AN INVESTIGATION ON THE REMOVAL EFFICIENCY FOR METAL IONS FROM POROUS SAND-PACKED COLUMNS BY A BIOSURFACTANT WITH THE FOAM-ENHANCED FLUSHING TECHNIQUE

Bode Haryanto\(^1\), Jo-Shu Chang \(^1\), and Chien-Hsiang Chang \(^1\)

\(^1\)Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan
\(^2\)Department of Chemical Engineering, University of Sumatera Utara, Medan 20135, Indonesia
email: chanchg@mail.ncku.edu.tw

ABSTRACT
This study investigated the potential application of a biosurfactant, surfactin, for metal ion removal in the contaminated soil remediation. Sand was contaminated with copper and cadmium ions with concentrations of 13.45 and 5.84 mg/kg, respectively, with the model of inner sphere adsorption. Dynamic foam capacity of surfactin was evaluated at a concentration of 5 times critical micelle concentration. The zeta potential of surfactin micelles was evaluated by a zeta sizer. An experimental column containing metal ion-contaminated sand was then used to evaluate the removal efficiency for the metal ions by using the biosurfactant solution and foam-enhanced flushing approaches. When the sand-packed columns containing metal ions were flushed by surfactin solutions, the removal efficiency was not over than 4% for copper ion and 14% for cadmium ion, respectively. When the sand-packed columns were flushed by surfactin solutions with foams, the removal efficiency was increased to 15% and 24% for copper and cadmium ions, respectively. The foam-enhanced flushing approach could apparently improve the removal efficiency for the metal ions. The less removal efficiency for the metal ions by surfactin might be related to the porous structures of the sand and the metal ion-sand interaction with the inner sphere sorption model. The copper ion is more water soluble and it is found that pure water has higher removal efficiency for the copper ions than the surfactin solution. However, the foam-enhanced approach could be applied to decrease the channeling effect in the sand-packed column and thus to improve the removal efficiency for the metal ions.

Keywords: biosurfactant, foam-enhanced solution flushing, soil remediation, solution flushing, surfactin

1. INTRODUCTION

Heavy metal ions are the most toxic inorganic pollutants which occur in soils and can be of natural or of anthropogenic origin [1]. A number of remediation technologies have been developed for removing heavy metal ions from contaminated soils. Surfactant solution flushing with foam-enhanced technique has been developed to increase the efficiency in soil remediation because the ability to control the migration of surfactant solutions can be improved by foam. This technique is attractive due to the low usage of surfactants [1-5]. Applications of biosurfactant in the environmental protection have received more attention due to their biodegradability, low toxicity, and effectiveness in enhancing biodegradation and solubility of hydrophobic compounds [6-8]. Surfactin is a biosurfactant, produced by various strains of Bacillus subtilis. It has been reported that surfactin molecules can form rod micelle structures with a critical micelle concentration (cmc) of about 10 ppm in 0.1 M NaClO\(_4\) (pH 8.7) [9-11].

The purpose of this study to evaluate the potential of surfactin to remove metal ion contaminated sands. Applying the foam-enhanced surfactant solution flushing technique to remove the metal ions from contaminated sand packed column was performed. The metal ion contaminated sand was prepared with copper and cadmium ions.

2. EXPERIMENTAL

The biosurfactant surfactin was produced from Bacillus subtilis ATCC 21332 and was kept in a refrigerator with a temperature of -80°C [11]. The surfactin purity was analyzed by HPCL and was found to be 90%. Research-grade Cu\(_2\)SO\(_4\)·5H\(_2\)O and CdCl\(_2\) purchased from Showa Chemical Co. Ltd.
Japan was chosen as the model contaminants. Sand was contaminated by copper (Cu) and cadmium (Cd) by mixed cleanse sand with metal ion solutions.

Cleanse sand surface was analyzed by SEM. Zeta potential of surfactant molecules or micelles was measured by a Zetasizer (model 300 HS, Malvern U.K.). Purified water with a resistivity of 18.2 MΩ·cm used for experiments was obtained from a Milli-Q plus purification system (Millipore, USA) and was used in all experiments.

A typical setup of a foam-enhanced surfactant solution flushing approach was following Huang and Chang [3]. A glass column of foam-generator with a length of 5 cm and an outside diameter of 3.5 cm was used to control the foam generation in the presence of surfactin solution and nitrogen gas. The dynamic foam capacity of surfactin was considered when the volume of foams in the column foam generator was constant. A glass column with a length of 7.5 cm and an outside diameter of 1.5 cm was used in the column experiments to simulate the soil remediation situation. Sand with an average diameter of 320 μm was used as the porous medium.

All experiments were performed at room temperature. Surfactin solutions were prepared in 10⁻³ M phosphate buffer with a pH value of 8.0. Surfactin solution flow rate was fixed at 2 ml/min and 1.5 cm/min N₂ flow rate was used. The surfactin solution with a concentration of 5x cmc was used to flush the contaminated sand-packed column. The flushing solution was collected every 4 pore volumes for analysis by AA.

3. RESULTS AND DISCUSSION

Negative charge characteristic of surfactin was indicated by a zeta potential of ~55 mV for a surfactin solution at a concentration of 5x cmc. Decreasing the surfactin concentration reduced the charges as demonstrated in Fig. 1. Because of the negative charges, surfactin should have the ability of associating with metal ions in contaminated soils. The foaming properties of surfactin solutions have been investigated before [12]. The foam has reached steady state after about 30 minutes. The surfactin solution has the foam capacity about 5 cm², as shown in Fig. 2. The foam capacity of a surfactant solution will affect the pressure when flushing the column, as a surfactant with the higher foam capacity is easier to penetrate into porous space of soil. However, surfactin has the lowest foam capacity as compared to that of rhamnolipid and SDS.

<table>
<thead>
<tr>
<th>Metal ion source</th>
<th>Initial Conc. (ppm)</th>
<th>Treatment</th>
<th>Sorption density (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>20</td>
<td>Shaking</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>Shaking</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>Without shaking</td>
<td>5.5</td>
</tr>
<tr>
<td>Cd</td>
<td>50</td>
<td>Shaking</td>
<td>6</td>
</tr>
</tbody>
</table>

Metal ions-sand sorption results are shown in Table 1. The sorption density was influenced by the metal initial concentration (Co) and shaking effect. For the Cu ion with concentrations of 20 and 50
ppm, with the shaking effect, the sorption densities were about 11 and 13 mg/kg, respectively. With 50 ppm Cd ion, the sorption density was about 6 mg/kg. At Co^2+ 50 ppm without shaking, the sorption density of copper ions on sand was about 5.5 mg/kg.

From the results, one can see that the shaking operation can increase the sorption density of metal ions.

The sand surface morphology has been observed by SEM. The sand surface is somewhat craggy at outer surface and porous structure was found for the sand. By shaking, the metal ions can go further into the porous areas of sands then the sorption density becomes higher.

In this study, the ion sorption might follow the inner sphere adsorption model. The pressure of N₂ gas was used to remove all solution from the sands then let the metal ions with positive charges interact with negatively charged surface of the sands.

![Figure 3. Removal efficiency for copper ions after flushing contaminated sand-packed columns with surfactant foam-solution, surfactant solution and water at a flow rate of 2 ml/min.](image)

Metal ion removal efficiency is presented in Fig. 3. The total removal efficiency of copper ions in the sand-packed column by a surfactant solution with foams was about 15% after 20 PV. By using surfactant solution and water, 3% and 8%, respectively were found for the removal efficiency. The total removal efficiency of Cd ions after 20 PV by a surfactant solution with foams was about 24%. By using surfactant solution and water, 13 and 12%, respectively were obtained for the removal efficiency. Possible reason for water with high removal efficiency is probably that water has strong attraction for copper ions.

The removal efficiency was affected by the contaminant position on sand and the flushing technique was applied. With the model of inner sphere adsorption, most of contaminants may be located at the surface inside the sand and will be difficult to be removed. Surfactant solution flushing with foams was possible to increase the removal efficiency in compared with that of solution flushing without foam. With a solution without foam the channeling effect might occur and it would decrease the removal efficiency.

The zeta potential of surfactin molecules is very low, and it is possible for surfactin micelles to associate with the metal ions in the sand. The potential to exchange metal ions with surfactin micelles should be supported by the higher flushing contact within the sand. The possible pressure resulting from surfactin foam into the sand-packed column might be not enough to increase the contact until the surface inside the porous sand was covered.

### 4. CONCLUSION

Surfactin has the potential of removing metal ions from contaminated sands with its zeta potential characteristic and solution foaming property. One can improve the metal ion-sand sorption density by a shaking operation. The copper ion-sand sorption density was increased from 5.5 to 13 mg/kg by shaking 150 rpm for 24 hours. Cadmium ion-sand sorption was about 6 mg/kg at the same condition. For the sand with porous structure, the adsorption occurred at the surface inside the sand and the inner sphere adsorption resulted in the difficult for the removal efficiency of the ions. Removal efficiency of surfactin solution with foam-enhanced flushing technique was increased about 10% as compared to that of the flush operation by surfactin solution only. By the foam-enhanced surfactin solution flushing technique, the channeling effect inside the sand-packed column became insignificant.

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