第24回 環境化学討論会
24th Symposium on Environmental Chemistry
Program and Abstracts

環境化学の新たな展開
—— 環境毒性学の視点を加えて ——

日時：2015年6月24日水～26日木
Dates: 24th-26th June 2015

会場：札幌コンベンションセンター
Venue: Sapporo Convention Center

後援：北海道大学
Supported by Hokkaido University

協力：SETAC JAPAN
 Graduate School of Veterinary Medicine, Hokkaido University

[主催]一般社団法人日本環境化学会
Organized by Japan Society for Environmental Chemistry
Removal of heavy metals from mine tailings by rhamnolipid biosurfactant using a continuous column laboratory system

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[Introduction]
The use of biosurfactants to enhance the removal of organic and inorganic contaminants has been widely studied in recent years. In comparison to their chemically synthesized equivalents, biosurfactants have numerous advantages, such as high specificity, biodegradability, low toxicity and the ability to be produced from renewable feedstock. Consequently, technology based on these natural products can be considered as environmentally friendly and nondestructive methods for remediation of polluted water, soil or sediments.

Heavy metals pose a persistent threat to all living organisms due to their toxic nature and, unlike organic contaminants, non-biodegradability. One of the main sources of heavy metals is mining activity – besides degradation of large areas of land, the disposal of large volumes of flotation tailings can cause serious ecological problems with time, particularly if the tailing pond is not properly stabilized. Bor region in east Serbia has been characterized as an environmental hot spot due to copper industry activities. It is estimated that during more than 100 years of exploitation of copper ore, 207 Mt of flotation tailings and 450 Mt of overburden were disposed of on the territory of this region1.

The aim of this study is to evaluate the effect of rhamnolipid, a glycolipid surfactant, on removal of heavy metals from mine tailings originating from the copper mine Veliki Krivelj (the Copper Mining and Smelting Complex Bor), in a continuous column laboratory system. Two aspects are of particular importance: 1) to predict environmental behavior of metals from mine tailings due to exposure to naturally occurring biosurfactants and 2) to assess whether rhamnolipids can be used in the remediation procedure.

[Methods]
Rhamnolipid was prepared from fermentation broth of Pseudomonas aeruginosa D3 (Genbank JN995664) by acidic precipitation and chloroform–methanol (2:1, V/V) extraction.2 To evaluate the extraction efficiency of rhamnolipid, a mine tailings sample was washed with biosurfactant solution in a model system with continuous flow to simulate a potential in situ flow. The sample (20g) was packed in a column (diameter 50 mm) with glass wool and quartz sand. Five successive elution steps were performed with 200 ml 0.1 % rhamnolipid solution in NaOH (pH 11.0), where each volume circulated four times through column. NaOH solution (pH 11.0) was used as a control. Flow rate was 2.4 ml/min. Content of heavy metals in all eluates was determined by ICP-OES after digestion with HNO3.
[Results and discussion]
The total content of Fe, Cu, Mn, Zn and Cr in the mine tailings sample was 32584, 485, 270, 98 and 42 mg/kg respectively. The pH value (1:2.5 H₂O) was measured to be 9.85, weight loss at 550° C was 3.57% and S content was 3.81%.
The effect of rhamnolipids from *Pseudomonas sp.* D3 on removal of heavy metals from the mine tailings sample is shown in Figure 1. Rhamnolipids form complexes and/or micelles with metals, and due to the reducing interfacial tension, these complexes are desorbed from the solid matrix to the solution. The main functional groups of rhamnolipids that interact with metals are probably the carboxylic groups.

![Figure 1. Sequential removal of metals from Veliki Krivelj mine tailings by rhamnolipids during elution](image)

In control series, the cumulative removal for Fe, Cu, Zn, Mn and Cr was 9559 (0.03), 1135 (0.23), 3444 (3.52), 232 (0.09) and 163 (0.39) µg/kg (%) respectively. For rhamnolipid biosurfactant, the cumulative removal for Fe, Cu, Zn, Mn and Cr was 30838 (0.09), 33458 (6.9), 8257 (8.44), 645 (0.24) and 197 (0.47) µg/kg (%) respectively. The highest percentages of removal achieved for Cu and Zn are in accordance with the results reported by other authors. Also, in elution series with rhamnolipids, high positive correlations between mobilization of Fe and Cr and Fe and Mn was found.

[Conclusion]
The results of this research have shown that the presence of rhamnolipid biosurfactant could increase mobilization of heavy metals, especially Cu and Zn, from mine tailings. At the same time and based on the percentage of metal removed, the treatment with rhamnolipids could be used as an initial procedure for continuous treatment methods such as solidification or bioremediation.

[References]
2. Rikalovic M. *et al.*, J. Surfactants Deterg. 16 (2013) 673–682