cu(II), Ni(II), Zn(II) and Cr(VI) ions, respectively by candidate biomass.

Introduction

Electroplating sector and other industrial units in Pakistan are contributing their major part in deteriorating the country environment at massive scale due to accumulation of heavy metals in the aqueous environment (Javaid & Bajwa, 2008). 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. Owing to severe water crisis problems in Pakistan, the notorious heavy metal pollution requires an urgent solution.

A number of physico-chemical protocols are currently being used world-wide to depollute water loaded with heavy metals. However, these methods are carried with inherently problematic in their application and are not economically feasible (Volesky, 2001; Sharma, 2003; Okoronkwo *et al*., 2007). Biological process like biosorption has acquired due attention owing to number of advantages and engaged the scientists from all over the world to identify the potent biomass type (Khan *et al*., 2009; Al-Masri *et al*., 2010; Xiao *et al*., 2010). Environmentally ubiquitous fungi are structurally unique organisms that contribute to the significant removal of metal ions from wastewater than other microbes. This is because of their great tolerance towards heavy metals and other adverse conditions such as low pH, and their intracellular metal uptake capacity (Gadd, 1987).

---

*Corresponding author E-mail: aamnaa29@yahoo.com

Among the groups of fungi, basidiomycetes (wood rotting fungi) are useful source of mycelial biomass for biosorption of metal ions, being easy to cultivate, acquire high yield and generally regarded as safe. Therefore, biosorbents made from these fungi can be easily accepted by public when applied practically. The potential of wood rotting fungi to remove metal ions is limited to a few examples in comparison with micromycetes and role of macromycetes in this field has been known only for few decades (Veit *et al*., 2005; Jarosz-Wilkolazka *et al*., 2006; Gonen *et al*., 2008; Vimala & Das, 2009). In some cases, their ability to bind metals is same or even better, than that of lower fungi and yeast (Javaid, 2008). 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 (Bayramoglu *et al*., 2007; Razmovski & Šćiban, 2008).

Current investigation was designed to explore the metal [Cu(II), Ni(II), Zn(II) and Cr(VI)] removal capacity of a wood rooting fungus, *Schizophyllum commune* from aqueous solution. The influence of initial pH, contact time, temperature and initial metal ion concentration on biosorption was evaluated. To determine the feasibility and efficiency of a biosorption process, metal uptake potential of test fungus was examined in real effluent of electroplating under predetermined experimental conditions.

Material and Methods

Physicochemical analysis of electroplating effluents: Wastewater samples were collected from outlet pipes of Electroplating Industry of Pakistan. The samples were analyzed for various important water pollution parameters (Table. 1).

Biosorbent preparation: The pure cultures of test fungal species viz., *S. commune* was obtained from First Fungal Culture Bank of Pakistan, Institute of Mycology and Plant Pathology, Punjab University Lahore, Pakistan. The biomass of the test fungus was prepared in 2% malt extract broth. After harvesting, biomass was dried in on oven at 60 ^{o}C, and was utilized in further biosorption studies.

Batch biosorption assays: The biosorption of Cu(II), Ni(II), Zn(II) and Cr(VI) ions was investigated by oven dried biomass of *S. commune* in batch biosorption experiments. The metallic ion solutions prepared in mixture form were comprised of Cu(II) 23.56 mg L^{-1}, Ni(II) 54.83 mg L^{-1}, Zn(II) 42.87 mg L^{-1} and Cr(VI) 93.54 mg L^{-1}, as working concentrations selected on the basis of analysis of electroplating effluents. The stock solutions of respective metal ion (1.0 g L^{-1}) were prepared from their nitrate salts of analytical grade in double distilled water.

Batch experiments were performed by adding 0.2 g of biomass with a magnetic stirrer at 150 rpm and 25 $^{\circ}$C using 250 mL flasks containing test solutions comprised of Cu(II): 23.56, Ni(II): 54.83, Zn(II): 42.87 and Cr(VI): 93.54 mg L^{-1}. To study the effect of initial pH on metal ions sorption onto *S. commune* biomass, the pH values of the contact solutions were tested in the range of 2.0–6.0 (which was adjusted with HCl and NaOH at the beginning of the experiment not controlled afterward).

Biosorption kinetic assays were performed at different time intervals from 15-720 minutes containing reaction mixture. The variable temperature range chosen in experiments was from 20-45 ^{o}C with 5 ^{o}C difference, while keeping the values of other parameters same as stated above.

The effect of initial metal ions concentration on biosorption was studied at pH 5.0 and concentration of adsorption medium was varied between 20-100 mg L^{-1}. The competitive biosorption of various studied metallic ions from their mixture was investigated in the same manner. The medium containing 0.2 g L^{-1} was incubated at 25°C with 0.2 g of biosorbent in batch fashion (at 150 rpm).

Analytical procedure: After the desired incubation period (up to 180 min), the content of the biomass was successfully separated from aqueous solution. The supernatants were analyzed for residual metal ions concentration using an atomic absorption spectrophotometer (Model, Varian AA 1275 series). The amount of metallic ion biosorbed per gram of biomass (q) and the efficiency of biosorption (E) were calculated using following equations:

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

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) and V = volume of reaction mixture (mL).

All the experiments were laid down in triplicates and control experiments were also conducted without biomass addition.

Results and Discussion

Effect of pH: Biomass of *S. commune* exposed to heavy metal ions, exhibited maximum sorption capacity for the Cu(II), Ni(II) and Zn(II) in the pH range 5.0-5.5, above and below this pH substantial decline in metal uptake was evidenced which represents the pH factor being highly sensitizing element (Fig. 1). Low pH (4.0 and below) limits the biosorption of Cu(II), Ni(II) and Zn(II) ions on fungal biomass surfaces, probably due to the ion exchange between metallic species and competition effects with oxonium (hydronium) ion to some extent in the biosorption mechanism (Fourest & Volesky, 1997; Yin *et al*., 1999). In similar findings by earlier investigators it has been attributed to protonation or poor ionization of acidic functional group of cell wall at low pH, inducing a weak complexation affinity between the cell wall and the metal ions (Sag & Kutsal, 1996; Chergui *et al*., 2007). The reduction in metal ions uptake displayed by fungus at pH > 5.5 can be explained on the basis that at higher pH values the metal ions may accumulate inside the cells, and or the intra-fibular capillarities of the cell walls by a combined sorption microprecipitation mechanism, therefore, biosorption experiments are meaningless at higher pH (Beveridge, 1986).

Contrary to other metals, the uptake of Cr(IV) ions was significantly supported at low pH range of 2.0-3.0 and declined sharply at higher pH by biomass of *S. commune* (Fig. 1). Enhanced uptake at highly acidic pH could be due to the electrostatic binding of negatively charged chromium species (chromate/dichromate) to positively charged group such as amines of chitosan on fungal cell walls elevating biosorption capacity of the biosorbents to Cr(VI) ion (Bai & Abraham, 2002; Bajpai *et al*., 2004; Bayramoglu *et al*., 2005).

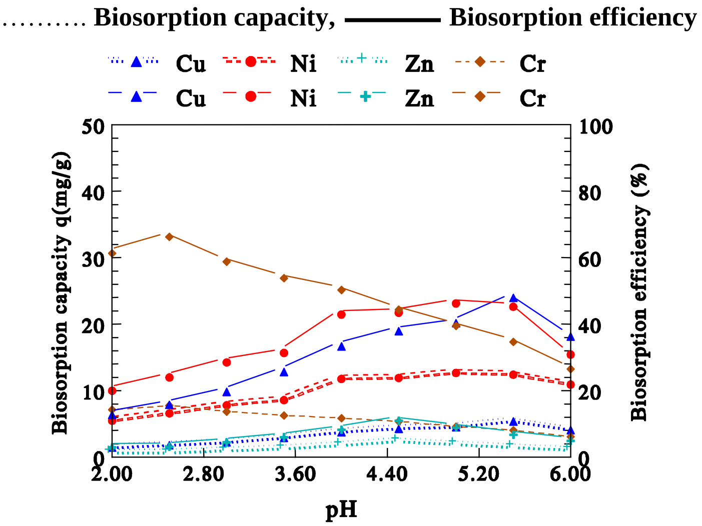

Fig. 1. Effect of pH on biosorption of Cu(II), Ni(II), Zn(II) and Cr(VI) ions by *S. commune* biomass. Initial concentration of Cu(II): 23.56, Ni(II): 54.83, Zn(II): 42.87 and Cr(VI): 93.50 mg L^{-1} ions in the reaction mixture. Biosorption conditions: biosorbent concentration, 0.2 g 100 mL^{-1}; pH range (2.0-6.0); 150 rpm and 25°C for 3 hours.

Effect of contact time: Time-course profiles for the adsorption of various metallic ions by *S. commune* revealed equilibrium time of 1 hour for of all four metal ions (Fig. 2). Almost 80% removal of all the heavy metal ions was recorded during first 15 minutes followed by saturation level of ~ 90% of the total biomass after 30 minutes of contact. Among the four metal ions, Ni(II) was removed most proficiently followed by Cu(II), Zn(II) and Cr(VI) at various tested time intervals. The plateau values i.e., adsorption equilibrium gradually reached to saturation level within 45 minutes for Cu(II) and Ni (II) and within 60 minutes for Zn(II) and Cr(VI) ions. The findings verify the two phases of biosorption, an initial rapid uptake due to surface adsorption and subsequent slow uptake due to membrane transport of metal ions into cytoplasm of cell or slow intracellular diffusion (Saglam *et al*., 2001). Similar results were obtained by Volesky & Holan (1995) and Cerbasi & Yetis (2001), while in some other studies single-step uptake has been suggested for different biosorbents (Huang *et al*., 1990). From the view point of savings in power and time consumption, rapid kinetics certainly will economize the daily running costs of treatment plant (Atkinson *et al*., 1998).

Biosorption kinetic modeling: Two different kinetic models i.e., Lagergren first-order (Lagergren, 1898) and Ritchie second-order (Ritchie, 1977) were used to fit the experimental data obtained on biosorption rate of heavy metal ions by the test fungus.

$$\text{Lagergren first - order} \quad \log\,(q_{eq} - q_t) = \log\, q_{eq} - \frac{k_1 t}{2.303}$$

$$\text{Ritchie second - order} \quad \frac{t}{q_t} = \frac{1}{k_2 q^2 eq} + \frac{1}{q_{eq}}\,t$$

where, $\boldsymbol{q_{eq}}$ = the amount of metal ions adsorbed at equilibrium (mg g^{-1}); $\boldsymbol{q_t}$ = the amount of metal ions adsorbed (mg g^{-1}) at any given time t; $\boldsymbol{k_1}$ = rate constant of pseudo-first order biosorption (min^{-1}); $\boldsymbol{q_{eq} - q_t}$ = the amount of metal ions adsorbed at equilibrium and at time t.

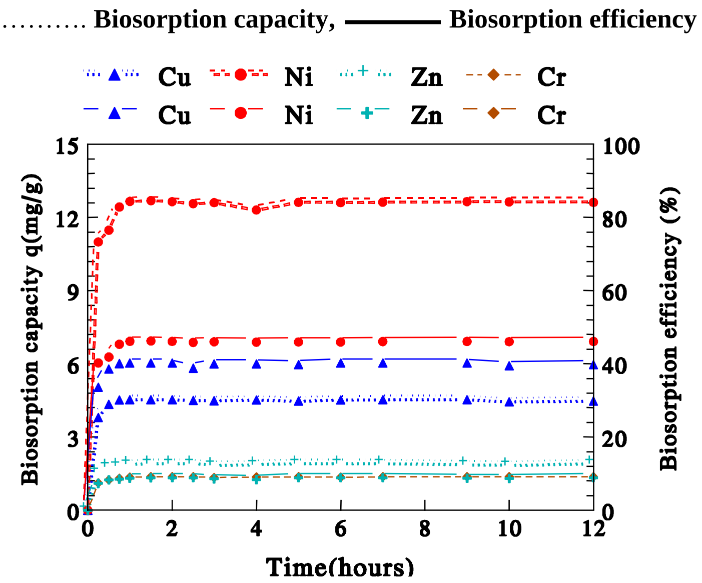

Fig. 2. Kinetic profiles of metal ions biosorption by *S. commune*.
Initial concentration of Cu(II): 23.56, Ni(II): 54.83, Zn(II): 42.87 and Cr(VI): 93.50 mg L^{-1} ions in the reaction mixture. Biosorption conditions: biosorbent concentration, 0.2 g 100 mL^{-1}; pH, 5.0; 150 rpm and 25°C for 12 hours.

Table 2. Kinetic parameters of the pseudo first-order and pseudo second-order rate equations for the biosorption of metal ions on to biomass of *S. commune*.

Metal ions	Experiment	First-order kinetic constant			Second-order kinetic constant		
	q_{eq} (mg g^{-1})	k_1	q_{eq}	R^2	k_2	q_{eq}	R^2
		(h^{-1})	(mg g^{-1})		(g mg^{-1} h^{-1})	(mg g^{-1})	
Cu(II)	4.54	1.72	4.56	0.99	2.36	4.60	0.99
Ni(II)	12.68	1.48	13.01	0.95	2.94	12.67	0.99
Zn(II)	1.92	1.00	1.25	0.97	3.10	2.00	0.99
Cr(VI)	9.23	1.19	9.24	0.96	2.59	9.25	0.99

The results on applicability of the Legergren first-order and Ho second-order based on solid capacity for the biosorbents are presented in Table 2 & Fig. 3. The coefficients of determination (R^2) of both the models were more or less greater than 0.9, indicating that second-order adequately describes the data acquired presently in metal ions biosorption assays (Fig. 3 A&B).

The findings suggest applicability of second-order kinetics, based on assumption that the biosorption/chemisorption may be a rate limiting step that involves valence forces. Through sharing or exchange of electrons between biosorbent and sorbate, it provides the best correlation of data in explaining the kinetics of biosorption (Preetha & Viruthagiri, 2005; Xiangliang *et al.*, 2005; Ho, 2006).

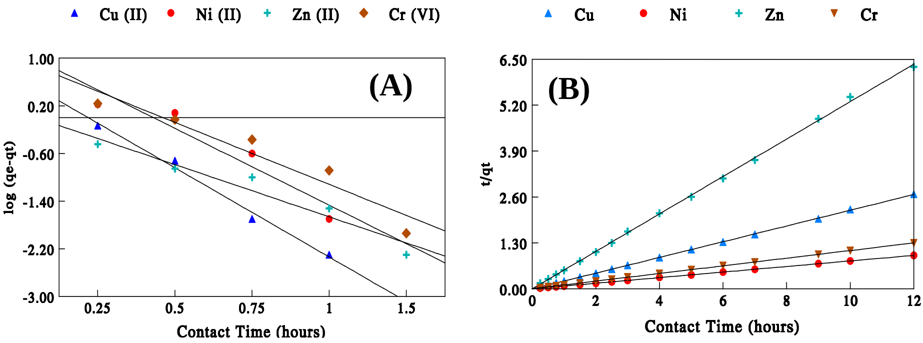

Fig. 3 A & B. Kinetic analysis of Cu(II), Ni(II), Zn(II) and Cr(VI) ions biosorption by linear plot of (A) pseudo first-order, (B) pseudo second-order rate equations by *S. commune* biomass.

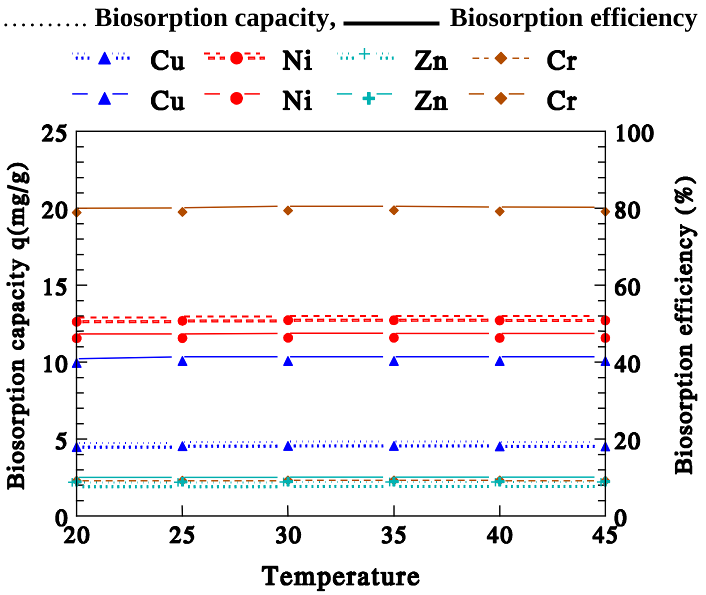

Fig. 4. Effect of temperatures (°C) on biosorption of Cu(II) , Ni(II), Zn(II) and Cr(VI) ions by *S. commune* biomass.

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, 0.2 g 100 mL^{-1}; pH, 5.0 at 150 rpm for 3 hours.

Effect of temperature: The temperature range of 20-45°C apparently exhibited no significant influence on biosorption potential of test fungal species (Fig. 4). The findings are in conformity with the earlier works which have also negated the effect of temperature on biosorption performance within this range, probably due to exothermic reaction (Saglam *et al*., 2002).

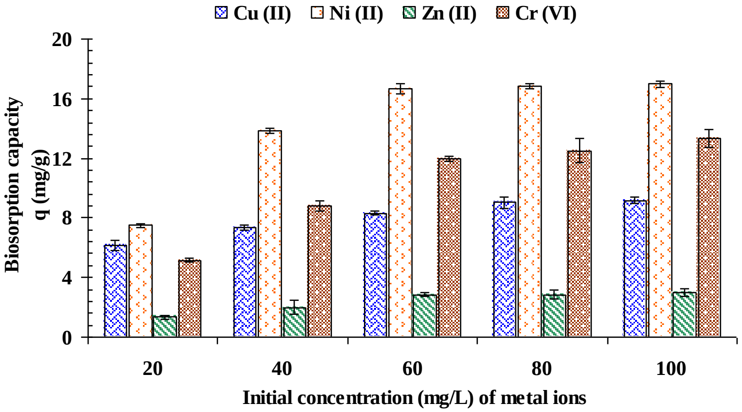

Fig. 5. Effect of various concentrations on biosorption capacity of *S. commune* for Cu(II) , Ni(II), Zn(II) and Cr (VI) ions in single metal systems.
Biosorption conditions: biosorbent concentration, 0.2 g 100 mL^{-1}, pH, 5.0; 150 rpm and 25°C for 3 hours. Vertical bars show standard errors of means of three replicates.

Influence of initial concentration of metal ions

Single metal studies: The graphical presentation for the effect of initial metal ion concentrations on biosorption capacity of the test fungi is depicted in Fig. 5. In case of Cu(II), on intensifying concentration limits 20-100 mg L^{-1}, perceptible biosorption capacity was 6.17-9.16 mg g^{-1}. However, the test fungus exhibited tremendous potential for Ni(II) in comparison to other three metals on appliance of metal concentration thus acquired capacity of 7.5-17.0 mg g^{-1} at 20-100 mg L^{-1}. In case of Zn(II) ion, test fungus exhibited capacity of 2.83 mg g^{-1} at 60 mg L^{-1}, while capacity reduced half-time at 80 and 100 mg L^{-1}. For Cr(VI), biomass of test fungus hold biosorption potential of 5.16, 8.83, 12.0, 12.67 and 13.33 mg g^{-1} at 20, 40, 60, 80 and 100 mg L^{-1}, respectively. The results of present findings clearly indicate that the sorption capacity increased and reached a saturation value as the metal ion concentration increased in aqueous medium. This assessment is in line with previously reported data on metal ion sorption by many other similar studies (Arica *et al.*, 2003; Veit *et al.*, 2005; Sheng *et al.*, 2007).There is evidence that at high metal ion concentration the number of ions sorbed is more than at low metal concentration, where more binding sites were free for interaction (Mukhopadhyay *et al.*, 2007).

Multi metal studies: It was observed in multiple metal components, total biosorption capacity of the test fungus was recorded to be less than in single metal conditions (Table 3). Whereas, biosorption capacity for Ni(II) and Cu(II) was least stressed by the presence of other metal ions at various applied concentrations. However, for Zn(II) interference of other three metal ions in mixture resulted in considerable reduction in fungal sorption capacity particularly at high concentrations regimes. The metal depicted bitter response to the test fungal candidate at low concentration ranges was Cr(VI), but removal was recorded to increase substantially on elevating concentrations in the presence of other three metal ions. The results obtained are in good agreement with some earlier findings representing that the total amount of metal ions biosorption in multiple metal systems is lower than in single system (Figueira *et al*., 1997; Utigikar *et al*., 2000; Hussein *et al*., 2004). However, reduction in sorption capacity in multiple metal systems could also be due to changes in ionic strength rather than competition between the heavy metals. The preferential order of metal binding in multiple metal isotherm study was same as recorded in single metal system i.e., Ni(II) > Cr(VI) > Cu(II) > Zn(II) by test fungus. This trend might be explained on the basis of differences in binding constants and the order of stability for metal-ligand complexes (Gardea *et al*., 1998).

Isotherm assessment

Single metal ion isotherm studies: Isotherm studies are basic requirement to design biosorption application procedures. For this purpose the empirical models viz., Langmuir (1916) and Freundlich (1906) for single solute system and modified Langmuir for multiple situations were employed to describe the biosorption equilibria of the test fungus.

$$\text{``Langmuir model} \quad \frac{q_{eq} = q_{\max} bC_{eq}}{1 + bC_{eq}} \text{''}$$

$$\text{``Freundlich model} \quad q_e = K_F (C_e)^{1/n} \text{''}$$

where, $\boldsymbol{q}_{\mathbf{eq}}$ = metallic ions adsorbed per unit of weight of adsorbents at equilibrium (mg g^{-1}); $\boldsymbol{q}_{\mathbf{max}}$ = maximum possible amount of metallic ions adsorbed per unit of weight of adsorbents (mg g^{-1}); $\boldsymbol{b}$ = constant related to the affinity of binding sites for metal ions(L mg^{-1}); $\boldsymbol{C}_{\mathbf{eq}}$ = equilibrium concentration (mg L^{-1}); $\boldsymbol{K}_{\mathbf{F}}$ = Freundlich characteristic constant of the system, incorporating parameters affecting the adsorption process, such as adsorption capacity; $\boldsymbol{n}$ = Freundlich characteristic constant of the system, incorporating parameters such as effect of concentration on the adsorption capacity and represents the adsorption intensity (dimensionless).

The parameter resulted from the Langmuir & Freundlich plots for Cu(II), Ni(II), Zn(II) and Cr(VI) ions by the test fungus are presented in Table 4. The plot of $1/q_{\mathrm{eq}}$ vs $1/C_{\mathrm{eq}}$ and In q_{eq} vs In C_{eq} in various initial concentrations range (20-100 mg L^{-1}) of four metal ions were found to be linear indicating the applicability of classical Langmuir & Freundlich adsorption isotherm to single metal ion solution of Cu(II), Ni(II), Zn(II) and Cr(VI) (Fig. 6 A&B). The coefficients of determination (R^2) of both models are more or less greater than 0.90, indicating that models adequately describe the experimental data of all four metal ions biosorption. The maximum capacity (q_{m}) determined from the Langmuir isotherm point calculated by the model in function of the experimental values of q_{eq} shows a linear tendency among the observed and predicted values. The Langmuir isotherm "*b"* the stability complex formed between metals ions and fungal cell wall under specific experimental conditions clearly demonstrated the small values.

The magnitude of intercept K_{F} and n (Freundlich constant) were calculated from Freundlich plots. The value of n, which is related to the distribution of bonded ions on the sorbent surface was greater than unity. The magnitude of Freundlich constant expresses easy separation of metal ions from aqueous medium and indicates favorable adsorption.

Table 4. Isotherm model parameters for the biosorption of metal ions onto biomass of *S. commune*.

Metal ions	q_{exp} (mg g^{-1})	Langmuir			Freundlich		
		q_m (mg g^{-1})	b (mg L^{-1})	R^2	K_F	n	R^2
Cu(II)	9.16	9.00	0.25	0.94	4.24	5.25	0.98
Ni(II)	17.00	21.27	0.12	0.98	5.38	3.29	0.90
Zn(II)	4.54	4.83	0.02	0.99	3.14	1.96	0.97
Cr(VI)	13.33	18.54	0.04	0.99	2.00	2.00	0.97

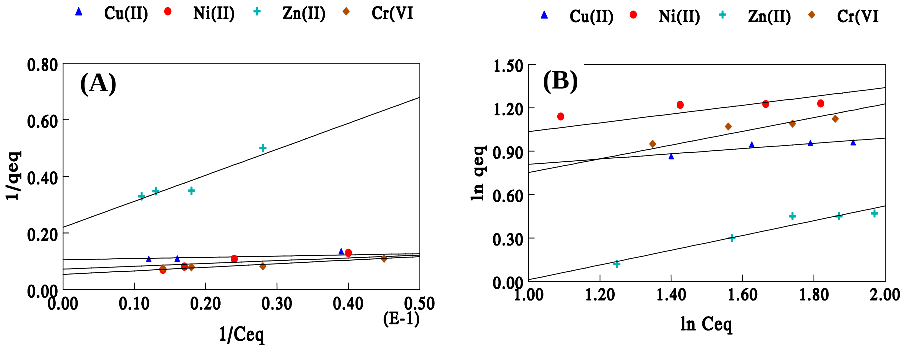

Fig. 6A &B: The linearized Langmuir (A) and Freundlich (B) adsorption isotherm for Cu(II) , Ni(II), Zn(II) and Cr (VI) ions biosorption by the *S. commune*.

Multiple metal isotherm studies: Extensions of several common isotherms were used to analyze the multi component experimental data. For this reason the extended Langmuir model and the Jain Soneyix modified extended Langmuir model have been proposed and applied. However, the extension of the basic Langmuir model proved to be reliable for the description of competitive phenomena. The formulation of this model was first planned by Schwab (1928). This model is based on the same assumption as was the original Langmuir like model and can be formulated as:

“Extended Langmuir model

$$q_{e,i} = \frac{q_{\max,i} b_i C_{e,i}}{1 + \sum_{i=1}^{n} b_i C_{e,i}}$$

”

where, $q_{max,i}$ and b_i = derived from the corresponding individual Langmuir isotherm equation; $q_{e,i}$ and $C_{e,i}$ = uptake and final concentration, respectively when adsorption equilibrium is reached; n = number of metal ions in the solution.

The parameters of Langmuir model for single solute system were used to calculate modified Langmuir equation for multiple metal systems. The non-linear adsorption isotherm presented in Fig. 7 clearly indicates the model is applicable to all experimental data of the test fungus. The order of maximum capacity for the biosorption of metal ions for *S. commune* was found in the order Ni(II) > Cu(II) > Cr(VI) > Zn(II). The application of the modified Langmuir model on sorption capacity of the test fungus in multi-component adsorption isotherm data clearly indicates that adsorbents are competing for same binding sites (Wurster *et al*., 2000).

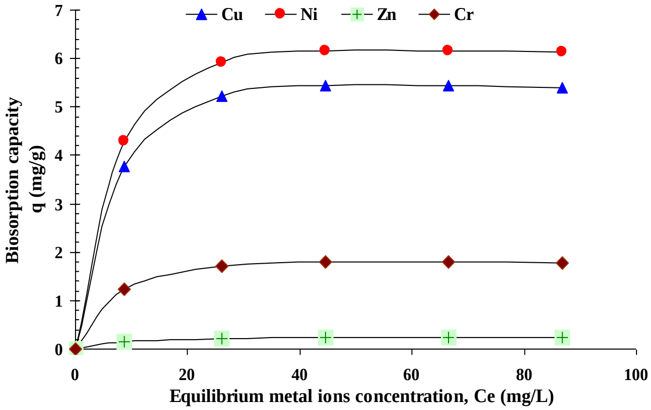

Fig. 7. Non-linear modified competitive Langmuir model for sorption of metal ions by *S. commune* in multiple metal systems.

Real industrial effluents: The feasibility and efficiency of a biosorption process depends not only on the properties of the biosorbents, but also on successful application of biosorbent in industrial effluents. Therefore, perusal of data obtained from aforementioned findings was used to conduct experiment with wastewater of electroplating industry. The biomass of *S. commune* removed all the four heavy metal ions significantly and exhibited same preference order of Ni(II) > Cu(II) >Cr (VI) > Zn(II) as was obtained with synthetic solution. Under optimized conditions, the biomass of *S. commune* exhibited significantly greater removal of Cu(II) (3.14 mg g^{-1}) and Ni(II) (10.54 mg g^{-1}) ions, while prevailed analogous adsorption capacity for both Zn(II) (1.08 mg g^{-1}) and Cr(VI) (23.67 mg g^{-1}) ions as with synthetic solution mixture. Moderate to slight reduction in heavy metal ions recorded in sorption potential of the from industrial effluents than from synthetic solutions could be due to various impurities present in electroplating industrial effluents in the form of anions i.e., SO_4^{-2}, NO_3^-, Cl^- and TDS that may compete for binding sites on the fungal cell walls. The high COD could also be a further compounding factor in reducing uptake of metallic ions from effluents. Besides low uptake can also be attributed to possible interference of Cl^- ions in biosorption process as compared to SO_4^{-2}, and NO_3^- as has been observed in other studies (Kovacevic *et al*., 2000).

Conclusion

The present study concludes, the test fungal specie *S. commune* employed in this study, can be classified as efficient biosorbents on the basis of rapid kinetics, remarkable biosorption capacity and selective removal of metal ions from electroplating industrial effluents. This biosorbents hold a potential for large scale application to remove toxic heavy metal ions from electroplating effluents.

References

Al-Masri, M.S., Y. Amin, B. Al-Akel and T. Al-Naama. 2010. Biosorption of Cadmium, Lead, and Uranium by Powder of Poplar Leaves and Branches. *Appl. Biochem. Biotechnol.*, 160: 976-987.

Anonymous. 1999. National Environmental Quality Standards for Municipal and Liquid Industrial Effluents (NEQS), Pakistan.

Anonymous. 2006. *Guidelines for drinking-Water Quality*. World Health Organization (WHO). 3rd eds.Vol 1.

Atkinson, B.W., F. Bux and H.C. Kasan.1996. Bioremediation of metal-contaminated industrial effluents using waste sludges. *Water Sci. and Tech*., 34: 9-15.

Bai R.S. and T.E. Abraham. 2002. Studies on enhancement of Cr(VI) biosorption by chemically modified biomass *Rhizopus nigricans, Water Res*., 36: 1224-1236.

Bajpai, J., R. Shrivastava and A.K. Bajpai. 2004. Dynamic and equilibrium studies on adsorption of Cr(VI) ions onto binary bio-polymeric beads of cross linked alginate and gelatin, Colloids *and Surfaces A: Physicochem. Eng. Aspects*, 236: 81-90.

Bayramoglu, G., G. Celik, E. Yalcin, M. Yilmaz and M.Y. Arica. 2005. Modification of surface properties of *Lentinus sajor-caju* mycelia by physical and chemical methods: evaluation of their Cr^{6+} removal efficiencies from aqueous medium. *J. Hazard. Mat.*, 119: 219-229.

Beveridge, T.G. 1986. The immobilization of soluble metals by bacterial walls, *Biotech. Bioengin.*, 16: 127-140.

Çeribasi, I.H. and U. Yetis. 2001. Biosorption of Ni(II) and Pb(II) by *Phanerochaete chrysosporium* from a binary metal system, Kinetics. *Water SA*., 27: 15-20.

Chergui, A., M.Z. Bakhti, A. Chahboub, S. Haddoum, A. Selatnia and G.A. Junter. 2007. Simultaneous biosorption of Cu^{2+}, Zn^{2+} and Cr^{6+} from aqueous solution by *Streptomyces rimosus* biomass. *Desalination*, 206:179-184.

Figueira, M.M., B. Volesky and V.S.T. Ciminelli. 1997. Assessment of interference in biosorption of a heavy metal. *Biotechnol. Bioengin*., 54: 344-350.

Fourest E. and B. Volesky. 1997. Alginate properties and heavy metal biosorption by seaweed biomass. *Biotechnol. Appl. Biochem*., 67: 215-226.

Freundlich, H.M.F. 1906. Over the adsorption in solution. *J. Phys. Chem*., 57: 385-470.

Gadd, G.M., 1987. Fungal response towards heavy metals. In: *Microbes in Extreme Environmentals*. (Eds.): R.A. Hebert and G.A. Codd. Academic Press, London. pp. 84-109.

Gardea-Torresdey, J.L., J H. Gonzalez, K.J. Tiemann, O. Rodrignuez and G. Gamez. 1998. Phytofiltration of hazardous cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (Alfalfa). *J. Hazard. Mat*., 57: 29-39.

Gonen, T.F., M.Yamac, A. Cabuk and Z. Yildiz. 2008. Selection of newly isolated mushroom strains for tolerance and biosorption of zinc in vitro. *J. Microbiol. Biotechnol.* 18: 483-489**.**

Ho, Y.S., 2006. Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods. *Water Res*., 40:119-125.

Huang, C.P., C.P. Huang and A. Morehart. 1990. The removal of Cu(II) from dilute aqueous solutions by *Saccharomyces cerevisiae*. *Water Res.*, 4: 433-439.

Hussein, H., S.F. Ibrahim, K. Kandeel and H. Moawad. 2004. Biosorption of heavy metals from wastewater using *Pseudomonas* sp. *Electron. J. Biotechnol*., 7: 195-201.

Jarosz-Wilkolazka, A., M. Graz, B. Braha, S. Menge, D. and G.J. Krauss. 2006. Species-specific Cd-stress response in the white rot basidiomycetes Abortiporus biennis and Cerrena unicolor. *Biometals*. 19: 39-49.

Javaid, A. and R. Bajwa. 2008. Biosorption of electroplating heavy metals by some basidiomycetes. *Mycopath*, 6:1-6.

Khan, M.S., A. Zaidi and P.A. Wani. 2009. Role of plant growth promoting rhizobacteria in the remediation of metal contaminated soils. *Environ. Chem. Lett.,* 7: 1-19**.**

Kovacevic, Z.F., L. Sipos and F. Briski. 2000. Biosorption of chromium, copper, nickel and zinc ions onto fungal pellet of *Aspergillus niger* 405 from aquous solution. *Food Technol. Biotechnol*., 38: 211-216.

Lagergren, S. 1898. About the theory of so called adsorption of soluble substances, Kungliga svenska vertenskapsakademiens. *Hand linger.,* 24: 1-39.

Langmuir, I. 1916. The constitution and fundamental properties of solids and liquids, Part. I: Solids. *J. Amer. Chem. Soc*., 38: 2221-2295.

Mukhopadhyay, M., S.B. Noronha and G.K. Suraishkumar. 2007. Kinetic modeling for the biosorption of copper by pretreated *Aspergillus niger* biomass. *Bioresour. Technol*., 98:1781-1787.

Okoronkwo, N.E., J.C. Igwe and I.J. Okoronkwo. 2007. Environmental impacts of mercury and its detoxification from aqueous solutions. *Afr. J. Biotechnol.,* 6: 335-340.

Preetha, B. and T. Viruthagiri. 2005. Biosorption of zinc(II) by *Rhizopus arrhizus*: equilibrium and kinetic modeling. *Afr. J. Biotechnol*., 4: 506-508.

Razmovski, R. and M. Šćiban. 2008. Iron(III) biosorption by *Polyporus squamosus***.** *Afri. J. Biotechnol*., 7: 1693-1699.

Ritchie, A.G., 1977. Alternative to elovich equation for kinetics of adsorption of gases on solids *J. Chem. Soc*. *Faraday Trans*., 73: 1650.

Saglam, A., Y. Yalcinkaya, A. Denizli, M.Y. Arica, O. Gene and S. Bektas. 2002. Biosorption of mercury by carboxymethylcellulose and immobilized *Phanerochaete chrysosporium. Microchem. J*., 71: 73-81.

Schwab, G.M. 1928. Theoretische und experimentelle Foortschritte auf dem Gebiete der heterogenen Gasreakionin Ergebnisse der Exakten Naturwissenschaften. *Berlin Springer,* 7: 276-341.

Sharma, Y.C. 2003. Cr(VI) from industrial effluents by adsorption on an indigenous low cost material. *Colloids and Surfaces A*: *Physicochem. Engin. aspects*, 215: 155-162.

Sheng, P.X. and J.P. Ting. 2007. Biosorption of heavy metal ions (Pb, Cu and Cd) from aqueous solution by the Marine Alga *Sargassum* sp., in single and multiple metal systems. *Indus. Engin. Chem. Res.,* 46: 2438-2444.

Shin, E.W. and R.M. Rowell. 2005. Cadmium ion sorption onto lignocellulosic biosorbent modified by sulfonation: The origin of sorption capacity improvement, *Chemosphere,* 60: 1054-1061.

Utigikar, V., B.Y. Chen, H.H. Tabak, D.F. Bishop and R. Govind. 2000. Treatment of acid mine drainage. Equilibrium biosorption of zinc and copper on non-viable activated sludge. *Int. Biodegrad. Biodet* ., 46: 19-28.

Veit, M.T., R.G. Tavares, S.M. Gomes-da-Costa and T.A. Guedes. 2005. Adsorption isotherms of copper(II) for two species of dead fungi biomass. *Proc. Biochem*., 40: 3303-3308.

Vimala, R. and N. Das. 2009. Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: A comparative study. *J. Hazard. Mater*., 168**:** 376-382**.**

Volesky, B., 2001. Detoxification of metal-bearing effluents: Biosorption for the next century. *Hydromet.,* 59: 203-216.

Xiangliang, P., W. Jianlong and Z. Daoyong. 2005. Biosorption of Pb(II) by *Pleurotus ostreatus* immobilized in calcium alginate gel. *Proc. Biochem*., 40: 2799-2803.

Xiao, X., S.L. Luo, G.M. Zeng, W.Z.Y. Wan and L. Chen. 2010. Biosorption of cadmium by endophytic fungus (EF) Microsphaeropsis sp LSE10 isolated from cadmium hyperaccumulator *Solanum nigrum* L. *Bioresour. Technol.,* 101: 1668-1674.

Yin, P.H., Q.M. Yu and Z. Ling. 1999. Biosorption removal of cadmium from aqueous solution by using pre-treated fungal biomass cultured from starch wastewater. *Water Res*., 33:1960-1963.

(Received for publication 29 July 2009)