

Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk)

Asma Saeed^a, Muhammed Iqbal^{a,*}, M. Waheed Akhtar^b

^a Environment Biotechnology Group, Biotechnology and Food Research Center, PCSIR Laboratories Complex, Lahore-54600, Pakistan

^b Institute of Biochemistry and Biotechnology, University of Punjab, Lahore, Pakistan

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Abstract

The study reports removal of heavy metals when present singly or in binary and ternary systems by the milling agrowaste of *Cicer arietinum* (chickpea var. black gram) as the biosorbent. The biosorbent removed heavy metal ions efficiently from aqueous solutions with the selectivity order of $Pb > Cd > Zn > Cu > Ni$. The biosorption of metal ions by black gram husk (BGH) increased as the initial metal concentration increased. Biosorption equilibrium was established within 30 min, which was well described by the Langmuir and Freundlich adsorption isotherms. The maximum amount of heavy metals (q_{max}) adsorbed at equilibrium was 49.97, 39.99, 33.81, 25.73 and 19.56 mg/g BGH biomass for Pb, Cd, Zn, Cu and Ni, respectively. The biosorption capacities were found to be pH dependent and the maximum adsorption occurred at the solution pH 5. Efficiency of the biosorbent to remove Pb from binary and ternary solutions with Cd, Cu, Ni and Zn was the same level as it was when present singly. The presence of Pb in the binary and ternary solutions also did not significantly affect the sorption of other metals. Breakthrough curves for continuous removal of Pb from single, binary and ternary metal solutions are reported for inlet-effluent equilibrium. Complete desorption of Pb and other metals in single and multimetal solutions was achieved with 0.1 M HCl in both shake flask and fixed bed column studies. This is the first report of removal of the highly toxic Pb, Cd, and other heavy metals in binary and ternary systems based on the biosorption by an agrowaste. The potential of application for the treatment of solutions containing these heavy metals in multimetal solutions is indicated.

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1. Introduction

Industrial effluents loaded with heavy metals are a cause of hazard to humans and other forms of life. The environmental impact due to their toxicity has led to the enforcement of stringent standards for the maximum allowable limits of their discharge into open landscapes and water bodies [1]. Authorities enforcing these standards further require the treatment procedures to be environment friendly [2]. Conventional methods for the removal of heavy metals from wastewaters, however, are often cost prohibitive having inadequate efficiencies at low metal concentrations, particularly in the range

of 1–100 mg/l [3–5]. Some of these methods, furthermore, generate toxic sludge [6], the disposal of which is an additional burden on the techno-economic feasibility of treatment procedures. These constraints have caused the search for alternative technologies for metal sequestering to cost-effective environmentally acceptable levels. The ability of biological materials to adsorb metal ions has received considerable attention for the development of an efficient, clean and cheap technology for wastewater treatment at metal concentrations as low as 1 mg/l [7]. Several materials in the categories of microbial biomass and plant wastes have been successfully used for metal biosorption [8–10].

Whereas numerous studies have reported the biosorption of metals by materials of diverse biological origin, these have remained limited to single species of heavy metal ions and

* Corresponding author. Tel.: +92 42 9230688; fax: +92 42 9230705.
E-mail address: iqbalmdr@brain.net.pk (M. Iqbal).

very little information is available for two and multimetal biosorption systems [11,12]. Wastewaters, however, contain multiple metals, which are likely to cause interactive effects depending on the number of metals competing for binding sites, the combination of these metals, levels of initial metal concentrations, the equilibrium steady state concentration of different metal ion species, limitations presented by the binding sites, and the nature and quantity of the biosorbent biomass [7,13]. Among the few multimetal biosorption systems investigated are the removal of Ni and Cr by cyanobacterium *Microcystis* [14]; Cd, Cu and Zn by seaweed *Ascophyllum* [7]; Ni and Cu by *Sphagnum* moss peat [15]; Cu, Cr, Fe, Ni, and Pb by fungus *Rhizopus* [12,16]; Cu and Cd by bacterium *Arthrobacter* [17]; Cd, Pb and Zn by bacterium *Alteromonas* [18]; Cd and Cu by alga *Nostoc* [19]; and Cd, Cu and Ni by pine bark [11]. The biological materials used in most of these studies were of microbiological origin, which inevitably add to the cost and complexity of biosorption procedures. No study has yet been carried out on the removal of metals by agrowastes in multimetal solutions, although several materials have been reported to efficiently biosorb them from single metal solutions [8]. Most of the multimetal sorption studies, furthermore, were done in shake flasks, which cannot be extrapolated for designing an operational technology without the data obtained from a continuous flow system.

Validity of the phenomenon of metal biosorption by a variety of biological materials is sufficiently established. Attention now needs to be focused on the search of cheaper and more efficient biosorbents capable of binding toxic metals from multimetal solutions in a continuous flow system. Husk of black gram (*Cicer arietinum*) has been recently reported to remove 100% Cd from 10 mg/l solution within 30 min and regenerating completely by desorbing 99.9% of the adsorbed metal [20]. Similar efficiencies were noted when Cd solution was passed in a continuous flow system through a fixed bed column packed with the husk. The agrowaste is available at no cost. These are sufficient indicators for developing a cheap and efficient procedure for the treatment of wastewater, containing several metals. Biosorption efficiency of the agrowaste is presently reported for the removal of Cd, Cu, Ni, Pb and Zn in single metal solutions, and different combinations of Pb and Cd, two of the three most toxic metals, in binary and ternary solutions in batch and continuous flow fixed bed column reactor.

2. Materials and methods

2.1. Adsorbent material

Black gram husk (BGH) was used for the metal biosorption studies. Black gram, also called Bengal gram or common gram, a variety of *C. arietinum* Linn (Family: Leguminosae), is distinguishable from the more common white variety chickpea (Spanish: garbanzo) by its smaller size and coffee-black husk. BGH is the seed coat comprising testa and tegumen, which is generated as a waste of no utility during the seed-splitting milling process. Proximate composition, lignocellulosic constituents of the crude fibre fraction, and particle size profile of BGH are given in Table 1 to indicate general physico-chemical nature of the adsorbent. The composite mixture of all particle sizes of BGH, as generated after milling, was used since an earlier study showed no significant difference in the biosorption of Cd by the composite mixture in comparison with individual fractions of different particle sizes [8]. BGH was thoroughly washed for 2–3 h in running tap water followed by boiling in double distilled water, changed repeatedly, till water was clear of all colouration. The washed and boiled BGH was then oven dried at 80 °C for 24 h and kept stored in desiccator till use. Quantity of the BGH biomass was varied, as respectively mentioned for different investigations.

2.2. Metal solutions

Atomic absorption spectroscopy grade metal solutions of Cd, Cu, Ni, Pb and Zn (nitrate salts in 0.5 mol/l HNO₃) concentration 1000 ± 2 mg/l (Merck), were diluted in ion-free double distilled water to the desired metal concentration. Adsorption was investigated from single metal solutions, from binary solutions containing Pb and another metal in different combinations, and Pb with Cd + Cu and Pb with Ni + Zn in ternary solutions. The solution pH was adjusted to 5, or as stated otherwise, with 0.1 M HCl or 0.1 M NaOH. Fresh dilutions were made for each study.

2.3. Metal analysis

Concentration of each metal, remaining in solution as the residual metal after adsorption, was determined us-

Table 1
Proximate composition, crude fibre composition, and the particle size profile of black gram husk (consolidated from published data: [8,20])

Proximate composition		Composition of crude fibre		Particle size fraction	
Contituents	%	Constituents	%	Sieve size	% by weight
Protein	3.32	Cellulose	69.0	<4	8.27
Fat	0.70	Hemicellulose	11.98	4	14.43
Crude fibre	51.90	Lignin	19.14	5	27.46
Ash	4.93			7	33.74
Moisture	15.50			8	11.60
Nitrogen-free extract (by difference)	39.15			12	4.44

British standard sieves of mesh size <4, 4, 5, 7, 8, and 12 with aperture size of >4, 4, 3.35, 2.8, 2.0, and 1.4 mm, respectively.

ing atomic absorption spectrophotometer (UNICAM-969). Analyses were done on triplicate samples. Controls comprised of adsorbent in double distilled water blank and adsorbent-free metal solutions. Analytical values were statistically analysed according to Duncan's multiple range test.

2.4. Shake flask biosorption

Batch biosorption assays were carried out in 250 ml Erlenmeyer flasks by transferring 100 ml of 10 mg/l single metal solutions and 1 g BGH. The flasks were tightly stoppered and the BGH–metal solution suspension was shaken on orbital shaker for 60 min at 150 rpm at $25 \pm 2^\circ\text{C}$ followed by centrifugation at 5000 rpm for 5 min to separate BGH from the metal solution. The supernatant was analysed for residual metals from which the quantity of metal biosorbed by BGH was computed. For the determination of rate of biosorption and the biosorption equilibrium time, the residual metal in the supernatant was determined by allowing BGH–metal contact for different periods between 5 and 60 min. The BGH–metal sorption suspension was equilibrated at different pH values of 2–7 for determining the effect of pH on biosorption. For the adsorption isotherm studies, metal concentrations used for biosorption by BGH were 10–800 mg/l. For studies on metal biosorption by BGH from binary and ternary solutions, the concentration of each metal in the solution was 10 mg/l, so that total multimetal concentrations, respectively, were 20 and 30 mg/l. The biosorption procedure was the same as for single metals described above.

2.5. Column biosorption

Fixed bed biosorption was done in glass columns of internal diameter 1.7 cm and height 28 cm, packed with 10 g BGH, packing height 25.0 cm. For single metal biosorption, 10 mg/l Pb solution was pumped upwards through the BGH-packed column, at a flow rate of 5 ml/min by a peristaltic pump (Cole Parmer). Effluent was collected manually after every 500 ml of the Pb solution passed through the column. Each fraction was analysed for residual Pb. The solution was continued to pass till the attainment of inlet–outlet Pb concentration equilibrium, which indicated no further metal sorption was occurring. Similar procedure was followed for metal biosorption from binary and ternary metal solutions. The quantity of each metal in the solution was 10 mg/l, so that total metal concentrations were 20 and 30 mg/l for the binary and ternary metal solutions, respectively.

2.6. Desorption of metal-loaded adsorbent

For the desorption of BGH after metal sorption in shake flasks, the metal-laden biosorbent was treated with HCl, which has been reported to be an efficient metal desorbent [15,20,21]. Desorption was done by transferring 1 g BGH loaded with different metals during the biosorption process to flasks containing 20 ml of 0.1 M HCl. The flasks were

shaken at 150 rpm for 30 min at $25 \pm 2^\circ\text{C}$. The flask contents were centrifuged to remove BGH and the residual content of Pb, Cu, Cd, Ni, Zn in the supernatant was determined. The metal-loaded BGH-pack in fixed bed column was desorbed by passing 0.1 M HCl through the same BGH-packed column used for the removal of Pb from single, binary and ternary metal solutions in the upward direction at the flow rate of 5 ml/min. Effluent from the column was manually collected after every 20 ml desorbent HCl passed. Each fraction was analysed for Pb content.

2.7. Adsorption isotherms

Langmuir and Freundlich isotherms were used to analyse the biosorption data. The Langmuir isotherms model is valid for monolayer adsorption on to surface containing finite number of identical sorption sites which is described by the following equation:

$$q_{\text{eq}} = \frac{q_{\text{max}} b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (1)$$

where q_{eq} and q_{max} are the observed and maximum uptake capacities (mg/g biosorbent), respectively; C_{eq} the equilibrium concentration (mg/l solution); b the equilibrium constant. The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants as below:

$$\frac{C_{\text{eq}}}{q_{\text{eq}}} = \frac{1}{b q_{\text{max}}} + \frac{C_{\text{eq}}}{q_{\text{max}}} \quad (2)$$

The Freundlich equation, on the other hand, is purely empirical based on sorption on heterogeneous surface, which is commonly presented as:

$$q_{\text{eq}} = K_{\text{F}} C_{\text{eq}}^{1/n} \quad (3)$$

where K_{F} and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich equation can be linearized in logarithmic form for the determination of Freundlich constants as below:

$$\ln q_{\text{eq}} = \frac{1}{n} \ln C_{\text{eq}} + \ln K_{\text{F}} \quad (4)$$

3. Results and discussion

3.1. Biosorption from single metal solutions in shake flasks

For determining the optimal conditions and efficiency of metal biosorption by black gram husk (BGH), as the primary data for elucidating comparative sorption in binary and ternary systems, single metal solutions of Cd, Cu, Ni, Pb and Zn were investigated for time course and pH effect at 10 mg/l metal ion and 10 g/l biosorbent concentration, and the initial metal ion concentration varying between 10 and 800 mg/l.

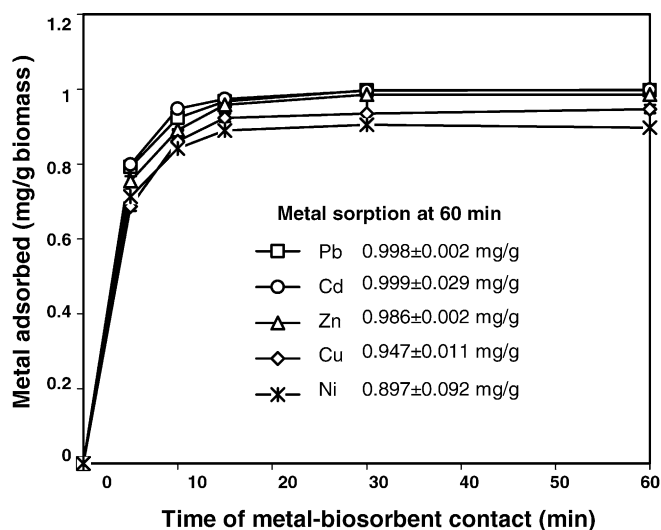


Fig. 1. Sorption at different periods of metal-biosorbent contact for 10 mg/l 100 ml metal solution per gram black gram husk, pH 5.0, during orbital shaking at 150 rpm at 25 ± 2 °C. All values are mean of three independent observations.

3.1.1. Time-course relationship

The biosorption equilibrium, in terms of metal-biosorbent contact time, was achieved very rapidly, within the short period of 30 min (Fig. 1). The sorption process, nevertheless, proceeded in two distinct phases. The rates of adsorption for all metals were very fast initially, the percent removal, respectively, for 5 and 10 min for the five metals was, Cd (79.9, 94.8), Cu (68.7, 86.1), Ni (71.3, 84.2), Pb (79.2, 92.3) and Zn (75.4, 89.1). The rate of metal removal declined appreciably during the next 20 min to attain the sorption equilibration in 30 min for the percentage removal of Cd (100), Cu (93.5), Ni (90.5), Pb (99.7) and Zn (98.6). This amounted to the mg removal of these metals, respectively, 9.99, 9.35, 9.05, 9.97 and 9.86 from 10 mg/l metal solution with 10 g BGH in 30 min. Similar two-phase biosorption has been reported during studies with Cd, Fe and Pb removal by *Schizomeris leibleinii* [22], and Cu sorption by oil-palm fibres, which was very rapid during the first 10 min followed by a slower process [23]. The fast-phase sorption may be explained as the passive uptake through physical adsorption, or the biosorbent surface ion exchange [24]. Since the adsorption phenomenon characteristically tends to attain instantaneous equilibrium [25] and many agricultural wastes act as natural ion exchange agents [26], the rapid-phase biosorption of metals by BGH is within the foregoing considerations. It is also relevant to point out that since active sorption sites in a system is a fixed number and each active site can adsorb only one ion in a monolayer [27], the metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for decreasing availability of active sites intensifies by the metal ions remaining in solution. The rate of metal removal is of greatest significance for developing a biosorbent-based water-treatment technology. The ability of BGH to rapidly biosorb all the five metals,

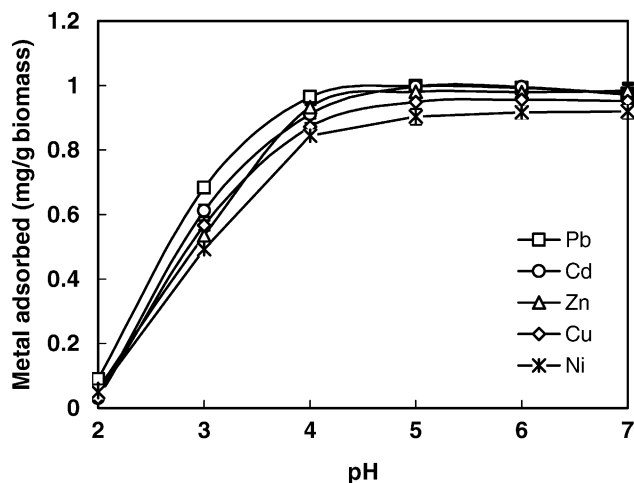


Fig. 2. Biosorption of various metals from solutions of different pH, by 1 g BGH mixed in 100 ml of 10 mg/l metal solution contained in 250 ml flasks during orbital shaking of 60 min at 150 rpm incubated at 25 ± 2 °C.

particularly the highly toxic Pb and Cd completely, within 30 min, is indicative of the efficient biosorption ability of this biowaste.

3.1.2. Effect of pH

Sorption of all metals at pH 2 was negligible, increasing with increase of pH, attaining optimum at the range of 5–6 (Fig. 2). Availability of negatively charged groups at the biosorbent surface is necessary for the sorption of metals to proceed [28], which at the highly acidic pH 2 is unlikely as there is a net positive charge in the biosorption system due to H^+ and H_3O^+ . In such a system H^+ compete with metal ions [23], resulting in active sites to become protonated to the virtual exclusion of metal binding on the biosorbent surface [29]. This means that at higher H^+ concentration, the biosorbent surface becomes more positively charged thus reducing the attraction between biomass and metal cations [8]. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake [30]. Metal sorption, accordingly, was noted to increase significantly as the pH was increased, such that at pH 4 and biosorbent-metal contact time of 60 min, Pb, Cd, Zn, Cu and Ni removal was 0.96, 0.91, 0.93, 0.87 and 0.84 mg/g, respectively. It is commonly agreed that the sorption of metal cations increased with increasing pH as the metal ionic species became less stable in the solution [31]. With further increase in pH, the solubility of metals decreases resulting in their precipitation as hydroxides, which at low metal concentrations is governed by the following equation [32]:

$$[OH^-] = \frac{\sqrt{K_{sp}}}{[M^{2+}]} \quad (5)$$

where $[M^{2+}]$ is the metal ion concentration; K_{sp} solubility product constant, which for precipitation of $Pb(OH)_2$, $Cd(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$ and $Ni(OH)_2$, respectively,

are 1.2×10^{-15} , 2.5×10^{-14} , 2.2×10^{-20} , 1.2×10^{-17} and 2.0×10^{-15} at 25 °C [33].

Water occurs as:

$$[H^+][OH^-] = K_w \quad (6)$$

or

$$[H^+] = \frac{K_w}{[OH^-]} \quad (7)$$

where K_w is the ion product constant of water, which is 1×10^{-14} , pH of precipitation, from the above equation can be calculated as:

$$pH = \log \frac{1}{[H^+]} \quad (8)$$

The hydroxide precipitation of Pb, Cd, Zn, Cu and Ni from their solutions of 10 mg/l was mathematically calculated to occur, respectively, at pH 8.7, 9.2, 7.4, 6.0, and 8.5. Since metal ion precipitation is pH dependent, all biosorption studies were done at pH 5, which is much below the pH at which the studied metals precipitate at 10 mg/l.

3.1.3. Adsorption isotherms

Initial concentrations (C_i) of metals in the solution were varied between 10 and 800 mg/l for sorption by the constant quantity of BGH biomass of 10 g/l. However, C_i for Cu was limited to 10–400 mg/l, as the metal commences to precipitate at 500 mg/l at pH 5. The data so obtained were converted to Langmuir and Freundlich isotherms, shown, respectively, in Figs. 3 and 4. Various parameters calculated from the adsorption isotherms, namely, adsorption capacity (q_{max}), adsorption efficiency (b) and correlation coefficient (r^2) for the Langmuir isotherms, and sorption capacity of the adsorbent (K_F), sorbability of the metal ($1/n$) and correlation coefficient (r^2) for the Freundlich isotherms are shown in Table 2. The values of r^2 are regarded as a measure of the goodness-of-fit of experimental data on the isotherm models [11], which

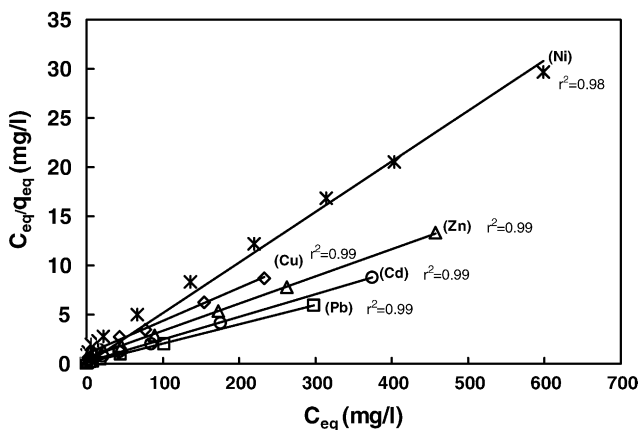


Fig. 3. The Langmuir adsorption isotherms of sorption of various metals (Pb, Cd, Cu, Ni, Zn) by BGH, where C_{eq} is the equilibrium concentration of metals and q_{eq} the quantity of metals biosorbed. All values are mean of three independent observations.

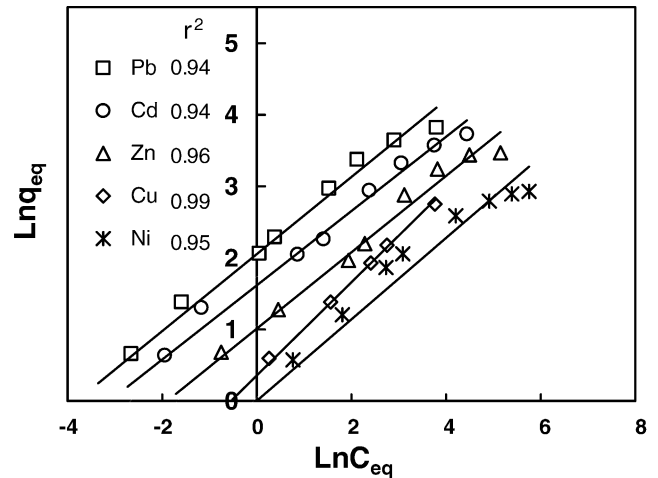


Fig. 4. The Freundlich adsorption isotherms of sorption of various metals (Pb, Cd, Cu, Ni, Zn) for initial concentration in the range of 10–800 mg/l by BGH, where $\ln C_{eq}$ is the natural log equilibrium concentration of metals and $\ln q_{eq}$ the natural log of quantity of metals adsorbed at equilibrium. All values are mean of three independent observations.

for all the metals in the Langmuir model, being very close to 1, are near perfect. The maximum amounts of metals adsorbed (q_{max}) were found to be 49.97, 39.99, 33.81, 25.73 and 19.56 mg/g BGH biomass for Pb, Cd, Zn, Cu and Ni, respectively. Working with various biosorbents, Sing and Yu [34] concluded that higher is the value of b , the higher is the affinity of adsorbent for the metal biosorbed. It is evident from the values of b for various metals, that the affinity of BGH to biosorb them followed the same pattern as was noted for r^2 and q_{max} in relative order from the highest to the lowest of $Pb > Cd > Zn > Cu > Ni$. These observations confirm that experimental data on the capacity of BGH to biosorb different metals fit the Langmuir model well. The r^2 values of the Freundlich model between 0.94 and 0.96 for different metals were not as close to the value of 1 as was in the case of the Langmuir model. Working with the adsorption of Pb by the fungal biomass of *Aspergillus niger*, nevertheless, the correlation coefficient of 0.93 was regarded as a high value for the experimental data to conform well to the Freundlich model [35]. Since the r^2 values for all metals in the present study were higher than 0.93, the experimental data

Table 2

Experimental values of total quantity of various metals biosorbed (q_{max}), Langmuir and Freundlich parameters of different heavy metals biosorbed on BGH for contact period of 60 min at an initial metal concentration 800 mg/l and the biosorbent 10 g/l

Metal ions	Experimental	Langmuir parameters			Freundlich parameters		
	q_{max}	q_{max}	b	r^2	K_F	$1/n$	r^2
Pb	50.20	49.97	0.590	0.999	7.33	0.452	0.941
Cd	42.56	39.99	0.373	0.993	4.96	0.440	0.946
Zn	34.28	33.81	0.160	0.995	2.87	0.477	0.962
Cu	27.97	27.73	0.057	0.996	1.73	0.511	0.959
Ni	20.15	19.56	0.056	0.982	1.38	0.470	0.955

All values are mean of three independent observations.

Table 3

The Freundlich adsorption isotherm values for different metals biosorbed on BGH for contact period of 60 min at different initial metal concentration (C_i) range of 300–800 mg/l and biosorbent 10 g/l

C_i (mg/l)	r^2 values				
	Pb	Cd	Zn	Cu	Ni
300	0.991	0.987	0.993	0.997	0.987
400	0.991	0.989	0.993	0.988	0.978
500	0.987	0.985	0.985	N.D	0.970
600	0.971	0.972	0.976	N.D	0.964
800	0.941	0.949	0.962	N.D	0.955

N.D: not determined due to precipitation of Cu after 400 mg/l. All values are mean of three independent observations.

may be regarded to reasonably fit the Freundlich model. Compared with K_F and $1/n$ for the Pb–*Aspergillus niger* biosorption system, 1.69 and 0.39, respectively [35], these values for the metal–BGH biosorption system in the present study were significantly higher (except the K value for Ni), pointing to the better efficiency of BGH to sequester heavy metals (Table 2).

The parameters calculated from the two models point to the Langmuir isotherm model to be closer to the experimental data than the Freundlich model for the C_i range of 10–800 mg/l by 10 g/l BGH. Relevant with the Langmuir equation assumptions, therefore, the metal sorption by BGH biomass was a chemically equilibrated and saturable mechanism [36]. The reasonable fit of the experimental data to the Freundlich model, however, needs to be critically considered in the light of the suggestion that lower but acceptable r^2 value is related to low adsorption capacity, resulting in higher experimental uncertainties [37]. Validity of the Freundlich equation, furthermore, is limited to low solute concentrations [25,38]. The experimental data were thus fragmented to determine the optimum range of maximum metal C_i at which the r^2 values were high enough to minimize experimental uncertainties (Table 3). The r^2 values of 0.99 for all metals at the C_i range of 10–300 mg/l (Fig. 5) indicate that biosorption capacity of BGH perfectly fit the Freundlich model at these metal concentrations. It is appropriate to note that sorption by biosorbents has been projected in literature for metal sequestering at low metal concentrations, particularly in the range of 1–100 mg/l [3–5], and the level of >300 mg/l not likely to

Table 4

Sorption of Pb from single, binary and ternary metal solutions by BGH

Metals	Metal adsorbed (%)						
	Single metal solution	Binary metal solution				Ternary metal solution	
		Pb + Ni	Pb + Zn	Pb + Cu	Pb + Cd	Pb + Ni + Zn	Pb + Cd + Cu
Pb	99.6 ± 0.28	98.5 ± 0.8	98.9 ± 0.3	99.1 ± 0.7	98.1 ± 0.6	99.7 ± 0.2	99.5 ± 0.3
Ni	90.5 ± 1.42	86.4 ± 1.7				86.3 ± 1.3	
Zn	98.6 ± 0.13		97.8 ± 0.5			96.5 ± 0.9	
Cu	93.5 ± 0.79			94.1 ± 0.9			93.8 ± 1.6
Cd	99.9 ± 0.02				98.8 ± 0.4		92.3 ± 1.1

Experimental conditions: BGH 10 g/l, metal concentration 10 mg/l each, pH 5.0, incubation at 150 rpm at 25 ± 2 °C for 30 min. All values are mean of three independent observations.

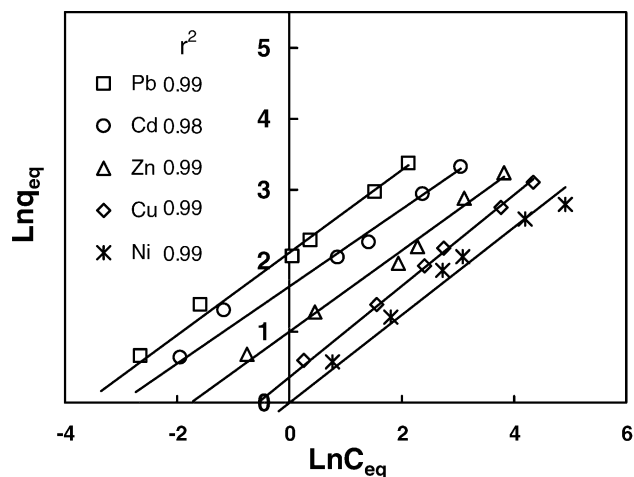


Fig. 5. The Freundlich adsorption isotherms for various metals (Pb, Cd, Cu, Ni, Zn) for initial concentration in the range of 10–300 mg/l by BGH, where $\ln C_{eq}$ is the natural log equilibrium concentration of metals. All values are mean of three independent observations.

be present in industrial effluents. The BGH–metal biosorbent system, therefore, validly fits the Freundlich isotherms model at the low metal concentrations at which it is expected to be applied under practical conditions.

3.2. Biosorption of Pb from binary and ternary metal solutions in shake flasks

3.2.1. Binary metal solutions

The efficiency of BGH to biosorb Pb from binary solutions with Cd, Cu, Ni and Zn was maintained at the same level as it was from the single metal solution, remaining within the statistical limits of no significant variation (Duncan's new multiple range test at $P=0.05$) (Table 4). The presence of Pb, likewise, did not interfere in the sorption of Cd, Cu and Zn, which also showed no significant difference for the level of sorption from their respective single metal solutions. Although the 86.41% sorption of Ni in the presence of Pb may be rated as high, the statistical difference was significant when compared with sorption from its single metal solution. The performance of BGH to biosorb Pb, Cd, Cu and Zn (even Ni, considering 86.41% sorption to be high) from the binary metal solutions was as good as noted for sorption from sin-

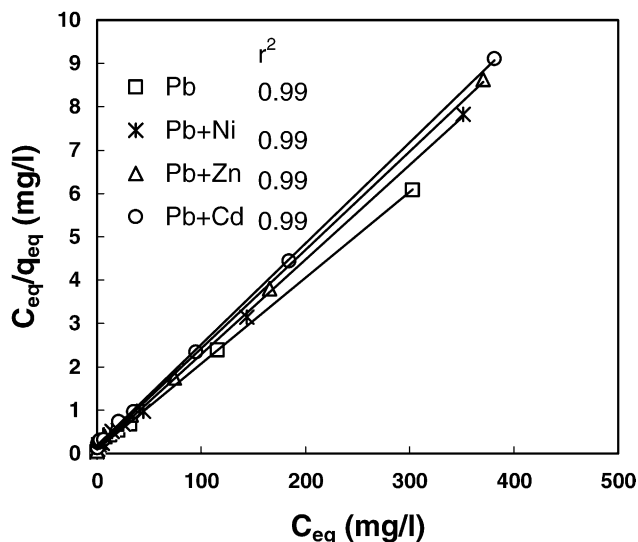


Fig. 6. The Langmuir adsorption isotherms for the sorption of lead when present singly or in binary solutions with nickel, zinc and cadmium for initial concentration of lead in the range of 10–800 mg/l. All values are mean of three independent observations.

gle metal solutions. The adsorption of Pb in the presence of other metals in the binary system was found to typically fit the Langmuir adsorption isotherms model and to the Freundlich model in the Pb concentration range of 10–800 mg/l in the same manner as was noted for sorption from single metal solution (Figs. 6 and 7).

3.2.2. Ternary metal solutions

Non-significant statistical differences were noted when Pb sorption was considered from ternary solutions containing

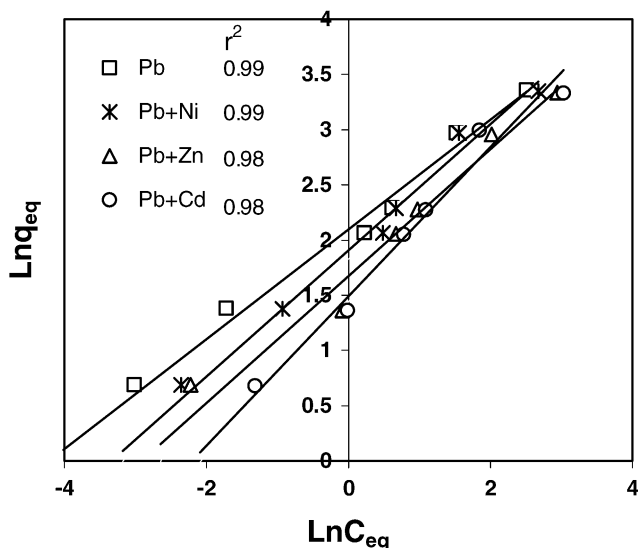


Fig. 7. The Freundlich adsorption isotherms for the sorption of lead when present singly or in binary solutions with nickel, zinc and cadmium for initial concentration of lead in the range of 10–800 mg/l, where $\ln C_{eq}$ is the natural log equilibrium concentration of metals and $\ln q_{eq}$ the natural log of quantity of metals adsorbed at equilibrium.

Pb + Ni + Zn and Pb + Cd + Cu (Table 4). Sorption of Cu, Ni and Zn from these ternary solutions also showed no significant difference from the level of their sorption from binary solutions. The sorption of Cd, however, declined to 92.32%, in comparison with its sorption of 99.99 and 98.86% from single metal and binary metal solutions, respectively. This slight drop in the sorption of Cd from ternary solutions may be attributed to the greater cumulative occupancy of the binding surface of BGH by the larger ion size of Pb and Cd. Ionic radii of the metals are—Cd: 0.97 Å; Cu: 0.72 Å; Ni: 0.72 Å; Pb: 1.2 Å; Zn: 0.74 Å [33]. Surface area occupancy by an ion each of the tri-component ternary systems can be calculated from the radii by applying the formula πr^2 as below:

$$Pb + Ni + Zn = 4.52 \text{ \AA} + 1.63 \text{ \AA} + 1.72 \text{ \AA} = 7.87 \text{ \AA}$$

$$Pb + Cd + Zn = 4.52 \text{ \AA} + 2.96 \text{ \AA} + 1.63 \text{ \AA} = 9.11 \text{ \AA}$$

These calculations clearly show that surface area occupancy was significantly greater in the ternary system of Pb + Cd + Zn in comparison with Pb + Ni + Zn, which may be the cause of slight Cd sorption decline. A generalized conclusion from the above observations is that BGH has the ability to biosorb Pb from binary and ternary systems at about the same efficiency as from single metal solution. The presence of Pb also did not significantly affect the sorption of other heavy metals in binary and ternary systems, however, exerting some limitation to the sorption of Cd, which had ionic radius greater than Zn and Ni. The insignificant competition between metal ions, in the binary and ternary systems, for sorption on BGH may be attributed to their low C_i (10 mg/l) and sufficient availability of adsorption sites. Similar conclusions of no competition at low metal concentration were drawn when Cd, Cu and Ni (C_i : 10 mg/l each metal), in binary and ternary systems, were biosorbed on seaweeds and seaweed-derived materials [2], and Hg and Cd (C_i : 100 mg/l each metal) in a binary system were biosorbed on brown seaweeds [39]. These findings suggest that BGH has the potential of application when simultaneous removal of more than one metal species is desired to be done at low metal ion concentrations.

3.2.3. Biosorption of Pb from ternary metal solutions in fixed bed column

A fixed bed column packed with BGH biomass was designed, as reported earlier [20], to operate as a continuous liquid flow system for the biosorption of Pb from binary solutions of Pb + Ni and Pb + Zn, and the ternary solution of Pb + Ni + Zn. The volume of single, binary and ternary metal solutions passed through the biosorption column was 90 l each. Two stages have been considered in the breakthrough curves for the sorption of Pb from these solutions (Fig. 8). One was the metal solution passed through the column at influent–effluent equilibrium for Pb sorption of zero (V_{max}), which was noted to occur at $74 l_{(Pb)}$, $70 l_{(Pb+Ni)}$, $79 l_{(Pb+Zn)}$ and $81 l_{(Pb+Ni+Zn)}$. This represents the stage of breakthrough curves for the total metal retention capacity of the biosorbent,

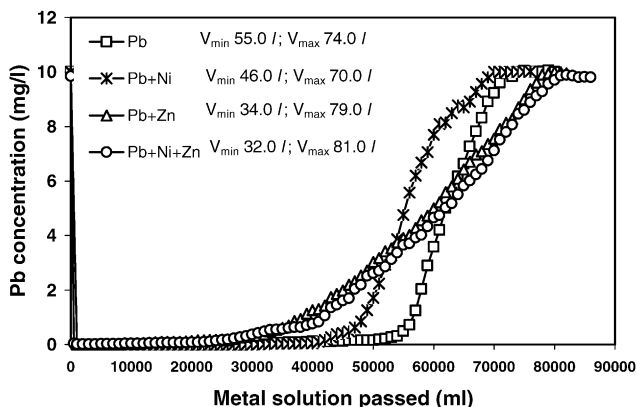


Fig. 8. Biosorption breakthrough curves for the removal of lead(II) in a fixed bed column bioreactor based on BGH biomass for single metal, and binary and ternary solutions with nickel and zinc. Conditions: column internal diameter 1.7 cm, height 28 cm; BGH biomass 10 mg; 10 mg/l lead in single metal solution, with additional 10 mg/l of either zinc or nickel in binary solution (total metal load 20 mg/l) and 10 mg/l each of zinc and nickel (total metal load 30 mg/l); flow rate 5 ml/min. V_{min} : volume passed at 0.1 mg/l lead at discharge, V_{max} volume passed at influent–effluent equilibrium at 10 mg/l.

which has been reported in literature to signify the metal sorption efficiency of algal, microbial and plant biomass [40–42]. Such breakthrough curves are grossly misleading, as they do not take into account the limits of respective metals permitted in industrial effluent discharge (V_{min}). This stage of metal sorption (V_{min}) is, therefore, the more appropriate stage of breakthrough curves for consideration of the metal sorption efficiency of biosorbents, which in present studies was the metal solution passed at which the Pb discharge remained below 0.1 mg/l. For the sorption of Pb, V_{min} from single metal solution was 55 l (Pb), which progressively decreased to 46 l (Pb+Ni), 34 l (Pb+Zn) and 32 l (Pb+Ni+Zn). These findings expectedly show that as the metal load increases from single to binary to ternary metal solutions, respectively, 10, 20 and 30 mg/l, full occupancy of the biosorbent surface is reached on the passage of lesser and lesser volumes of metal solutions. V_{min} for Pb from the single metal solution was thus the highest and from the ternary metal solution the lowest. This was expected, since as the metal load increased, BGH was simultaneously sorbing other metals along with Pb. The solution volume outflowing between V_{min} and V_{max} contained Pb from 0.1 to 10 mg/l. This volume of the breakthrough curves in effect had undergone partial treatment of varying degrees for the removal of Pb, which can also be rendered fit for discharge by inserting a secondary fixed bed treatment column.

3.2.4. Desorption of metals

During an earlier study using a variety of desorbing agents, 0.1 M HCl was noted to most effectively desorb $99.89 \pm 0.22\%$ Cd biosorbed by BGH [20]. Desorption of Pb, Cu, Ni and Zn from the metal-laden BGH in flasks with 0.1 M HCl resulted in 99.96 ± 0.03 , 93.36 ± 0.77 , $96.39 \pm 0.1.18$ and $84.85 \pm 1.47\%$ recovery of these metals, respectively.

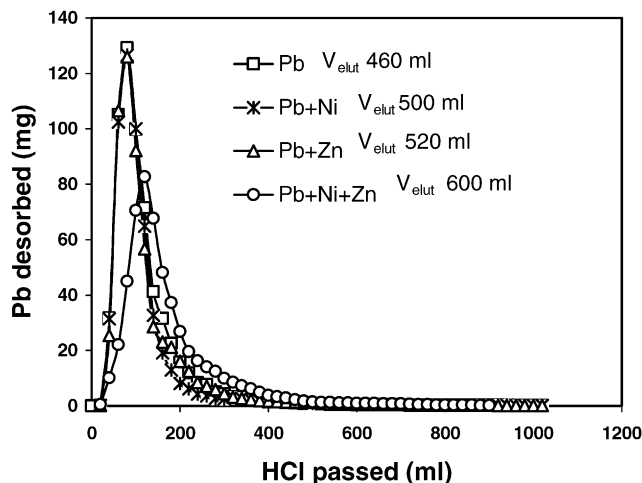


Fig. 9. Desorption breakthrough curves for the elution of lead from single metal and binary and ternary solutions with nickel and zinc in a fixed bed column bioreactor based on BGH biomass. Conditions: column internal diameter 1.7 cm, height 28 cm; BGH biomass 10 g; 0.1 M HCl desorbent; flow rate 5 ml/min. V_{elut} : volume of HCl discharged at 0.1 mg/l metal solution.

It may be noted from the elution breakthrough curves that desorption of Pb from single, binary and ternary metal solutions was complete (Fig. 9). The elution volume (V_{elut}), for the desorption required to achieve 0.1 mg/l Pb in the effluent discharged from single, binary and ternary metal solutions was 460 ml (Pb), 500 ml (Pb+Ni), 520 ml (Pb+Zn) and 600 ml (Pb+Ni+Zn). These observations show that as the load of metals on the biosorbent surface increased from single to binary to ternary metal solutions, the volume of desorbing agent needed for the recovery of Pb was more. This was expected as along with Pb, other metals were also being removed.

4. Conclusions

On the basis of good adsorption ability shown by BGH for several individual metals (Pb, Cd, Cu, Ni and Zn), Pb in the presence of other metals, desorption of various metal species with mild acid treatment, and their removal in binary and ternary systems in a fixed bed column suggest that this biosorbent (BGH) has the potential of application for the simultaneous removal of several heavy metals contained in effluent solutions.

References

- [1] UNEP, United Nations Environmental Programme, Industry and Environment Office, Paris, 1989.
- [2] D. Aderhold, C.J. Williams, R.G.J. Edyvean, *Bioresour. Technol.* 58 (1996) 1.
- [3] J.S. Davila, C.M. Matos, M.R. Cavalcanti, *Water Technol.* 26 (1992) 2309.
- [4] A. Kapoor, T. Viraraghavan, *Bioresour. Technol.* 53 (1995) 195.
- [5] E.W. Wilde, J.R. Benemann, *Biotechnol. Adv.* 11 (1993) 781.

- [6] E. Sandau, P. Sandau, O. Pulz, *Acta Biotechnol.* 16 (1996) 227.
- [7] K.H. Chong, B. Volesky, *Biotechnol. Bioeng.* 47 (1995) 451.
- [8] A. Saeed, M. Iqbal, M.W. Akhtar, *Pakistan J. Sci. Ind. Res.* 45 (2002) 206.
- [9] S. Schiewer, B. Volesky, in: D.R. Lovely (Ed.), *Environmental Microbe–Metal Interactions*, ASM Press, Washington, DC, 2000, p. 329.
- [10] D.A.J. Wase, C.F. Forster, *Biosorbents of Metal Ions*, Taylor and Francis, London, 1997, p. 1.
- [11] S.F. Al-Asheh, R. Banat, Z. Al-Omari, *Duvnjak, Chemosphere* 41 (2000) 659.
- [12] Y. Sag, B. Akcael, T. Kutsal, *Process Biochem.* 37 (2001) 35.
- [13] Z. Aksu, U. Acikel, *Process Biochem.* 34 (1999) 589.
- [14] S. Singh, B.N. Rai, L.C. Rai, *Process Biochem.* 36 (2001) 1205.
- [15] Z.R. Holan, B. Volesky, I. Prasetyo, *Biotechnol. Bioeng.* 41 (1993) 819.
- [16] Y. Sag, T. Kutsal, *Process Biochem.* 31 (1996) 561–572.
- [17] F. Pagnanelli, M. Trifoni, F. Becolchini, A. Esposito, L. Toro, F. Veglio, *Process Biochem.* 37 (2001) 115.
- [18] M. Loaec, R. Olier, J. Guezennec, *Water Res.* 31 (1997) 1171.
- [19] B.B. Prasad, U.C. Pandey, *World J. Microbiol. Biotechnol.* 16 (2000) 819.
- [20] A. Saeed, M. Iqbal, *Water Res.* 37 (2003) 3472.
- [21] P.R. Puranik, K.M. Paknikar, *J. Biotechnol.* 55 (1997) 113.
- [22] A. Ozer, D. Ozer, H.I. Ekiz, *Process Biochem.* 34 (1999) 919.
- [23] K.S. Low, C.K. Lee, K.P. Lee, *Bioresour. Technol.* 44 (1993) 109.
- [24] Y.P. Ting, F. Lawson, I.G. Prince, *Biotechnol. Bioeng.* 34 (1989) 990.
- [25] D.N. Bajpai, *Advanced Physical Chemistry*, S. Chand and Company, New Delhi, India, 1998.
- [26] J.M. Randall, E. Hautala, G. McDonald, *J. Appl. Polym. Sci.* 22 (1978) 379.
- [27] I. Langmuir, *J. Am. Chem. Soc.* 40 (1918) 1361.
- [28] E. Luef, T. Prey, C.P. Kubicek, *Appl. Microbiol. Biotechnol.* 34 (1991) 688.
- [29] I. Aldor, E. Fourest, B. Volesky, *Can. J. Chem. Eng.* 73 (1995) 516.
- [30] J.S. Chang, R. Law, C.C. Chang, *Water Res.* 31 (1997) 1651.
- [31] B. Volesky, S. Schiewer, in: M.C. Flickinger, S.W. Drew (Eds.), *Encyclopedia of Bioprocess Engineering*, Wiley, New York, 1999, p. 433.
- [32] I.M. Kolthoff, E.B. Sandell, E.J. Mehan, S. Bruckenstein, *Quantitative Chemical Analysis*, Macmillan, London, 1971.
- [33] J.A. Dean, *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, New York, 1985.
- [34] C. Sing, J. Yu, *Water Res.* 32 (1998) 2746.
- [35] W. Jianlong, Z. Xinmin, D. Decai, Z. Ding, *J. Biotechnol.* 87 (2001) 273.
- [36] P.R. Puranik, N.S. Chabukswar, K.M. Paknikar, *Appl. Microbiol. Biotechnol.* 43 (1995) 1118.
- [37] N. Chiron, R. Guilet, E. Deydier, *Water Res.* 37 (2003) 3079.
- [38] W.J. Moore, *Physical Chemistry*, Longman, Scientific and Technical, Essex, UK, 1972.
- [39] M.W. Wilson, R.G. Edyvean, *Inst. Chem. Eng. Symp. Ser.* 132 (1993) 185.
- [40] Z. Aksu, T. Kutsal, *Process Biochem.* 33 (1998) 7.
- [41] E. Maranon, H. Sastre, *Bioresour. Technol.* 38 (1991) 39.
- [42] J.T. Matheickal, Q. Yu, G.M. Woodburn, *Water Res.* 33 (1999) 335.