Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.943059

54 (2015) 3177–3183
June

Taylor & Francis
Taylor & Francis Group

Effects of rhamnolipid on the adsorption of Pb^{2+} onto compost humic acid

Haiyan Fu[a,*], Tian Chai[a], Guohe Huang[a], Panfeng Gao[a], Zhifeng Liu[b]

[a]*Department of Environmental Engineering, Xiamen University of Technology, Xiamen 361024, China, Tel. +86 592 6291151; Fax: +86 592 6291138; emails: fhyan@126.com, fuhy@xmut.edu.cn (H. Fu), Tel./Fax: +86 592 6291138; email: chait@xmut.edu.cn (T. Chai), Tel. +86 592 6291160; Fax: +86 592 6291138; email: huanggh@xmut.edu.cn (G. Huang), Tel. +86 592 6291620; Fax: +86 592 6291138; email: Smilegaopf@126.com (P. Gao)*
[b]*College of Environmental Science and Engineering, Hunan University, Changsha 410082, China, Tel./Fax: +86 731 88823701; email: lzf18182002@163.com*

Received 22 July 2012; Accepted 2 July 2014

ABSTRACT

Biosurfactants can be applied to improve the micro-environment and efficiency of composting, but their biosurfactant effects on the adsorption of heavy metals and humic acid (HA) remain undefined. This study aims to deal with the effects of biosurfactant rhamnolipid (RL) on the adsorption of Pb^{2+} onto compost HA at various concentrations, temperatures, and pH values. Adding RL solution influenced the adsorption of Pb^{2+} onto compost HA without fitting the Langmuir or the Freundlich isotherm. Moreover, Pb^{2+} adsorption onto compost HA was accelerated by RL at low concentrations until maximum at $40\,\mathrm{mg\,L^{-1}}$. However, the adsorption was weakened at sufficiently high RL concentration. Furthermore, Pb^{2+} adsorption was enhanced with increasing pH values and was weakened with rising temperature. This study provides reference for applying biosurfactants in compost.

Keywords: Rhamnolipid; Compost; Humic acid; Pb^{2+}; Adsorption

1. Introduction

Composting is a biochemical process which facilitates the transformation of biodegradable organic matters into stable humus in artificial conditions utilizing micro-organisms existing widely in nature, such as bacteria, actinomycetes, and fungi [1,2]. Therefore, humus is a crucial component of compost in its later stages. Organic solid wastes used for compost, which are accumulated from a wide range of sources, contain toxic substances, such as organic contaminants and heavy metals, etc. Since heavy metals are non-biodegradable, they have been threatening our lives and environment for a long time [3–6]. However, the toxicity of heavy metals depends not only on their concentrations, but also on their form and mobility [7]. Meanwhile, humus plays an essential role in the transformation of heavy metals [8]. Thus, the relationship between humus and heavy metals has attracted worldwide attention [9–11]. The adsorption characteristics of humus from various sources may differ [12] because the molecular weight and chemical structure of humus determine its complexation with heavy metals [13].

On the other hand, biosurfactants, which are environmentally friendly [14,15], have been utilized to wash or remove heavy metals in environmental remediation [16]. Besides, Miller [17] proposed two mechanisms for the desorption of heavy metals from soil by biosurfactants, including the complexation with free heavy metals in soil solution and the reduction of interfacial tension resulting from the adsorption of

---

*Corresponding author.

heavy metals onto soil that entered the solution and were further complexed with the biosurfactants. Doong et al. [18] found that the mechanisms of removing heavy metals by biosurfactants included ion exchange, precipitation–dissolution, and anti-charge combination. Moreover, Mulligan et al. [19] revealed that heavy metals were removed by surfactants through the adsorption of surfactants onto soil surface and subsequent complexation. The complex was then transferred to the solution within soil where it was further complexed with the micelles therein. Mulligan and Wang [20] discovered that biosurfactants could remove heavy metals from sediments, and the removal efficiency of Cu was 65% by rhamnolipid (RL). However, the biosurfactants were also adsorbed onto the soil during functioning. Urum and Pekdemir [21] verified that 75% of biosurfactants were adsorbed onto soil in the suspension of soil/surfactant. In addition, the adsorption ability of RL for heavy metals was remarkably higher than that of many components of polluted soil [4]. Fu et al. [15] showed that applying biosurfactants in composting can improve microenvironment and augment efficiency. Thus, biosurfactants may be able to change the interactions between compost humus and heavy metals, and to prevent heavy metals from re-entering the environment. Nevertheless, relevant mechanisms and applications have seldom been referred hitherto. Since different humic acids (HAs) show various adsorption capacities [12], compost HAs that have been extensively investigated in our group were selected as the study objects. Furthermore, there are no reports concerning the mechanisms of composting for the influences of biosurfactants on the interactions between compost humus and heavy metals, nor whether these effects might be related to environmental factors, such as temperature and pH. Thereby motivated, Pb was employed as the heavy metal to study the adsorption of Pb^{2+} onto compost HA, as well as the effects of temperature and pH values on adsorption.

2. Materials and methods

2.1. Preparation and characterization of HA

The 20-d compost sample was taken from the Shanghai Meishang solid waste treatment plant to render the experimental results more applicable to practical situation. The sample, which comprised 8.02% paper, 13.93% plastic, 1.43% bamboo, 2.87% fiber, 54.67% kitchen residue, 13.69% pericarp, and 5.41% clay, was air-dried, passed through a 2-mm screen, and then mixed.

Compost HA was extracted by the method of Kang and Xing [22]. Ten grams of the compost sample was dispersed in 100 mL of 0.1 M $Na_4P_2O_7{\cdot}10H_2O$ solution using a 250-mL conical flask. Air in the flask was displaced by N_2, and the mixture was shaken for 24 h at room temperature and 200 rpm. Then, the suspension was centrifuged at 3,000 g for 15 min, and the supernatant was collected for acidification (pH 1.5 with 6 M HCl) to obtain the first HA fraction (Fig. 1). Then, the precipitate was extracted seven times with 0.1 M $Na_4P_2O_7$ and then twice more with 0.1 M NaOH. For each extraction, the supernatant after centrifugation was acidified and precipitated as described above. Each precipitated HA was centrifuged at 5,000 g for 30 min, redissolved in 0.1 M $Na_4P_2O_7$ or 0.1 M NaOH, acidified, and centrifuged. Then, the precipitated HA was mixed and de-ashed with 0.1 M HCl/0.3 M HF solution, washed with deionized water, freeze-dried, gently ground to pass through a 100-μm screen, and stored for subsequent use.

One milligram of the crude compost HA sample was mixed with 600 mg KBr and compressed to create a pellet. Absorption spectra were obtained using a WQF-410 FTIR Spectrometer and scanned 32 times from 400 to 4,000 cm^{-1} with the resolution of 4 cm^{-1}.

2.2. Production, purification, and characterization of the biosurfactants

The method of Zeng et al. [23] was used for the production and purification of RL. The purified biosurfactants were characterized following the method of Yuan et al. [24].

2.3. Adsorption experiments

2.3.1. Pb^{2+} adsorption onto compost HA in the presence of RL

The effects of RL at different concentrations on the isothermal adsorption of Pb^{2+} on HA were examined at 25℃. The critical micelle concentration of RL used herein was about 58 mg L^{-1}. One hundred milliliters of 0, 20, 40, 100, and 500 mg L^{-1} RL and 0, 50, 100, 250, 500, 750, 1,000, 1,500, 2,000, and 5,000 μM $Pb(NO_3)_2$ were adjusted to pH 5.0, respectively, and transferred to Erlenmeyer flasks with 40 mg HA. The resulting mixture was incubated at 25℃, shaken in a water-thermostatic reciprocal shaker at 100 rpm for 24 h until adsorption equilibrium. Each experiment was performed in duplicate and the average was calculated.

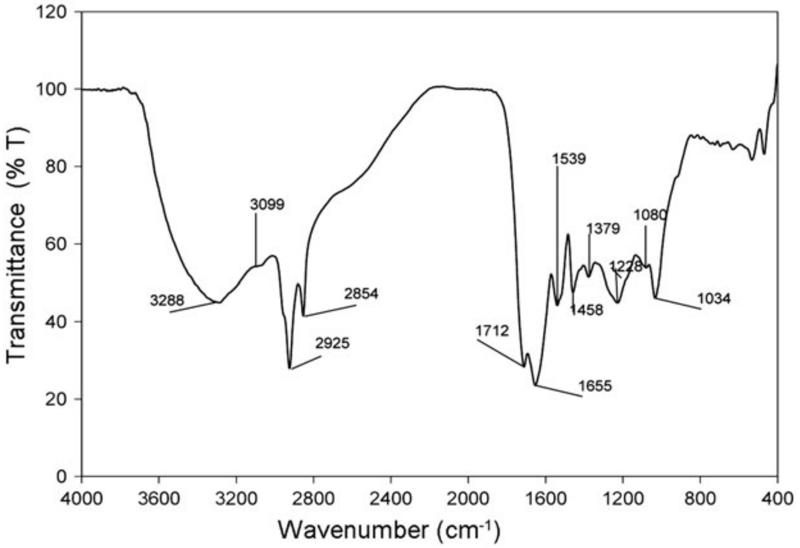

Fig. 1. FTIR spectra of compost HA.

2.3.2. Effect of pH values and temperature on the adsorption

The effect of pH on the adsorption was studied at 25℃ with 0, 40, and $100\,\mathrm{mg\,L^{-1}}$ RL and 0, 100, and 1,000 μM Pb^{2+} utilizing the optimal solid–liquid ratio. The same experiments were also performed at 45℃ to explore the effect of temperature. Similarly, each experiment was performed in duplicate and the average was reported.

3. Results and discussion

3.1. Characterization of HA

IR spectra of compost HA are shown in Fig. 1, which are similar to those obtained by Jerzykiewicz [25]. Table 1 exhibits the infrared vibrational frequencies of some organic compound functional groups, indicating that active functional groups, such as carboxyl, hydroxyl, alcoholic hydroxyl, and phenolic hydroxyl in compost HA, may participate in the complexation.

3.2. Effect of RL on the adsorption of Pb^{2+} onto compost HA

As shown in Fig. 2, the adsorption isotherms of Pb^{2+} on HA are similar to the systems of RL at different concentrations. When the initial concentration of Pb^{2+} was low, i.e. from 0 to 750 μM, the adsorption rate of Pb^{2+} by HA was high, and the adsorption amount increased rapidly with rising Pb^{2+} concentration and eventually leveled off. Meanwhile, RL at different concentrations obviously influenced the adsorption of heavy metals on HA which peaked with $40\,\mathrm{mg\,L^{-1}}$ RL. The above results suggest that RL at low concentrations enhanced the adsorption of Pb^{2+} on HA, which may be related to the surfactant form in the solution. RL at low concentrations existed as single molecules in the solution, the hydrophilic groups of which combined heavy metal ions through complexation. It could also be adsorbed onto the HA surface through hydrophobic interactions between the non-polar groups and HA. The non-polar adsorption sites were transformed to polar ones once most molecules of low-concentration RL were adsorbed onto the HA surface. The polarizing effect increased the adsorption sites of Pb^{2+} on the HA surface, which subsequently increased the adsorption of heavy metals by HA. Conversely, RL at high concentrations inhibited the adsorption of Pb^{2+} on HA. The easily saturated HA surfaces in the presence of highly concentrated RL benefited the formation of micelles that complexed with Pb^{2+} and retained Pb^{2+} in the solution. Therefore, less Pb^{2+} was adsorbed on the HA surface, which is consistent with previous findings that RL could remove heavy metals from sediments [19,20,26].

Additionally, RL at different concentrations affected the adsorption of heavy metals on HA differently using a similar pattern. Meanwhile, Pb^{2+} adsorption on compost HA did not fit the Langmuir or the Freundlich isotherm with RL, which is not in

Table 1
Assignment of absorption bands in FTIR spectra of HA

Wave number (cm^{-1})	Vibration type
3,240–3,245	Hydroxyl group of phenol
3,099	Alkenes anti-symmetric stretching
2,925	Alkane CH_2 anti-symmetric stretching
2,854	Alkane CH_2 symmetric stretching
1,712	C=O stretching vibration in COOH
1,655	Aromatic –C=C stretching
1,539	N–H variable vibration in secondary amide of acid, indicating high content of N
1,458	CH_3 anti-symmetric bending vibration
1,379	CH_3 symmetric bending vibration
1,228	Tertiary butyl alcohol C–OH stretching
1,080	Alcohol C–OH stretching
1,034	Aromatic ester C–O–C symmetric stretching

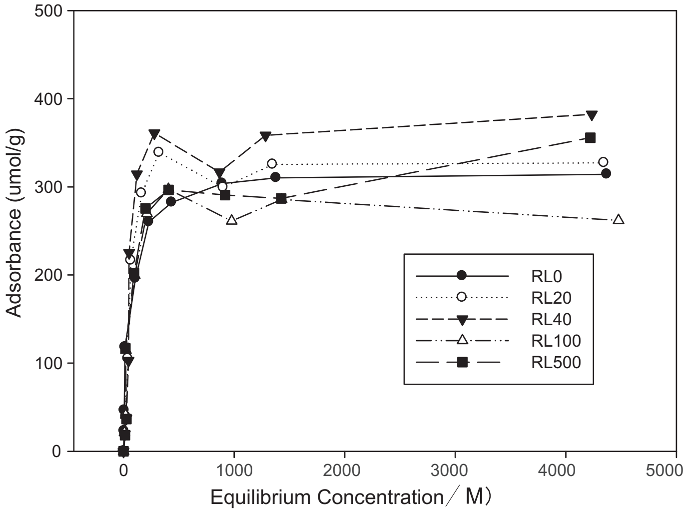

Fig. 2. Adsorption isotherm of Pb^{2+} on compost HA in the presence of RL at different concentrations.

agreement with the results of Fu et al. [27] that Pb^{2+} was adsorbed onto HA following the Langmuir isotherm. In other words, RL may change the mechanism of Pb^{2+} adsorption on compost HA.

FTIR spectra of free compost HA in the absence or presence of RL (Fig. 3) show that the structure of HA scarcely changed upon the addition of RL. The intensity of the absorption peak changed without any shifts, denoting that no new structures emerged during the adsorption of RL onto HA.

3.3. Effects of pH and temperature on adsorption

As exhibited in Fig. 4, the adsorption of Pb^{2+} (100 and 1,000 μM) on HA increases with elevating pH. However, when the Pb^{2+} concentration was lower than 100 μM, this phenomenon became negligible since all Pb^{2+} was adsorbed onto HA.

Moreover, increasing the temperature reduces the adsorption ability of compost HA for Pb^{2+} (Fig. 4). Compost HA was determined using FTIR at different temperatures to clarify the mechanisms (Fig. 5). The peak at 1,080 cm^{-1} (alcohol C–O–C stretching) shifts to 1,169 cm^{-1} (inverse C–O–C symmetry stretching of aliphatic ester and inner ester, inverse C–O–C symmetry stretching of aromatic ester), suggesting that the alcohol bonds of compost HA were destroyed at high temperatures. Therefore, Pb^{2+} was desorbed from compost HA with rising temperature due to the reduced adsorption ability of HA.

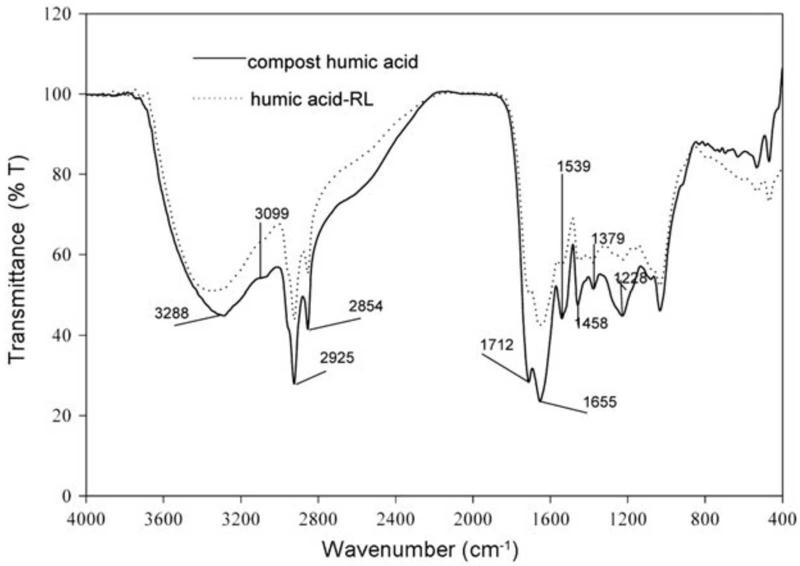

Fig. 3. FTIR spectra of HA and HA-RL.

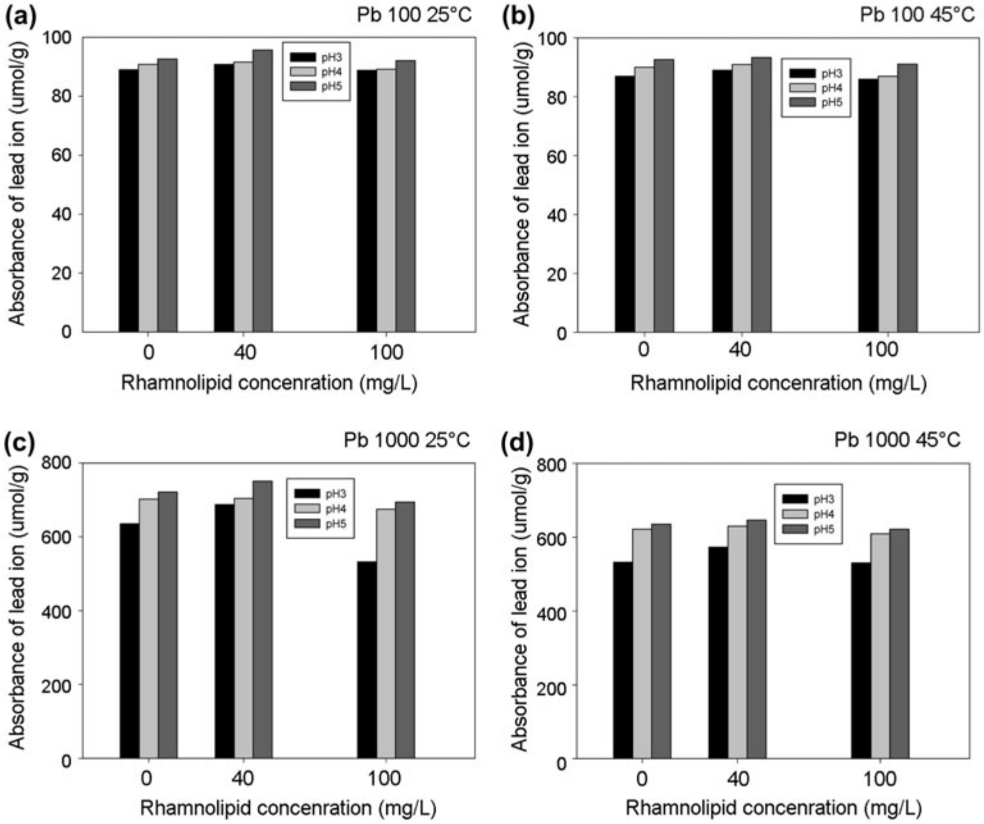

Fig. 4. Effects of pH and temperature on Pb^{2+} adsorption onto compost HA. (a) 100 μM Pb^{2+}, 25°C; (b) 100 μM Pb^{2+}, 45°C; (c) 1,000 μM Pb^{2+}, 25°C; (d) 1,000 μM Pb^{2+}, 45°C.

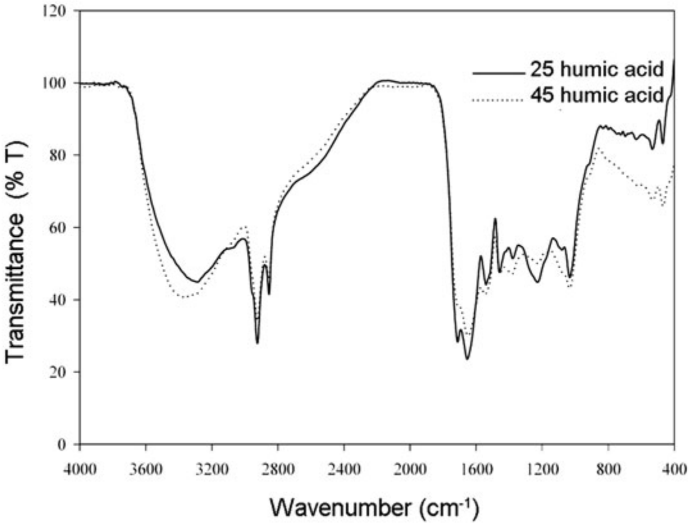

Fig. 5. Effect of temperature on FTIR spectra of compost HA.

4. Conclusions

The effects of RL, pH, and temperature on the adsorption of heavy metal Pb^{2+} onto compost HA have been thoroughly investigated in this study. The conclusions are as follows:

(1) Low-concentration RL enhanced the adsorption of Pb^{2+} onto compost HA with the maximum at 40 mg/L. However, high-concentration RL reduced the adsorption of Pb^{2+} onto HA.
(2) The adsorption of over 100 μM Pb^{2+} onto compost HA increased with elevating pH, while the adsorption ability decreased with rising temperature.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China [51109181], Foundation of Fujian Educational Committee [JA11236, JA12243].

References

[1] E. Smet, H. Van Langenhove, I. De Bo, The emission of volatile compounds during the aerobic and the combined anaerobic/aerobic composting of biowaste, Atmos. Environ. 33 (1999) 1295–1303.
[2] Y.C. Zhao (Ed.), The Mechanism and Technology of Resource of Domestic Garbage, Chemical Industry Press, Beijing, 2002.
[3] K. Elgh Dalgren, S. Waara, A. Düker, Anaerobic bioremediation of a soil with mixed contaminants: Explosives degradation and influence on heavy metal distribution, monitored as changes in concentration and toxicity, Water, Air Soil Pollut. 202 (2009) 301–313.
[4] L.Y. Ji, W.W. Zhang, D. Yu, Y.R. Cao, H. Xu, Effect of heavy metal-solubilizing microorganisms on zinc and cadmium extractions from heavy metal contaminated soil with Tricholoma lobynsis, World J. Microbiol. Biotechnol. 58 (2012) 45–53.
[5] N.N.M. Yusof, Y. Kikuchi, T. Kobayashi, Predominant hosting lead(II) in ternary mixtures of heavy metal ions by a novel of diethylaminomethyl-calix resorcinarene, Int. J. Environ. Sci. Technol. 11 (2014) 1063.
[6] D.L. Huang, G.M. Zeng, X.Y. Jiang, Bioremediation of Pb-contaminated soil by incubating with *Phanerochaete chrysosporium* and straw, J. Hazard. Mater. 134 (2006) 268–276.
[7] M.C. Ramos, Metals in vineyard soils of the Penedès area (NE Spain) after compost application, J. Environ. Manage. 78 (2006) 209–215.
[8] X. Xiong, Y.X. Li, J. Han, Formation and transformation of humus in composting and its impacts on bioavailability of toxic metals, J. Agro-Environ. Sci. 27 (2008) 2137–2142 (in Chinese).
[9] Y. Laor, C.H. Zolkov, R. Armon, Immobilizing humic acid in a sol−gel matrix: A new tool to study humic-contaminants sorption interactions, Environ. Sci. Technol. 36 (2002) 1054–1060.
[10] H.T. Lin, M.C. Wang, G.C. Li, Complexation of arsenate with humic substance in water extract of compost, Chemosphere 56 (2004) 1105–1112.
[11] Z.Y. Hseu, Evaluating heavy metal contents in nine composts using four digestion methods, Bioresour. Technol. 95 (2004) 53–59.
[12] V.P. Evangelou, M. Marsi, Composition and metal ion complexation behaviour of humic fractions derived from corn tissue, Plant Soil 229 (2001) 13–24.

[13] P. Zhou, H. Yan, B.H. Gu, Competitive complexation of metal ions with humic substances, Chemosphere 58 (2005) 1327–1337.

[14] J.H. Liu, Y.T. Chen, R.D. Xu, Y.P. Jia, Screening and evaluation of biosurfactant-producing strains isolated from oilfield wastewater, Ind. J. Microbiol. 53 (2013) 168–174.

[15] H.Y. Fu, G.M. Zeng, H. Zhong, Effects of rhamnolipid on degradation of granular organic substrate from kitchen waste by a *Pseudomonas aeruginosa* strain, Colloids Surf., B 58 (2007) 91–97.

[16] A.K. Singh, S.S. Cameotra, Efficiency of lipopeptide biosurfactants in removal of petroleum hydrocarbons and heavy metals from contaminated soil, Environ. Sci. Pollut. 20 (2013) 7367–7376.

[17] R.M. Miller, Biosurfactant-facilitated remediation of metal-contaminated soils, Environ. Health Perspect. 103 (1995) 59–62.

[18] R.A. Doong, Y.W. Wu, W.G. Lei, Surfactant enhanced remediation of cadmium contaminated soils, Water Sci. Technol. 37 (1998) 65–71.

[19] A.N. Mulligan, R.N. Yong, B.F. Gibbs, Heavy metal removal from sediments by biosurfactants, J. Hazard. Mater. 85 (2011) 11–125.

[20] C.N. Mulligan, S.L. Wang, Remediation of a heavy metal-contaminated soil by a rhamnolipid foam, Eng. Geol. 85 (2006) 75–81.

[21] K. Urum, T. Pekdemir, Evaluation of biosurfactants for crude oil contaminated soil washing, Chemosphere 57 (2004) 1139–1150.

[22] S.H. Kang, B.S. Xing, Phenanthrene sorption to sequentially extracted soil humic acids and humins, Environ. Sci. Technol. 39 (2005) 134–140.

[23] G.M. Zeng, H.Y. Fu, H. Zhong, Co-degradation with glucose of four surfactants, CTAB, Triton X-100, SDS and Rhamnolipid, in liquid culture media and compost matrix, Biodegradation 18 (2007) 303–310.

[24] X.Z. Yuan, F.Y. Ren, G.M. Zeng, Adsorption of surfactants on a *Pseudomonas aeruginosa* strain and the effect on cell surface lypohydrophilic property, Appl. Microbiol. Biotechnol. 76 (2007) 1189–1198.

[25] M. Jerzykiewicz, Formation of new radicals in humic acids upon interaction Pb(II) ions, Geoderma 122 (2004) 305–309.

[26] J.G. Shi, X.Z. Yuan, G.M. Zeng, Removal of heavy metals from sediment by rhamnolipid, Environ. Chem. 24 (2005) 55–58 (in Chinese).

[27] H.Y. Fu, T. Chai, B. Yan, The adsorption of lead ion on the compost humic acid and its mechanism, Sci. Technol. Rev. 27 (2009) 71–74.