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REMOVAL OF Pb(II), Cu(II) AND Cd(II) FROM AQUEOUS SOLUTION BY SOME FUNGI AND NATURAL ADSORBENTS IN SINGLE AND MULTIPLE METAL SYSTEMS

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Abstract

Six fungal and 10 natural biosorbents were analyzed for their Cu(II), Cd(II) and Pb(II) uptake capacity from single, binary and ternary metal ion system. Preliminary screening biosorption of assays revealed 2 fungi (*Aspergillus niger* and *Cunninghamella echinulata*) and three natural [*Cicer arietinum* husk, *Moringa oleifera* flower & soil (clay)] adsorbents hold considerable high adsorption efficiency and capacity for 3 metal ions amongst the adsorbents. Further biosorption trials with five elected adsorbents showed a considerable reduction in metal uptake capability of adsorbents in binary- and ternary systems as compared to singly metal system. Cd(II) manifested the highest inhibitory effect on the biosorption of other metal ions, followed by Pb(II) and Cu(II). On account of metal preference, the selectivity order for metal ion towards the studied biomass matrices was Pb(II) (40-90%) > Cd(II) (2-53%) > Cu(II) (2-30%).

Introduction

Biosorption is a practice that utilizes inexpensive biomass to sequester toxic heavy metals and is particularly useful for the removal of trace levels of contaminants from industrial effluents (Volesky, 2003). Since 1970s, after discovery of biosorption technique, scientists from all over the world have been engaged in identifying promising biosorbent owing to availability several kinds of adsorbents including microorganisms i.e., fungi (Zhang, 2009), bacteria (Hamzah *et al*., 2009), algae (Qunaibit *et al*., 2005) and plants (Melcakova and Ruzovic, 2010). After few decades, scientists have diverted their attentions to explore some low cost, naturally abundant and environment friendly adsorbents. In this case they have noticed tremendous metal sequestering ability of various type of agro waste (Qaiser *et al*., 2009). It is however imperative to notice, that all studies on biosorption have provided insight into the identification of several microbial biomass types for single-metal-ion solutions. The fact cannot be ignored that single toxic metallic species rarely exist in wastewaters. Infact, the presence of multiple metal ions often causes an interactive effect while insufficient attention seems to have been given to this problem (Choy *et al*., 2000, Hammaini *et al*., 2002, Sheng *et al*., 2007).

Relatively few studies on multimetal systems have been reported, though multimetal competitive interactions in solution with the sorbent material are amongst the basic factors affecting the degree of metal removal by biosorption (Ceribasi & Yetis, 2001, Javaid, 2008). For instance, Yan & Viraraghavan (2001) explored the biosorption ability of *Mucor rouxii* for Pb(II), Cd(II), Ni(II) and Zn(II) in binary and multi-metal ion solution. Mahvi *et al*., (2005) recorded 60-90% removal for Pb(II), Ni(II) and Cd(II) through application of tea waste from single metal solution and noticed a 3.5% decrease for Pb(II) adsorption whereas 12.2% for Ni(II) in mixture form Akar *et al*., (2006) explored the greater biosorption potential (22.79 mg g^{-1}) of *Ganoderma carnosum* for the removal of Pb(II) ion from aqueous solution and industrial effluents. In a similar investigation, the biosorption of 8 different metal ions i.e., Fe(II), Ni(II), Mn(II), Cu(II), Cd(II), Cr(III), Pb(II) and Zn(II) from aqueous solutions of combined industrial effluent by *Phanerochaete chrysosporium* was investigated with following affinity order: Cd(II) >Zn(II)> Mn(II)> Fe(II)> Ni(II)> Cr(III)> Cu(II)> Pb(II) by the test fungus (Pogaku & Kulkarni, 2006). Javaid, (2008) in her experimentation found potential capability of *Pleurotus ostreatus*, *Ganoderma lucidum* and *Schizophyllum commune* in adsorbing Cu(II), Ni(II), Cr(VI) and Zn(II) in single, multiple and real industrial solutions. However, like most of previous findings she noticed considerable reduction in sorption capacity of three fungi in competitive form and due to change in ionic strength rather than competition between the heavy metals. The present study aims to investigate the biosorption of divalent metal ions viz., Pb, Cd and Cu from single, binary and multi-component aqueous solutions using biomass of some fungi and plants.

Materials and Methods

Preparation of adsorbents: Six fungal and 10 natural adsorbents were selected for biosorption trials. The pure cultures of six fungal species viz., *Aspergillus niger* (FCBP 0074), *Aspergillus terreus* (FCBP 0058), *Rhizopus arrhizus* (FCBP 800), *Fusarium* sp., (FCBP 734), *Trichoderma harzianum* (FCBP 0139) and *Cunninghamella echinulata* (FCBP 0104) were provided by First Fungal Culture Bank (FCBP), in the Institute of Plant Pathology (IPP). A medium with 2 g L^{-1} malt extract was used for the cultivation of fungi and biomass preparation (Javaid & Bajwa, 2008).

Amongst natural, *Azadirachta indica* leaves, *Pinus* sp. bark and *Moringa oleifera* flower and leaves were collected from Botanical garden of Punjab University. However, *Citrus reticula* peels, *Oryza sativa* straw, *Luffa cylindrica* dried fruit and *Cicer arietinum* husk was acquired from local market. All adsorbents were washed thoroughly with tap water to remove dust and twice with distilled water. Finally, these candidate biosorbents were dried in oven at 100^{o}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). Waste charcoal was taken from Natural Product laboratory of Herbal Heritage Centre, IPP, Punjab University, and soil (clay) was collected from IPP lawn. Both of the biosorbents were dried at 60°C in an oven for 24 hours and sieved (mesh size 150μm) . The dried biomass of each adsorbent was utilized in biosorption experiments.

Batch screening experiments: The stock metal solutions at various concentrations were prepared by using nitrate salts of Pb(II), Cu(II) and Cd(II) (Merck, Germany). Preliminary screening batch experiments were conducted with 6 fungal and 10 natural biosorbents for each of three metal ions. Metal biosorption experiments were carried out in a 250mL flask at 25 ± 1°C in a rotary shaker at 150rpm. The flask was filled with 100mL (1000mg L^{-1}) of previously prepared solutions of each metal. An arbitrary amount of biosorbent biomass (0.1 g of dry cell weight mL^{-1}) was used. Each experiment was conducted for 4 hours, which was enough time to achieve steady state biosorption. The pH of each reaction mixture in flask was adjusted to the 4.5 using 0.1 N HNO_3 or 0.1 N NaOH. After desired contact time, the mixture was filtered through Whatmann filter paper No.1 and filtrate was analyzed using atomic absorption spectrophotometer (BMS-100 SERIES) to find out the amount of metal left after sorption.

Batch Experiments for binary- and multiple metal systems: Potential adsorbents obtained through biosorption screening trials were further subjected to batch examinations in binary and multiple metal mixture. For this purpose each metal ions [Cu(II), Cd(II) and Pb(II)] was taken in the equivalent concentration within the range of 100 mg L^{-1}. The proposed binary mixtures were in following combinations: Cu-Cd, Cu-Pb & Cd-Pb, whereas a grouping of Cu-Cd-Pb was taken as ternary aqueous phase. The adsorption experiment was carried out in a similar fashion as was performed for single metal cases.

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

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

where, C_i = initial concentration of the metallic ion (mg L^{-1}); C_f = final concentration of metallic ion (mg L^{-1}); m = dried mass of the biosorbent in the reaction mixture (g) and V = volume of reaction mixture (mL).

Results and Discussion

Quantitative screening of efficient biosorbents: Data presented in Table 1 reveals residual metal ion concentration (Cf) and biosorption efficiency (E) of different biosorbents with respect to their metal sequestering potential. Results presented clearly indicates that all selected adsorbents exhibited the highest removal efficiency for Pb(II) (40-90 %) in comparison to Cd(II) (2-53 %) and Cu(II) (2-30 %). In case of Cu(II) trend of biosorption by various adsorbents was recorded to follow the sequence of: *M. oliefera* flowers (50%) > *C. echinulata* and soil (30%) > *A. niger* and *C. arietinum* (21%). Assorted adsorbents possess following predilection for Cd(II) ions: *M. oliefera* flowers (53%) > *C. echinulta*, soil(clay) *Citrus reticula* peels, *M. oliefera* and *A. indica* leaves (50%) > *A. niger* and *A. terreus* (43%). For Pb(II) ions different metal sequesters tag along the following selectivity order : six fungal adsorbents (80-90%) > *M. oliefera* (leaves & flowers),*Citrus reticula* peels, Pinus bark and soil (80%) > *O. sativa* husk (60%). Thus, screening experiments demonstrated that two fungal species viz. *A. niger* and *C. echinulta* and three natural adsorbents i.e. *M. oliefera* flowers, *C. arietinum* husk and soil (clay) hold considerable greater biosorption efficiency and capacity for three metal ions (Cu, Cd & Pb) in comparison to rest of adsorbents. Therefore, these five efficient adsorbents were chosen for further biosorption assays. The assessment regarding screening of potent adsorbents for Cu(II), Cd(II) and Pb(II) revealed variable biosorption capacity of test species. Disparity in biosorption capacity of different adsorbents may be ascribed to the intrinsic ability of organism, its chemical composition of cell wall leading various types of interaction of metals with adsorbents (Gadd, 1993).

Table 1. Comparative representation of biosorption efficiency (%) of various biosorbents for metal ions. Biosorption conditions: biosorbents concentration, 0.1g 100 mL^{-1}; pH, 4.5; 150 rpm at 25°C for 4 hours.

	Biosorbents	Co g L^{-1}	Pb(II)		Cu(II)		Cd(II)	
			Ce g L^{-1}	E %	Ce g L^{-1}	E %	Ce g L^{-1}	E %
1.	*Aspergillus niger*	100	10	90	79	21	57	43
2.	*Rhizopus arrhizus*	100	13	87	92	8	82	18
3.	*Cunninghamella echinulata*	100	15	85	70	30	50	50
4.	*Fusarium* sp.	100	17	83	90	10	60	40
5.	*Trichoderma harzianum*	100	18	82	98	2	85	15
6.	*Aspergillus terreus*	100	19	81	90	10	57	43
7.	*Citrus reticula* peels	100	20	80	92	8	50	50
8.	Pinus sp. bark	100	20	80	90	10	98	2
9.	*Moringa oleifera* flowers	100	20	80	50	50	50	53
10.	*Moringa oleifera* leaves	100	20	80	90	10	50	50
11.	Soil (clay)	100	20	80	70	30	50	50
12.	*Oryza sativa* husk	100	40	60	96	4	70	30
13.	*Azadirachta indica* leaves	100	60	40	84	16	52	48
14.	*Luffa cylindrica* dried fruit	100	60	40	84	16	90	10
15.	*Cicer arietinum* husk	100	60	40	79	21	60	40
16.	Charcoal	100	60	40	88	12	90	10

Biosorption assays in binary and multiple metal systems: A comparison of the effect of Cu(II), Cd(II) and Pb(II) adsorption by selected adsorbents viz. *A. niger*, *C. echinulta*, *M. oliefera* flowers, *C. arietinum* husk and soil (clay) in single-, binary- and ternary metal systems is pooled in Tables 2 & 3. Data acquired revealed that, all five adsorbent species exhibited considerable metal uptake potency in the binary and ternary mixture. However, a considerable reduction in metal sequestering ability of the adsorbents was evident in binary and multiple metal systems in comparison to single metal system. Thus, in case of binary metal system all the chosen adsorbents exhibited the highest decline of 5-20% in adsorption efficiency for Cu(II) followed by 2-18%for Pb(II) and 5-12% for Cd(II) in comparison to single metal system (Table 2). While, a net reduction of 18-25%, 17-25% and 18-21% in uptake efficiency of adsorbents for Cu(II), Pb(II) and Cd(II), respectively was traced in ternary metal system in contrast to metal confiscating potential in single metal system (Table 3). The results in the binary and ternary systems clearly showed that the combined action of multiple ions was antagonistic. Thus, the metal removal efficiency was greater in the single-component systems in the comparison with the multi-component one. It is probably due to the absence of competitive processes between metals and biomass in single component system (Kovacevic *et al*., 2000). The most likely reason for the antagonistic effect is the competition for adsorption sites on the cell surfaces and/or the screening effect by the competing metal ions (Sheng *et al*., 2007). Results of present research also showed that Cd(II) exerted the most inhibitory effect on the biosorption of other metals, followed by Pb(II) and Cu(II). A similar phenomenon had been observed in the binary adsorption of Pb(II), Cu(II), Cd(II), and Ni(II) with a natural heterogeneous sorbent, where it was shown that Cd(II) and Ni(II) strongly competed with each other and were displaced in the presence of Pb(II) and Cu(II) (Papini *et al*., 2004).

Table 2. Comparative biosorption efficiency of various adsorbents in single metal systems (SMS) and binary metal systems (BMS) at 100 mg L^{-1}.

	Biosorbents	Cu(II)		Cd(II)	
		SMS	BMS	SMS	BMS
1.	*Aspergillus niger*	21%	18%	43%	41%
2.	*Cunninghamella echinulata*	30%	25%	50%	48%
3.	*Cicer arietinum* husk	21%	19%	40%	38%
4.	*Moringa oliefera* flowers	50%	44%	53%	50%
5.	Soil (clay)	30%	24%	50%	48%
	Biosorbents	**Cu(II)**		**Pb(II)**	
		SMS	**BMS**	**SMS**	**BMS**
1.	*Aspergillus niger*	21%	20%	90%	76%
2.	*Cunninghamella echinulata*	30%	24%	85%	77%
3.	*Cicer arietinum* husk	21%	20%	40%	37%
4.	*Moringa oliefera* flowers	50%	45%	80%	78%
5.	Soil(clay)	30%	25%	80%	70%
	Biosorbents	**Cd(II)**		**Pb(II)**	
		SMS	**BMS**	**SMS**	**BMS**
1.	*Aspergillus niger*	43%	40%	90%	75%
2.	*Cunninghamella echinulata*	50%	45%	85%	70%
3.	*Cicer arietinum* husk	40%	38%	40%	33%
4.	*Moringa oliefera* flowers	53%	47%	80%	70%
5.	Soil (clay)	50%	44%	80%	68%

Table 3. Comparative biosorption efficiency of various adsorbents in single metal systems (SMS) and ternary metal systems (TMS) at 100 mg L^{-1}.

	Biosorbents	Cu(II)		Cd(II)		Pb(II)	
		SMS	TMS	SMS	TMS	SMS	TMS
1.	*Aspergillus niger*	21%	16%	43%	35%	90%	67%
2.	*Cunninghamella echinulata*	30%	22.5%	50%	41%	85%	63%
3.	*Cicer arietinum* husk	21%	16%	40%	32%	40%	30%
4.	*Moringa oliefera* flowers	50%	41%	53%	42%	80%	66%
5.	Soil (clay)	30%	23%	50%	40%	80%	61%

Among the three metal ions, the five adsorbents exhibited the highest adsorption efficiency for Pb(II) and lowest for Cu(II). Cd(II) manifested the highest inhibitory effect on the biosorption of other metal ions, followed by Pb(II) and Cu(II). Generally, all the adsorbent demonstrated the highest uptake efficacy for Pb(II), followed by Cd(II) and Cu(II). Sheng *et al*., (2007) observed following preference order of metal ions: Pb(II) > Cu(II) > Cd(II) onto algal biomass and correlate this uptake trend with the electronegativities of the metal-ion hydroxides. The electronegative values of Pb(II) is 2.33, Cu(II): 1.90, Cd(II): and 1.69. According to them, higher electronegativity corresponds to a higher adsorption capacity owing to higher attraction of metal ions for electrons (Wang *et al*., 2006). In current study, the domino effect of Cd(II) over Cu(II), may be due to different pH value employed during biosorption experiments and dissimilarity in the nature of biomass. Ionic radius and hydration energy is an important factor in sorption process. The preferential sorption behavior of adsorbents for metal ions acquired in present investigations could also be explained in terms of ionic radii of the metal ions (Cu= 0.73 Å; Cd = 0.97 Å; Pb = 1.19 Å). Thus, the element with larger ionic radius will compete faster for exchange sites than those of smaller ionic radius. Adsorption may be related to the loss of the entire hydration sphere that precedes hydrolysis. According to Horsefall & Spiff (2005), smaller the ionic radius, the greater its tendency to hydrolyze leading to reduce sorption. The observed order indicates that Pb(II) may have greater accessibility to the surface of certain pores than Cd(II) and Cu(II) due to its larger ionic radius.

Results obtained from the present study conclude that:

1. *Cunninghamella echinulata* and *Moringa oleifera* flowers possess substantial adsorption potential for Cu(II), Cd(II) and Pb(II) in single- binary and ternary metal solution at metal concentration 100 mg L^{-1}.
2. The sorption of metal ions was reduced by the presence of co-ion(s), with the inhibitory effect increasing as the concentration of the co-ion(s) increased.
3. Adsorbents hold maximum uptake efficiency and capacity for Pb(II), followed by Cd(II) and Cu(II).
4. Cd(II) manifested the highest inhibitory effect on the biosorption of other metal ions, followed by Pb(II) and Cu(II).

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