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FTIR and kinetic modelling of fungal biosorbent *Trichoderma asperellum* for the removal of Pb(II), Cu(II), Zn(II) and Cd(II) from multi-metal solutions

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ABSTRACT

Metal biosorption potential of Pb(II), Cu(II), Zn(II) and Cd(II) by *Trichoderma asperellum* in multi-metal solutions was compared against single-metal solutions to mimic occurrence in natural wastewater. Significantly lower metal removal was observed in multi-metal solutions compared to single-metal solutions. Antagonistic metal interaction may have led to poor metal removal in multi-metal solution (equilibrium achieved after 360 min) although biosorption occurred more rapidly in single-metal solution (equilibrium detected as early as 120 min). Preference for metals was consistent in both metal solutions, preferring Pb(II) > Cu(II) > Zn(II) ≥ Cd(II), albeit lower levels removed in multi-metal solutions. Binding of metals involved functional groups such as amino (–NH_2), carbonyl (C=O) and sulphur (–S) discovered from ATR-FTIR analysis. Metal biosorption by *T. asperellum* in both metal solutions was mainly via a rate-limiting chemisorption, with compliance to pseudo-second order kinetic.

Keywords: ATR-FTIR analysis; Biosorption; Kinetic modelling; Multi-metal solution; Single-metal solution; *Trichoderma asperellum*

1. Introduction

Toxic metals such as aluminium (Al), cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) have been pollutants for decades, in forms of wastes and effluents. These common metals are discharged from mining and agricultural activities [1]. The presence of these metals in the environment is of great concern as they accumulate in the body and impact health, with varying degree of health effects, from skin irritation to malfunction of vital organs [2]. Various approaches have been used to remove heavy metals from the environment, which include physico-chemical and biological methods such as the use of bacteria, fungi and algae as biosorbents. Of these, fungi are highly preferred as they are relatively cheaper to culture and easily available. Fungi can remove metals either via biosorption or bioaccumulation where metals are adsorbed via chemical-physical interaction between the fungi (biosorbents) and the toxic metals, or moved across cellular structures, respectively [3].

To date, most biosorption studies were performed using single-metal solutions in which the removal efficacies from these solutions were relatively high due to the absence of complex metal interactions [4]. However, different metals are often present together in the environment and the interactions between metals complicate the removal process. As a result, biosorbents may not produce similar removal efficacy as observed in laboratory settings. Multi-metal solutions are therefore ideal as this model mirrors the natural wastewaters, hence are more appropriate and may yield more accurate results in respect of their environmental applications. The fungal species used in this study is *Trichoderma asperellum*, a strain isolated by [5] from river sediment. *T. asperellum*, a filamentous fungus, is ubiquitous, non-pathogenic and easy to cultivate; the species grows rapidly and is able to produce sufficient biomass. The mentioned isolated strain was successful in removing Cu(II) when used in live and dead form [5,6]. In single-metal solutions of Cu(II), Pb(II), Zn(II) and Cd(II), the strain showed higher removal potentials as compared to other *Trichoderma* species such as *T. viride*, *T. atroviride* and *T. longibrachiatum* [7,8].

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Therefore, in this study, the efficiency of *T. asperellum* in removing metals in multi-metal solutions is studied and compared against the single-metal solutions. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy analysis was also performed to characterize the functional groups present on *T. asperellum* and to further explain their influence on biosorption. Kinetic modelling was also employed to determine the possible kinetic models used by *T. asperellum* in multi-metal biosorption, as compared to single-metal solutions.

2. Materials and methods

2.1. Culture establishment and preparation of metal solutions

T. asperellum was first cultured on potato dextrose agar (PDA, Merck) at 25 ± 2°C. Eight mycelial plugs (of 5 mm diameter) were inoculated into 250 mL potato dextrose broth (PDB, Merck) and cultured for 3–5 d (25°C ± 2°C, 150 rpm). The mycelium was harvested using Whatman No. 1 filter paper, rinsed with sterile distilled water and autoclaved (121°C, 20 min) to obtain dead cells for the biosorption experiments. Autoclaved mycelium was dried overnight in 50°C oven, powdered using pestle and mortar and sieved using a siever (mesh size of 0.08 cm). The powdered sterile mycelium was kept in sterile bottles at room temperature (25°C ± 2°C) until further use.

Stock solutions of 1,000 mg L^{-1} metal salts were prepared by dissolving analytical grades of metal nitrates; $Pb(NO_3)_2$ (R&M Chemicals), $Cu(NO_3)_2{\cdot}3H_2O$ (Sigma-Aldrich), $Zn(NO_3)_2{\cdot}6H_2O$ (R&M Chemicals) and $Cd(NO_3)_2{\cdot}4H_2O$ (Sigma-Alrich) in Milli-Q water. This was followed by dilution of the nitrate stock solutions to 100 mg L^{-1} (used for biosorption experiment) with the initial pH of the solutions adjusted to pH 5 using 0.1 M HCl and 0.1 M NaOH.

2.2. Metal biosorption in multi-metal solutions compared to single-metal solutions

To prepare multi-metal solution, each of the nitrate solution (100 mg L^{-1} each) was mixed to a final volume of 15 mL (slight modifications from [4]). The multi-metal solution was then treated with 0.1 g biosorbent (powdered sterile mycelium of *T. asperellum*, Section 2.1) with the initial pH adjusted to pH 5. Similarly, biosorption in single-metal solutions was determined using each single metal nitrate solutions. After incubating for 15, 30, 60, 120, 240, 360 and 480 min on a rotary shaker, the samples were collected and filtered using Whatman No. 1 filter paper. Metal ions in the collected filtrates were analysed using an air-acetylene atomic absorption spectroscopy (AAS) (Agilent Technologies 240 Series AA), current pre-set at 15 mA. The wavelengths used for the detection of Pb(II), Cu(II), Zn(II) and Cd(II) were 217.0, 324.8, 213.9 and 228.8 nm, respectively. The AAS was calibrated using solution standards for every batch of analyses. Similarly, the procedure was repeated to determine metal biosorption in multi-metal solutions. The metal biosorption per g of biosorbent (mg g^{-1}) (Q) was calculated as follows:

$$Q = \left[(C_i - C_f) \cdot V \right] / M \quad (1)$$

where C_i is the initial metal concentration (mg L^{-1}); C_f is the final metal concentration (mg L^{-1}); V: total volume of solution (mL); M is the mass of dried biosorbents (g).

2.3. Characterization of functional groups of T. asperellum via ATR-FTIR

Powdered *T. asperellum* (Section 2.1) was used for the characterization of functional groups present using Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FTIR) spectroscopy [Thermo Scientific Nicolet™iS™ 10]. The scanning conditions include a spectral range of 4,000–400 cm^{-1} (resolution of 4 cm^{-1}, 16 scans).

2.4. Modelling of biosorption kinetics of T. asperellum in single- and multi-metal solutions

Kinetic modeling was applied to systems in which equilibrium was achieved. The pseudo-first and pseudo-second order kinetics were used. Based on the following Eqs. (2) and (3), the theoretical metal removal mechanism was determined by comparing the correlation coefficient (R^2) and experimental values of q_{eqex} to calculated q_{eq}.

Pseudo-first order kinetic:

$$\log(q_e - q_t) = \log q_e - (k_1 / 2.303)t \quad (2)$$

where q_e is the metal adsorbed at equilibrium determined experimentally (mg g^{-1}); q_t is the metal adsorbed at particular time (mg g^{-1}); k_1 is the rate constant derived from slope (min^{-1}); t is the time (min).

Pseudo-second order kinetic:

$$(t / q_t) = (1 / k_2 q_e^{\,2}) + (1 / q_t)t \quad (3)$$

where t/q_t is the time, t, since the start of experiment (min) divided by the metal adsorbed at time t; k_2 is the rate constant from y-intercept; q_e is the metal adsorbed at equilibrium determined experimentally from equation slope (mg g^{-1}); q_t is the metal adsorbed at particular time (mg g^{-1}).

2.5. Statistical analysis

All experiments were performed in triplicates and repeated once. Data collected was analysed with ANOVA using the Statistical Package for the Social Sciences (SPSS) version 20.0. Means were compared using T-test ($p < 0.05$).

3. Results and discussion

3.1. Metal biosorption in single- and multi-metal solutions

Biosorption of Pb(II), Cu(II), Zn(II) and Cd(II) were evidently inferior in multi-metal solutions compared to single-metal solutions. T-test indicated significant differences in amount of metals removed in multi-metal solutions compared to single-metal solutions, with amount of metals removed between 0.41 to 3.53 mg g^{-1} compared to 7.47 to 36.36 mg g^{-1}, respectively (Fig. 1). Biosorption of Pb(II) was highest in multi-metal and single-metal solutions, with 3.53 and 36.36 mg g^{-1} removed, respectively. Nevertheless, the amount of Pb(II) removed

in multi-metal solution was 10-folds lesser than the amount removed in single-metal solutions (Fig. 1). Similar observations were detected for Cu(II), Zn(II) and Cd(II), with 2.00, 0.41 and 0.50 mg g^{-1} removed in multi-metal solutions, which were significantly lower compared to 10.70, 9.60 and 7.47 mg g^{-1} in single-metal solutions, respectively (Fig. 1).

In multi-metal solutions (mimicking wastewaters), multiple factors such as concentration, physical and chemical properties between the biosorbents and metals, may have influenced and complicated the process [9]. Metal interaction particularly competition among metals for binding to functional groups are more intense in multi-metal solutions than in single-metal solutions [10]. As a result, biosorbents demonstrate lower metal removal efficacies. Metals also interact with one another, forming additive, antagonistic or synergistic interactions which led to equal, lower or greater efficacies compared to metals existing as individual components, respectively [11]. In this study, the sum of metals removed in multi-metal solutions was lower than their respective components in single-metal solutions, suggesting the occurrence of complex antagonistic interactions among the metals in the multi-metal solutions. This observation however, contradicts with [12] who discovered additive and synergistic removal of Cu(II) in the presence of Zn(II) and/or Pb(II) by *T. atroviride*. The contrast here was presumed attributed to the capability of metal ions to bind to available functional groups of specific fungal species, and their inherent metal properties.

T. asperellum demonstrated identical trend for metal preference in both multi-metal and single-metal solutions, with preference for Pb(II)> Cu(II)> Zn(II)≥ Cd(II) (Figs. 1 and 2). Preference of metals in the binding process is most likely influenced by the electronegativity of the metal cations as positively-charged metal cations bind easily to negatively-charged functional groups [13]. Each metal cation have specific electronegativity values with 2.33, 1.90, 1.69 and 1.65 Pauling for Pb(II), Cu(II), Zn(II) and Cd(II), respectively. Pb(II), with the highest electronegativity, can attract and bind more easily to functional groups compared to other metal cations, resulting in the higher amount of Pb removed in both single- and multi-metal solutions. By contrast, Zn(II) and Cd(II) with similar lower electronegativity values, had minimal amount removed. This metal uptake trend was similar to several studies using activated sludge, barley roots and fungi, and various biosorbents (bacteria, alga, plant and mineral soils) in removing metals from single- [14,15] and multi-metal solutions [16,17] respectively. It is evident that among all the tested metal cations (Cu(II), Zn(II) and Cd(II)), Pb(II) is the easiest to be adsorbed due to its ionic characteristic. Uptake of Cu(II), Zn(II) and Cd(II) in multi-metal solutions was significantly lower but increasing from 60 to 480 min.

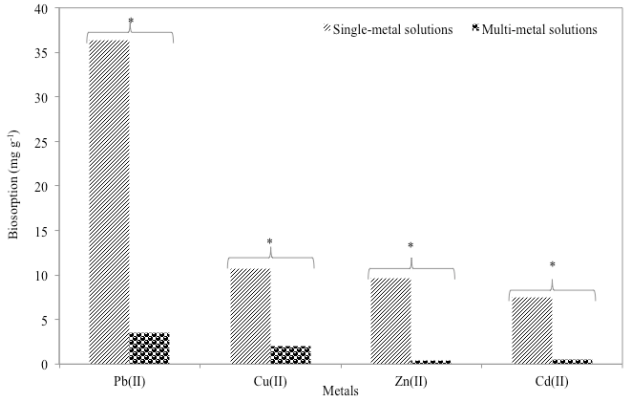

Fig. 1. Removal of Pb(II), Cu(II), Zn(II) and Cd(II) by *T. asperellum* in single- and multi-metal solutions after the experimental 480 mins. '*' indicates significant differences in the mean amount of metal removed in single- and multi-metal solutions based on *T*-test ($p < 0.05$).

3.2. Characterization of functional groups of T. asperellum via ATR-FTIR

A total of 14 peaks were observed for *T. asperellum* with wavenumbers 3,256.74, 2,925.79, 2,853.30, 1,744.62, 1,627.30, 1,548.18, 1,454.83, 1,376.88, 1,246.88, 1,149.38, 1,080.92, 1,023.06, 930.98 and 890.12 cm^{-1} (Fig. 3). These peaks

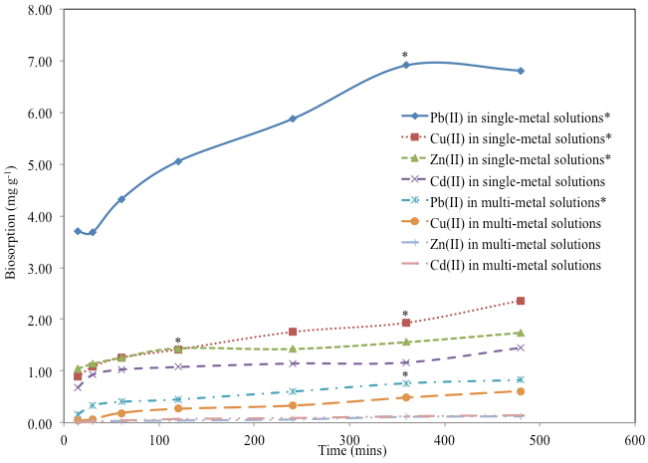

Fig. 2. Metal biosorption by *T. asperellum* in single- and multi-metal solutions throughout the experimental period (480 min). Equilibriums achieved are indicated with '*' in the single-metal solutions for Pb(II), Cu(II), Zn(II) and in the multi-metal solutions for Pb(II).

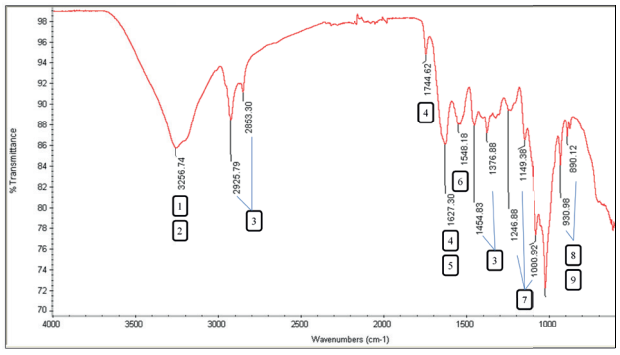

Fig. 3. ATR-FTIR spectra of powdered *T. asperellum* to identify the functional groups. Numbers from (1) to (9) represent the following functional groups: (1) hydroxyl (–OH), (2) amino ($–NH_2$), (3) methyl ($–CH_3$), (4) carbonyl (C=O), (5) alkene (C=C), (6) aromatic alkene (C=C), (7) carboxyl (-COOH), (8) phosphate ($–PO_4$) and (9) sulphur (–S).

Table 1
Pseudo-first and pseudo-second order kinetic constants for biosorption of Pb(II), Cu(II), Zn(II) and Cd(II) by *T. asperellum* in single- and multi-metal solutions at equilibrium

Metal solutions	Metals	Experimental q_{eqex} (mg g^{-1})	Pseudo-first order			Pseudo-second order		
			k_1 (min^{-1})	q_{eq} (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_{eq} (mg g^{-1})	R^2
Single	Pb(II)	6.91	0.02	35.31	0.90	1.48	7.32	0.99
	Cu(II)	2.36	0.01	2.31	0.99	0.11	2.41	0.97
	Zn(II)	1.51	0.02	0.48	0.91	0.13	1.73	0.99
Multi	Pb(II)	0.83	0.01	0.42	0.94	0.01	0.94	0.97

indicated the presence of the following groups; hydroxyl (–OH), amino (–NH_2), methyl (–CH_3), carbonyl (C=O), alkene (C=C), aromatic alkene (C=C), carboxyl (–COOH), phosphate (–PO_4) and sulphur (–S). Phosphate and methyl groups are attributed to nucleic acids and lipids, respectively [18]. Their low amount in the cells may suggest their less significant roles in fixing and complexing metals. On the contrary, hydroxyl, amino, carbonyl and carboxyl are commonly found in biosorbents of various origins and are key groups in metal-binding [19]. In addition to carboxyl being found in fungi and bacteria, hydroxyl and carbonyl are abundant in fungi [20,21] while phosphate is common in bacteria [22]. These functional groups are related to proteins, suggesting their prominent role in binding and removal of metals from the solutions. It has also been documented that different functional groups bind to metals differently; carbonyl and sulphur attracting mainly Pb(II), while oxygen and nitrogen-rich functional groups such as amino predominantly bind Cu(II), Zn(II) and Cd(II) [23]. This phenomenon of metal-competition particularly among Cu(II), Zn(II) and Cd(II) may have influenced metal removal in the multi-metal solutions where the amount of metals removed is significantly inferior compared to single-metal solutions.

3.3. Modelling of biosorption kinetics of T. asperellum in single- and multi-metal solutions

In this study, kinetic modelling using pseudo-first and pseudo-second order models were performed for four metal-systems with equilibrium points, i.e., Pb(II) in both solutions, and Cu(II) and Zn(II) in single-metal solutions (Fig. 2). As a biosorbent, *T. asperellum* complied with pseudo-second order kinetic as higher R^2 value were obtained (0.97 to 0.99) compared to R^2 values based on pseudo-first order (0.90–0.99) (Table 1). Compliance to pseudo-second order in single-metal solutions has been reported for studies using *Amanita rubescens*, sesame leaf and aquatic moss in removing Pb(II) and Cd(II) [24–26]. In multi-metal solutions, compliance to pseudo-second order was derived from studies using *Tricholoma lobayense* and algae to remove Pb(II), Cu(II) and Cd(II) [27,28]. Pseudo-second order fitted most metal biosorption processes as this model considers the interaction of valency forces between the biosorbents and metal cations. As such, pseudo-second model is often more accurate than pseudo-first order model in predicting the overall behaviour of the adsorption process [29]. Pseudo-second order was also a better model as values of calculated (q_e) amount of metal removed were similar to the experimental values (q_{eqex}) (Table 1). This suggested that *T. asperellum* mainly adsorbed the metal cations through chemisorption, a rate-controlled process. It was also evident that chemisorption is a mechanism that was not influenced by the presence of multiple metals in the solution. Therefore, biosorption behaviour of *T. asperellum* in terms of mechanism of sorption is consistent in single- and multi-metal solutions.

4. Conclusion

The biosorption behaviour of *T. asperellum* varies when applied in multi- and single-metal solutions. In multi-metal solution, biosorption efficacy was compromised by the presence of multi-metals and their subsequent antagonistic interaction with one another. As a result, amount of metals removed was 10-fold lesser compared to single-metal solution. Other factors such as presence of functional groups on fungal surface, mechanism of biosorption (chemisorption) and electronegativity of metal cations were unaffected by the presence of multiple metal cations in the solution. This study also revealed the potential complexity of using and reproducing efficient metal removal of metals in natural wastewater by *T. asperellum*.

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Symbols and abbreviations

AAS	—	Atomic absorption spectroscopy
ANOVA	—	Analysis of variance
ATR-FTIR	—	Attenuated total reflectance Fourier transform infrared
C_f	—	Final metal concentration, (mg L^{-1})
C_i	—	Initial metal concentration, (mg L^{-1})
k	—	Rate constant
M	—	Mass of dried biosorbents, (g)
PDA	—	Potato dextrose agar
PDB	—	Potato dextrose broth
Q	—	Metal biosorption per g of biosorbent, (mg g^{-1})
q_e	—	Metal adsorbed at equilibrium, (mg g^{-1})
q_t	—	Metal adsorbed at particular time, (mg g^{-1})
R^2	—	Correlation coefficient

SPSS — Statistical package for the social sciences
t — Time
t/q_t — Contact time divided with adsorption at particular time
V — Total volume of solution, (mL)

References

[1] C.S.T. Araujo, D.C. Carvalho, H.C. Rezende, I.L.S. Almeida, L.M. Coelho, N.M.M. Coelho, T.L. Marques, V.N. Alves, Bioremediation of waters contaminated with heavy metals using Moringaoleifera seeds as biosorbent, Eds. Y.B. Patil, P. Rao, Applied Bioremediation Active Passive Approaches, InTech, 2013. doi: 10.5772/56157.

[2] G.A. Drasch, An increase of cadmium body burden for this century- an investigation on human tissues, Sci. Total. Environ., 26 (1983) 111–119.

[3] A. Kapoor, T. Viraraghavan, Fungal biosorption- an alternative treatment option for heavy metal bearing wastewaters: a review, Bioresour. Technol., 53 (1995) 195–206.

[4] C.S.F. Sim, W.S. Tan, A.S.Y. Ting, Endophytes from *Phragmites* for metal removal: evaluating their metal tolerance, adaptive behaviour and biosorption efficacy, Desal. Wat. Treat., 57 (2016) 6959–6966.

[5] A.S.Y. Ting, C.C. Choong, Utilization of non-viable cells compared to viable cells of *Stenotrophomonas maltophilia* for copper (Cu(ii)) removal from aqueous solutions, Adv. Environ. Biol., 3 (2009) 204–209.

[6] W.S. Tan, A.S.Y. Ting, Efficacy and reusability of alginate-immobilized live and heat-inactivated *Trichoderma asperellum* cells for Cu(II) removal from aqueous solution, Biores. Resour., 123 (2012) 290–295.

[7] M. Yazdani, C.K. Yap, F. Abdullah, S.G. Tan, An *in vitro* study on the adsorption, absorption and uptake capacity of Zn by the bioremediator *Trichoderma atroviride*, Environ. Asia, 3 (2010) 53–59.

[8] A.I. Adeogun, S.O. Kareem, J.B. Durosanya, E.S. Balogun, Kinetics and equilibrium parameters of biosorption and bioaccumulation of lead ions from aqueous solutions by *Trichoderma longibrachiatum*, J. Microbiol. Biotechnol. Food Sci., 1 (2012) 1221–1234.

[9] K.S. Hui, C.Y.H. Chao, S.C. Kot, Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ask, J. Hazard Mater., 127 (2005) 89–101.

[10] Y. Göksungur, S. Dagbagli, A. Ucan, U. Guvenc, Optimization of pullulan production from synthetic medium by *Aureobasidium pullulans* in a stirred tank reactor by response surface methodology, J. Chem. Technol. Biotechnol., 80 (2005) 819–827.

[11] Y.P. Ting, W.K. Teo, Uptake of cadmium and zinc by yeast: effects of co-metal ion and physical/chemical treatments, Bioresour. Technol., 50 (1994) 113–117.

[12] E.L. Errasquin, C. Vazquez, Tolerance and uptake of heavy metals by *Trichoderma atroviride* isolated from sludge, Chemosphere, 50 (2003) 137–143.

[13] G.E.J. Brown, A.L. Foster, J.D. Ostergren, Mineral surfaces and bioavailability of heavy metal: a molecular-scale perspective, Proc. Natl. Acad. Sci. U.S.A., 96 (1999) 3388–3395.

[14] A. Hammaini, A. Ballester, F. Gonzalez, M.L. Blazquez, J.A. Munoz, Activated sludge as biosorbent of heavy metals, Process Metall., 9 (1999) 185–92.

[15] P. Yin, Q. Yu, B. Jin, Z. Ling, Biosorption removal of cadmium from aqueous solution by using pretreated fungal biomass cultured from starch wastewater, Water Res., 33 (1999) 1960–1963.

[16] H.A. Elliot, M.R. Liberati, C.P. Huang, Competitive adsorption of heavy metals by soils, J. Environ. Qual., 15 (1986) 214–219.

[17] S. Singh, S. Pradhan, L.C. Rai, Metal removal from single and multimetallic systems by different biosorbent materials as evaluated by differential pulse anodic stripping voltammetry, Process Biochem., 36 (2000) 175–182.

[18] G. Guibaud, N. Tixier, A. Bouju, M. Baudu, Relation between extracellular polymers' composition and its ability to complex Cd, Cu and Pb, Chemosphere, 52 (2003) 1701–1710.

[19] R.H. Crist, K. Oberholser, N. Shank, M. Nguyen, Nature of bonding between metallic ions and algal cell walls, Environ. Sci. Technol., 15 (1981) 1212–1217.

[20] G.M. Gadd, D.J. Gray, P.J. Newby, Role of melanin in fungal biosorption of tributyltin chloride, Appl. Microbiol. Biotechnol., 34 (1990) 116–121.

[21] G.M. Gadd, Interactions of fungi with toxic metals, New Phytol., 124 (1993) 25–60.

[22] T.J. Beveridge, Role of cellular design in bacterial metal accumulation and mineralization, Annu. Rev. Microbiol., 43 (1989) 147–171.

[23] G.D. Wang, X.Y. Chen, Detoxification of soil phenolic pollutants by plant secretory enzyme. Eds. N. Wiley, Phytoremediation: Methods and Reviews, Humana Press, Totowa, 2007, pp. 49–57.

[24] A. Sari, M. Tuzen, Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass, J. Hazard Mater., 164 (2009) 1004–1011.

[25] L.E. Liu, J.D. Liu, H.P. Li, H.Q. Zhang, J. Liu, H.Q. Zhang, Equilibrium, kinetic, and thermodynamic studies of lead (II) biosorption on sesame leaf, Bioresources, 7 (2012) 3555–3572.

[26] R.J.E. Martins, V.J.P. Vilar, R.A.R. Boaventura, Kinetic modelling of cadmium and lead removal by aquatic mosses, Braz. J. Chem. Eng., 31 (2014) 229–242.

[27] Y.R. Cao, Z. Liu, G.L. Cheng, X.B. Jing, H. Xu, Exploring single and multi-metal biosorption by immobilized spent *Tricholoma lobayense* using multi-step response surface methodology, Chem. Eng. J., 164 (2010) 183–195.

[28] A.H. Sulaymon, A.A. Mohammed, T.J. Al-Musawi, Competitive biosorption of lead, cadmium, copper, and arsenic ions using algae, Environ. Sci. Pollut. Res. Int., 20 (2013) 3011–3023.

[29] A.C. John, O.L. Ibironke, V. Adedeji, O. Oladunni, Equilibrium and kinetic studies of the biosorption of heavy metal (cadmium) on *Cassia siamea* bark, Am. Eurasian J. Sci. Res., 6 (2011) 123–130.