Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.929978

55 (2015) 1832–1839
August

Taylor & Francis
Taylor & Francis Group

Biosorption of Pb(II) and Zn(II) from aqueous solutions by living B350 biomass

Yanzhi Qu[a,b], Qingqiang Meng[a], Quanlin Zhao[a], Zhengfang Ye[a,*]

[a]*The Key Laboratory of Water and Sediment Sciences, Department of Environmental Engineering, Peking University, Ministry of Education, Beijing 100871, China, Tel. +86 10 62755914; emails: pkuqyz@163.com (Y. Qu), mengqingqiang@pku.edu.cn (Q. Meng), zhaoquanlin@pku.edu.cn (Q. Zao), Fax: +86 10 62756526; email: zhengfangye@163.com (Z. Ye)*

[b]*Research Center on Environmental Planning and Policies, National Engineering Research Center of Urban Environmental Pollution Control, Beijing Municipal Research Institute of Environmental Protection, Beijing 100037, China*

Received 18 December 2013; Accepted 21 May 2014

ABSTRACT

Beneficiation production wastewater is a kind of wastewater generated from exploiting minerals, where the main pollutants are heavy metals and organic agents. In this study, living B350 biomass (a mixture of various micro-organisms) was used to remove Pb(II) and Zn(II) from aqueous solutions. The effects of pH, biomass dosage and contact time on removal ratios of Pb(II) and Zn(II) were studied. Two kinetic models, pseudo-first-order and pseudo-second-order, were used to fit the experimental results. The chemical changes of B350 biomass before and after adsorption were monitored by Energy Dispersion X-ray (EDX) spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy. In addition, the feasibility of B350 to remove heavy metals and m-cresol simultaneously was investigated. The results showed that the removal ratios of heavy metals increased with increasing dosage of biosorbent. When B350 dosage was 1.0 g/L, 84.88% of Pb(II) and 38.06% of Zn(II) can be removed after 2 h of adsorption at 25°C. The adsorption of Pb(II) and Zn(II) on B350 was coincident with Langmuir and Freundlich isotherms, respectively. Pseudo-second-order model can best describe the adsorption process. EDX and FTIR results indicated that ion exchange and complexation might exist during the adsorption of Pb(II) and Zn(II). The living B350 biomass can not only adsorb heavy metal ions, but also biodegrade organic pollutants through metabolizing itself.

Keywords: Biosorption; Pb; Zn; B350 biomass; Kinetics

1. Introduction

Beneficiation production wastewater is a kind of wastewater generated from exploiting minerals, the main pollutants of which are heavy metals and organic agents. Heavy metals, such as lead and zinc, are difficult to biodegrade and can travel through the food chain by bioaccumulation, which will result in serious environmental pollution if it is discharged without effective treatment. In the last decades, various physicochemical methods, such as filtration [1–3], chemical precipitation [4], solvent extraction [5], ion exchange [6] and adsorption [7], have been investigated for removing heavy metals from wastewaters. However, these methods have the disadvantages of low efficiencies and high cost [8,9]. So it is necessary to find an alternative technique, which is efficient and cost effective.

*Corresponding author.

Biosorption, based on living or non-living micro-organisms or plants, could be such an alternative method, which can be used to treat high-volume wastewater containing low concentrations of heavy metals [10]. Metal ions uptake is complex and may involve the contribution of ion exchange, micro-precipitation, physical adsorption, electrostatic attraction and chelation [11,12]. In recent years, various kinds of microbial biomass were investigated as biosorbents to remove heavy metals, such as *Microsphaeropsis* [13], *R. opacus* [14], *Bacillus subtilis* [15] and *Geobacillus thermoleovorans* [16], most of which were dead microbial biomass, which were dried, ground and sieved before use. It is expected that whether living biomass can be used as biosorbent because it can biodegrade organics at the same time. To our knowledge, there are still few studies focused on biosorption with living biomass.

B350 is a mixture of various micro-organisms which has been used to remove organic pollutants from oil-field wastewater [17] and landfill leachate [18]. The objective of the present work was to investigate its feasibility of adsorbing Pb(II) and Zn(II) from aqueous solution. Effects of pH, biomass dosage and contact time on removal ratios of Pb(II) and Zn(II) were studied. Two kinetic models, pseudo-first-order and pseudo-second-order, were used to fit the experimental results. The chemical changes of B350 biomass before and after adsorption were monitored by Energy Dispersion X-ray (EDX) spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy. In addition, the feasibility of B350 to remove heavy metals and m-cresol simultaneously was investigated.

2. Materials and methods

2.1. Micro-organism and its culture conditions

The micro-organisms used in this study were B350, which were purchased from Bio-Systems Corporation (USA). It contains several kinds of enzymes, such as cellulase, amylase, lipase and hydrolase with the bulk density of 0.6–0.8 g/cm^3.

The culture medium is composed of beef extract (3.0 g/L), peptone (10.0 g/L), sodium chloride (5.0 g/L) and glucose (2.0 g/L), the pH of which was adjusted to 7.2–7.4.

The stock strain was prepared by cultivating 0.5 g B350 in a DDHZ-300 shaker (Taicang, China) at 30 ℃ and 200 rpm for 72 h in a 1,500 mL conical flask containing 500 mL sterilized culture medium. The strain was transferred weekly and stored at 2 ℃. Each time 5 mL strain was inoculated into a new sterilized medium. After the micro-organism multiplied, it was transferred to the centrifugal tube and centrifuged at 5,000 rpm for 10 min (Eppendorf 5804R, Germany). The supernatant was removed and the micro-organism was washed twice by deionized water to remove residual growth medium. The washed living biomass was immediately re-suspended in deionized water to prepare B350 suspension for later uses. Biomass concentration in suspension was determined by drying an aliquot to a constant weight at 80 ℃ in a pre-weighed glass container.

2.2. Metal solutions

The stock solutions of lead and zinc (1,000 mg/L) were prepared using a 500 mL volumetric flask by dissolving 2.2754 g $Zn(NO_3)_2{\cdot}6H_2O$ and 0.7993 g $Pb(NO_3)_2$ (GR grade) in deionized water, respectively. Working solutions were obtained by diluting stock solutions in a desired ratio with deionized water before experiment. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl.

2.3. Batch adsorption test

The batch adsorption test was used to investigate the influence of pH, B350 biomass dosage and contact time on removal of Pb(II) and Zn(II). The pre-weighed amount of pre-treated B350 (25 mg) was put into a 100 mL flask containing 25 mL water samples with certain pH value. The flasks were sealed and shaken at constant speed in a constant temperature oscillator (Taicang Laboratory Equipment Factory, Jiangsu Province, China). After the adsorption system reached equilibrium, the suspension was centrifuged at 10,000 rpm for 10 min, and then the concentrations of Pb(II) and Zn(II) in the supernatant were determined using a flame atomic absorption spectrophotometer (Jena AAS vario 6, Germany). The heavy metal removal $R\%$ was used to evaluate the adsorption efficiency, which can be calculated by the equation:

$$R\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_t (mg L^{-1}) represents metal concentration at contact time t and C_0 (mg L^{-1}) represents the initial metal concentration.

The following equation was used to calculate the adsorption capacity of B350:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where q_e (mg g^{-1}) represents the adsorption capacity of B350 at equilibrium time, C_0 and C_e represent the initial and equilibrium metal concentration, respectively. W (mg) represents the B350 mass and V (mL) represents the volume of water sample.

2.4. Adsorption kinetics

For the adsorption kinetics test, 25 mg of pre-treated B350 biomass was added to a 100 mL flask containing 25 mL water sample. At different time intervals, certain amount of solution was withdrawn and centrifuged, and the metal concentration of the supernatant was determined.

2.5. Adsorption isotherm

For the adsorption isotherm determination, 25 mL water sample with different initial concentrations (10, 20, 50, 100, 150 and 200 mg L^{-1}) was added to six flasks, each of which containing 25 mg pre-treated B350 biomass. After the adsorption equilibrium had been achieved, the solution was withdrawn and centrifuged, and then the metal concentration was determined.

2.6. EDX analysis

The change of B350s elemental composition before and after adsorption was studied by an EDX spectrometer accompanied with a Quanta 200F Environmental Scanning Electron Microscope (FEI, the Netherlands), with the accelerating voltage of 15 kV.

2.7. FTIR analysis

The chemical changes of B350 samples before and after adsorption were monitored by FTIR spectroscopy analysis using a Tensor 27 spectrometer (Bruker, Germany) with a resolution of 1 cm^{-1}.

2.8. Simultaneous biosorption and biodegradation study

In order to investigate the feasibility of B350 to biosorb heavy metal and biodegrade organics simultaneously, it was used to treat four synthetic water samples: (i) m-cresol 5 mg/L; (ii) m-cresol 5 mg/L + Pb (II) 10 mg/L; (iii) m-cresol 5 mg/L + Zn(II) 10 mg/L; (iv) m-cresol 5 mg/L + Pb(II) 10 mg/L + Zn(II) 10 mg/L, which contained the same basal ingredients (NH_4Cl 0.04 g/L, NaH_2PO_4 0.01 g/L and glucose 0.2 g/L). The pH value was controlled at 7.0. After the adsorption system reached equilibrium, the suspension was filtered through a 0.45 μm pore size filter, and then the metal concentrations were determined by AAS and the m-cresol concentration was determined by High-Performance Liquid Chromatography (HPLC).

3. Results and discussion

3.1. Effect of pH on removal of Pb(II) and Zn(II)

The solution pH can affect the chemical state of metal ions, which has important effect on the adsorption of heavy metals. Fig. 1 shows the effect of pH on removal of Pb(II) and Zn(II). The initial metal concentration was 20 mg/L. It can be seen that the influence of pH on Pb(II) removal is greater than that on Zn(II) removal. The removal ratio of Zn(II) increased continuously from 7.8 to 53.8% when pH increased from 2 to 7, while that of Pb(II) increased quickly from 1.5 to 84.9% when pH increased from 2 to 5, and then levelled off. This is because when pH increases, the amount of H^+ and H_3O^+ that would compete with heavy metal ions for adsorption sites decreases, resulting in the increase of Zn(II) and Pb(II) removal. It can also be noted that the removal ratio of Pb(II) decreased a little when the solution pH further increased from 5 to 7. This may be attributed to the formation of lead hydroxide, which would deposit on the micro-organism's surface and hence decrease adsorption of Pb(II). In the later study, pH 5 was selected as the optimum pH value.

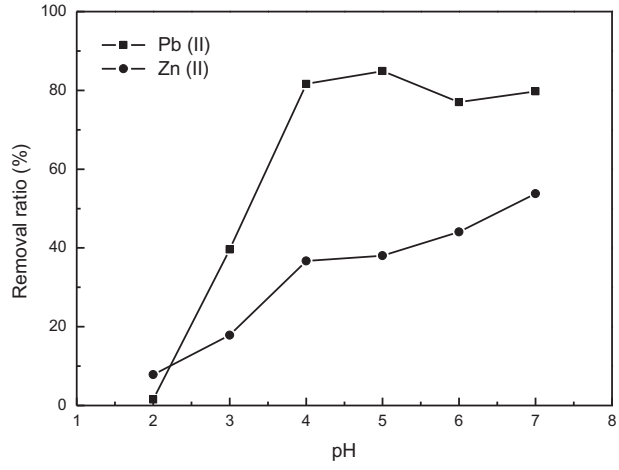

Fig. 1. Effect of pH on removal of Pb(II) and Zn(II) (conditions: initial metal concentration 20 mg L^{-1}, temperature 25°C, contact time 2 h and biomass dosage 1.0 g L^{-1}).

3.2. Effect of biomass dosage on removal of Pb(II) and Zn(II)

Fig. 2 illustrates the effect of B350 dosage on removal of Pb(II) and Zn(II). The removal ratios of Pb (II) and Zn(II) increased with increasing B350 dosage. When B350 dosage increased from 0.08 to 1.2 g/L, the removal ratios of Pb(II) and Zn(II) increased gradually from 23.0 and 5.4% to 87.50 and 42.2%, respectively. This is attributed to the increasing number of active sites on the biosorbent and exchangeable ions available for biosorption. It can also be observed that the removal ratio of Pb(II) is much higher than that of Zn (II), meaning that Pb(II) is easier to be removed by B350.

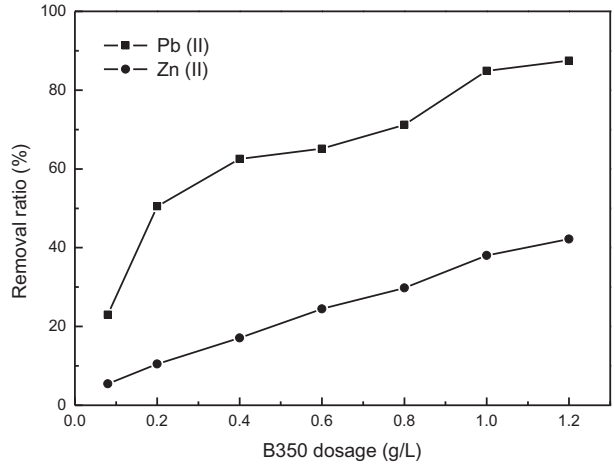

Fig. 2. Effect of B350 dosage on removal of Pb(II) and Zn (II) (conditions: initial metal concentration 20 mg L^{-1}, temperature 25°C, pH 5 and contact time 2 h).

3.3. Effect of contact time on removal of Pb(II) and Zn(II)

Fig. 3 shows the effect of contact time on removal of Pb(II) and Zn(II). It can be obviously observed that the removal ratio of Pb(II) is greater than that of Zn (II). In the first 5 min, the removal ratio of Pb(II) increased quickly from 0 to 71.1%, and then changed a little in the following times. The change of Zn(II) removal is similar to Pb(II) removal. It increased from 0 to 36.3% in the first 5 min and then kept almost unchanged in the following times. This result is attributed to biosorption, whereby metal ions are bound passively to the surface of bacterial cell wall by physical/chemical processes. This process occurs rapidly, and subsequently the metal ions are slowly transferred to the interior of the cell by microbial energy systems [19].

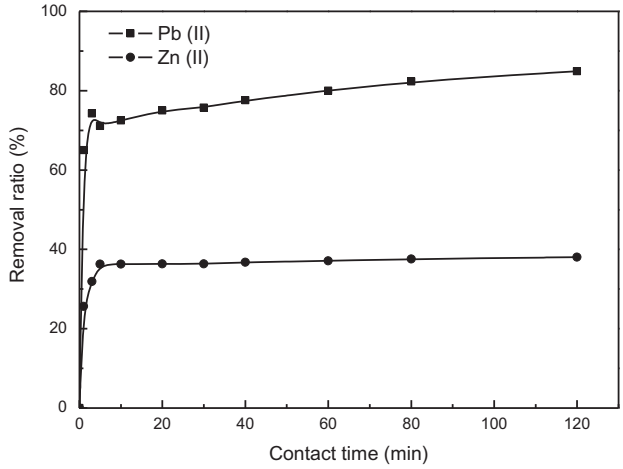

Fig. 3. Effect of contact time on removal of Pb(II) and Zn (II) (conditions: initial metal concentration 20 mg L^{-1}, temperature 25°C, pH 5 and biomass dosage 1.0 g L^{-1}).

3.4. Adsorption isotherm

In our study, Langmuir and Freundlich isotherm models were used to fit the experimental data. The saturated monolayer isotherm can be represented as Langmuir isotherm [20]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where C_e (mg L^{-1}) is the equilibrium concentration, q_e (mg g^{-1}) is the amount of metal ions adsorbed at equilibrium, q_m (mg g^{-1}) is q_e for a complete monolayer and K_L (L mg^{-1}) is the Langmuir adsorption constant. It can be linearized into the following form:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \tag{4}$$

Freundlich equation is an empirical formula that describes a multilayer adsorption [21], which can be expressed as:

$$q_e = K_F C_e^{1/n} \tag{5}$$

where q_e and Ce are the same parameters as in Eq. (3), K_F is the Freundlich constant ((L $mg^{-1})^{1/n}$ mg g^{-1}) and $1/n$ is an empirical constant. It can be linearized into the following form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

Table 1 lists the Langmuir and Freundlich isotherm parameters for the adsorption of Pb(II) and Zn(II) onto B350 at different temperatures. For Pb(II), the correlation coefficients for Langmuir isotherm model are higher than 0.99, which are much higher than that of Freundlich isotherm, meaning that Langmuir isotherm can be used to describe the adsorption of Pb(II) onto B350. The adsorption constant K_L decreased with increasing temperatures, suggesting that the adsorption of Pb(II) onto B350 maybe exothermic. For Zn(II), the correlation coefficients for both Langmuir and Freundlich isotherm models are higher than 0.93, meaning that these two models can be used to describe its adsorption. It can also be noted that the correlation coefficient R^2 for Freundlich model is a little higher than that for Langmuir model, suggesting that the adsorption of Zn(II) is more likely to be described by Freundlich model.

3.5. Adsorption kinetics

The adsorption kinetics was investigated using two models, pseudo-first-order and pseudo-second-order. Pseudo-first-order kinetic model can be expressed as [22]:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (7)$$

where q_e (mg g^{-1}) is the adsorption capacity at equilibrium, q_t (mg g^{-1}) is adsorption capacity at contact time t (min) and k_1(min^{-1}) is the rate constant of pseudo-first-order kinetic model. The values of q_e and k_1 can be obtained by plotting log ($q_e - q_t$) vs. t.

Pseudo-second-order kinetic model can be written as [23]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order kinetic model. The values of q_e and k_2 can be obtained by plotting t/q_t vs. t.

Table 2 lists the kinetics fitting results of these two models. For Pb(II) and Zn(II), the correlation coefficients of pseudo-second-order model ($R^2 > 0.99$) are higher than that of pseudo-first-order model, suggesting that the adsorption of Pb(II) and Zn(II) is a pseudo-second-order adsorption. It can also be noted that k_2 for Zn(II) (0.1612 g mg^{-1} min^{-1}) is higher than that for Pb(II) (0.0315 g mg^{-1} min^{-1}), indicating that Zn(II) can be adsorbed on B350 more rapidly that Pb (II).

3.6. EDX analysis

Fig. 4 shows the EDX spectra of B350 before and after adsorption. The raw B350 biomass consists of C, O, P, Na and Ca. After biosorption, the peak of Pb or Zn appeared, suggesting the existence of Pb or Zn after adsorption. Moreover, the intensity of Na and Ca peaks decreased after biosorption, inferring that Na and Ca participate in the biosorption process. The result indicates that biosorption may involve an ion-exchange process [24], where Na(I) and Ca(II) combined by cellular material are replaced by Pb(II) or Zn (II), resulting in partly removal of Pb(II) or Zn(II) from aqueous solution.

3.7. FTIR analysis

Fig. 5 shows the FTIR spectra of B350 biomass before and after biosorption. Several adsorption peaks can be observed in the spectrum of raw B350. The peak at 3,302 cm^{-1} is assigned to stretching vibration of hydroxyl or amino [25], while the peak at 2,928 cm^{-1} is attributed to methylene [26]. The peak at 1,725 cm^{-1} is characteristic absorption of stretching vibration of carbonyl in acid. The peaks at 1,653 and

Table 1
Langmuir and Freundlich isotherm parameters for the adsorption of Pb(II) and Zn(II) on B350 at different temperatures

		Langmuir			Freundlich		
Metal ions	Temperature (℃)	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F	n	R^2
Pb(II)	25	55.1876	0.1200	0.9954	9.5553	2.6174	0.7456
	35	63.8978	0.1055	0.9932	10.3811	2.5381	0.7441
	45	62.0347	0.07197	0.9803	9.7971	2.6295	0.5491
Zn(II)	25	22.9043	0.03405	0.9547	3.4627	2.9888	0.9817
	35	29.3255	0.02511	0.9322	2.7510	2.3684	0.9777
	45	19.9283	0.03071	0.9547	2.6776	2.8147	0.9793

Table 2
Kinetics fitting results of the adsorption data

Metal ions	Kinetic model	Parameters	R^2
Pb(II)	Pseudo-first-order	$k_1 = 0.0486$, $q_e = 6.3183$	0.8111
	Pseudo-second-order	$k_2 = 0.0315$, $q_e = 16.9492$	0.9986
Zn(II)	Pseudo-first-order	$k_1 = 0.0594$, $q_e = 1.9661$	0.8019
	Pseudo-second-order	$k_2 = 0.1612$, $q_e = 7.6104$	0.9998

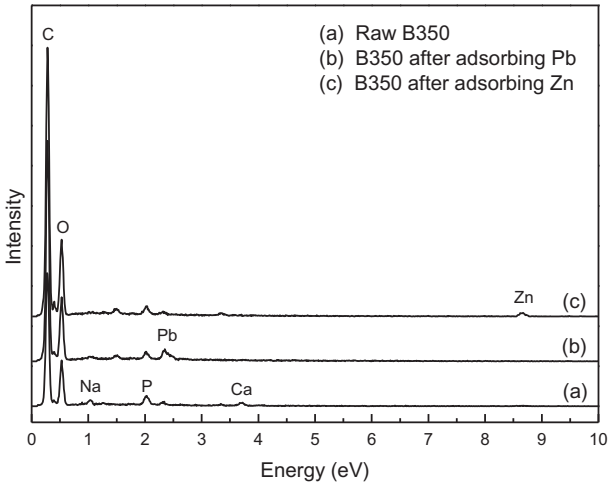

Fig. 4. EDX spectra of B350 before and after adsorbing Pb (II) and Zn(II).

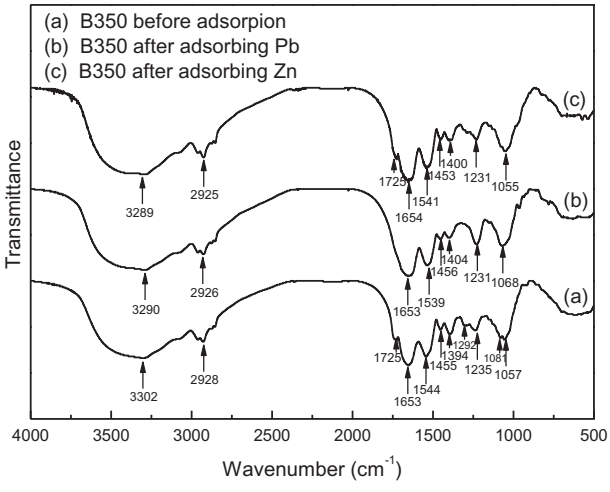

Fig. 5. FTIR spectra of B350 before and after adsorption.

1,544 cm^{-1} are assigned to C=O stretching vibration and N–H bending vibration, which are characteristics of amide. The peak at 1,455 cm^{-1} is assigned to bending vibration of methyl. The peak at 1,394 cm^{-1} is characteristic of carboxyl in uronic acid. The band at 1,292 cm^{-1} is assigned to C–N stretching vibration of amide. The peak at 1,235 cm^{-1} is assigned to C–O stretching vibration of carbohydrates and alcohols, along with the stretching bands of POO^- and $P(OH)_2$ from phosphates [27]. The peak at 1,081 cm^{-1} is assigned to C–O stretching vibration of sugar. The peak at 1,057 cm^{-1} is associated with different stretching vibrations of C–O bonds of the cyclic structure of polysaccharides [28].

After adsorption of Pb (II) and Zn (II), the bands corresponded to hydroxyl or amino red shifted to 3,290 and 3,289 cm^{-1}, the peak at 1,725 cm^{-1} disappeared or weakened. The peak at 1,292 cm^{-1} disappeared. The bands at 1,394 cm^{-1} blue shifted to 1,404 and 1,400 cm^{-1}, respectively. The peak at 1,235 cm^{-1} shifted to 1,231 cm^{-1}. The band at 1,057 cm^{-1} shifted to 1,068 and 1,055 cm^{-1}, respectively. These changes suggested that Pb(II) and Zn(II) might react with hydroxyl, amino, carboxyl and phosphate groups in the adsorption process.

3.8. Simultaneous biosorption and biodegradation

In our previous study [18], B350 showed an excellent capability of biodegrading refractory organic pollutants in landfill leachate. 98.3% of chemical oxygen demand (COD) could be removed when the influent COD was 5,550 mg/L. In this study, we investigated its feasibility of removing heavy metal ions (Pb^{2+} or Zn^{2+}) and organic pollutants simultaneously, where m-cresol was used as model organic pollutant, which was typical organic pollutant in beneficiation production wastewater.

Table 3 lists the removal ratios of m-cresol, heavy metals and total organic carbon (TOC) in different water samples. It can be seen that the removal ratio of TOC is higher than 90% (92.81–96.06%), meaning that B350 is bioactive for biodegrade organics. When Pb(II) or Zn(II) is present in water sample, the removal of m-cresol decreases from 93.35 to 82.36 or 80.24%, and the removal of Pb(II) or Zn(II) is 68.36 or 54.65%, respectively. When Pb(II) and Zn(II) coexist

Table 3
Removal ratios of m-cresol, heavy metals and TOC in different water samples (%)

	m-cresol	Pb(II)	Zn(II)	TOC
m-cresol	93.35			96.02
m-cresol + Pb(II)	82.36	68.36		93.43
m-cresol + Zn(II)	80.24		54.65	94.65
m-cresol + Pb(II) + Zn(II)	78.42	63.62	50.35	92.81

in the solution, m-cresol removal further decreases to 78.42% and the removal ratios of Pb(II) and Zn(II) are 63.62 and 50.35%, respectively. This result indicated that the micro-organisms not only adsorbed heavy metal ions, but also biodegraded organic pollutants through metabolizing itself. Pb(II) and Zn(II) ions have some inhibition effect on biodegradation of m-cresol by B350. It can also be noted that the removal ratios of m-cresol, Pb(II) and Zn(II) are lower when they coexist in solution than that when each of them is in the solution separately, which inferred that competition might exist between biosorption of heavy metals and biodegradation of organics.

4. Conclusions

B350 biomass can be used as an effective biosorbent to remove Pb(II) and Zn(II) from aqueous solution. When B350 dosage was 1.0 g/L, 84.88% of Pb(II) and 38.06% of Zn(II) can be removed after 2 h of adsorption at 25°C. The adsorption of Pb(II) and Zn(II) on B350 was coincident with Langmuir and Freundlich isotherms, respectively. Pseudo-second-order model can best describe the adsorption process. EDX and FTIR results indicated that ion exchange and complexation might exist during the adsorption of Pb(II) and Zn(II). The micro-organisms can not only adsorb heavy metal ions, but also biodegrade organic pollutants through metabolizing itself.

Acknowledgments

The authors are grateful for the financial support from the Major Special Technological Project on Water Pollution Control and Management of China, whose registered number is 2009ZX07212-001-04. The authors also gratefully acknowledge the reviewers for their comments which would significantly improve the quality of the manuscript.

References

[1] S. Liu, Z. Li, C. Wang, A. Jiao, Enhancing both removal efficiency and permeate flux by potassium sodium tartrate (PST) in a nanofiltration process for the treatment of wastewater containing cadmium and zinc, Sep. Purif. Technol. 116 (2013) 131–136.
[2] P. Yenphan, A. Chanachai, R. Jiraratananon, Experimental study on micellar-enhanced ultrafiltration (MEUF) of aqueous solution and wastewater containing lead ion with mixed surfactants, Desalination 253 (2010) 30–37.
[3] B. Rahmanian, M. Pakizeh, A. Maskooki, Micellar-enhanced ultrafiltration of zinc in synthetic wastewater using spiral-wound membrane, J. Hazard. Mater. 184 (2010) 261–267.
[4] M.M. Brbooti, B.A. Abid, N.M. Al-Shuwaiki, Removal of heavy metals using chemical precipitation, Eng. Tech. J. 29 (2011) 595–612.
[5] J. Konczyk, C. Kozlowski, W. Walkowiak, Lead (II) removal from aqueous solutions by solvent extraction with tetracarboxylresorcin[4]arene, Physicochem. Probl. Miner. Process 49 (2013) 213–222.
[6] N. Rahman, U. Haseen, M. Rashid, Synthesis and characterization of polyacrylamide zirconium (IV) iodate ion-exchanger: Its application for selective removal of lead (II) from wastewater, Arab. J. Chem. 2013, http://dx.doi.org/10.1016/j.arabjc.2013.06.029.
[7] L. Hajiaghababaei, A. Badiei, M.R. Ganjali, S. Heydari, Y. Khaniani, G.M. Ziarani, Highly efficient removal and preconcentration of lead and cadmium cations from water and wastewater samples using ethylenediamine functionalized SBA-15, Desalination 266 (2011) 182–187.
[8] R. Vimala, N. Das, Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: A comparative study, J. Hazard. Mater. 168 (2009) 376–382.
[9] G. Blazquez, M.A. Martin-Lara, G. Tenorio, M. Calero, Batch biosorption of lead (II) from aqueous solutions by olive tree pruning waste: Equilibrium, kinetics and thermodynamic study, Chem. Eng. J. 168 (2011) 170–177.
[10] H. Li, Y. Lin, W. Guan, J. Chang, L. Xu, J. Guo, G. Wei, Biosorption of Zn(II) by live and dead cells of Streptomyces *ciscaucasicus strain* CCNWHX 72-14, J. Hazard. Mater. 179 (2010) 151–159.
[11] V.K. Gupta, A. Rastogi, Equilibrium and kinetic modelling of cadmium (II) biosorption by nonliving algal biomass *Oedogonium* sp. from aqueous phase, J. Hazard. Mater. 153 (2008) 759–766.
[12] C. Mack, B. Wilhelmi, J.R. Duncan, J.E. Burgess, Biosorption of precious metals, Biotechnol. Adv. 25 (2007) 264–271.
[13] X. Xiao, S. Luo, G. Zeng, W. Wei, Y. Wan, L. Chen, H. Guo, Z. Cao, L. Yang, J. Chen, Q. Xi, Biosorption of cadmium by endophytic fungus (EF) *Microsphaeropsis* sp. LSE10 isolated from cadmium hyperaccumulator *Solanum nigrum* L, Bioresour. Technol. 101 (2010) 1668–1674.

[14] B.Y.M. Bueno, M.L. Torem, F. Molina, L.M.S. de Mesquita, Biosorption of lead(II), chromium(III) and copper(II) by *R. opacus*: Equilibrium and kinetic studies, Miner. Eng. 21 (2008) 65–75.
[15] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, B.B. Mamba, L. Marjanovic, T.G. Barnard, A comprehensive study of physical and physiological parameters that affect biosorption of metal pollutants from aqueous solutions, Phys. Chem. Earth 35 (2010) 672–678.
[16] S. Ozdemir, E. Kilinc, A. Poli, B. Nicolaus, K. Güven, Biosorption of Cd, Cu, Ni, Mn and Zn from aqueous solutions by thermophilic bacteria, *Geobacillus toebii* sub.sp. *decanicus* and *Geobacillus thermoleovorans* sub.sp. *stromboliensis*: Equilibrium, kinetic and thermodynamic studies, Chem. Eng. J. 152 (2009) 195–206.
[17] X. Zhao, Y. Wang, Z. Ye, A.G.L. Borthwick, J. Ni, Oil field wastewater treatment in biological aerated filter by immobilized microorganisms, Process Biochem. 41 (2006) 1475–1483.
[18] Z. Ye, H. Yu, L. Wen, J. Ni, Treatment of landfill leachate by immobilized microorganisms, Sci. China Chem. 51 (2008) 1014–1020.
[19] S.T. Akar, A. Gorgulu, B. Anilan, Z. Kaynak, T. Akar, Investigation of the biosorption characteristics of lead (II) ions onto *Symphoricarpus albus*: Batch and dynamic flow studies, J. Hazard. Mater. 165 (2009) 126–133.
[20] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. mishra, Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses, Colliods Surf., A 264 (2005) 17–28.
[21] C. Ma, G. Tao, J. Tang, Z. Lou, H. Wang, X. Gu, L. Hu, M. Yin, Preparative separation and purification of rosavin in *Rhodiola rosea* by macroporous adsorption resins, Sep. Purif. Technol. 69 (2009) 22–28.
[22] V. Gomez, M.S. Larrechi, M.P. Callao, Kinetic and adsorption study of acid dye removal using activated carbon, Chemosphere 69 (2007) 1151–1158.
[23] E. Rodrguez, A. Encinas, F.J. Masa, F.J. Beltran, Influence of resorcinol chemical oxidation on the removal of resulting organic carbon by activated carbon adsorption, Chemosphere 70 (2008) 1366–1374.
[24] L. Yao, Z. Ye, M. Tong, P. Lai, J. Ni, Removal of Cr^{3+} from aqueous solution by biosorption with aerobic granules, J. Hazard. Mater. 165 (2009) 250–255.
[25] M. Jain, V.K. Garg, K. Kadirvelu, Equilibrium and kinetic studies for sequestration of Cr (VI) from simulated wastewater using sunflower waste biomass, J. Hazard. Mater. 171 (2009) 328–334.
[26] N. Azouaou, Z. Sadaoui, A. Djaafri, H. Mokaddem, Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics, J. Hazard. Mater. 184 (2010) 126–134.
[27] M. Martins, M.L. Faleiro, A.M.R. da Costa, S. Chaves, R. Tenreiro, A.P. Matos, M.C. Costa, Mechanism of uranium (VI) removal by two anaerobic bacterial communities, J. Hazard. Mater. 184 (2010) 89–96.
[28] R.F.L. Ribeiro, S.M.S. Magalhaes, F.A.R. Barbosa, C.C. Nascentes, I.C. Campos, D.C. Moraes, Evaluation of the potential of microalgae *Microcystis novacekii* in the removal of Pb^{2+} from an aqueous medium, J. Hazard. Mater. 179 (2010) 947–953.