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Removing Adsorbed Heavy Metal Ions from Sand Surfaces *via* Applying Interfacial Properties of Rhamnolipid

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Abstract: In this study, the interfacial properties of biosurfactant rhamnolipid were investigated and were applied to remove adsorbed heavy metal ions from sand surfaces with flushing operations. The surface tension-lowering activity, micelle charge characteristic, and foaming ability of rhamnolipid were identified first. For rhamnolipid in water, the negatively charged characteristic of micelles or aggregates was confirmed and the foaming ability at concentrations higher than 40 mg/L was evaluated. By using the rhamnolipid solutions in a batch washing approach, the potential of applying the interfacial properties of rhamnolipid to remove adsorbed copper ions from sand surfaces was then demonstrated. In rhamnolipid solution flushing operations for sand-packed medium, higher efficiency was found for the removal of adsorbed copper ions with residual type than with inner-sphere interaction type, implying the important role of interaction type between the copper ion and the sand surface in the removal efficiency. In addition, the channeling effect of rhamnolipid solution flow in the sand-packed medium was clearly observed in the solution flushing operations and was responsible for the low removal efficiency with low contact areas between solution and sand. By using rhamnolipid solution with foam to flush the sand-packed medium, one could find that the channeling effect of the solution flow was reduced and became less pronounced with the increase in the rhamnolipid concentration, or with the enhanced foaming ability. With the reduced channeling effect in the flushing operations, the removal efficiency for adsorbed copper ions was significantly improved. The results suggested that the foam-enhanced rhamnolipid solution flushing operation was efficient in terms of surfactant usage and operation time.

Key words: biosurfactant, foam-enhanced solution flushing, rhamnolipid, solution flushing

1 INTRODUCTION

Heavy metal ions are toxic pollutants which are usually adsorbed onto soil[1]. The interactions between metal ion and soil can be classified as outer-sphere interaction and inner-sphere interaction. The outer-sphere interaction indicates the interaction between metal ions and the sand surfaces, involving the liquid phase or water molecules. The inner-sphere interaction describes the interaction between metal ions and functional groups at the sand surfaces, not involving a liquid phase between the adsorbed ions and the functional groups of the surfaces[1–5]. For sands, the tetrahedral silica with hydroxyl functional groups on the surfaces can be represented as $=Si–OH$[6]. The primary bonding in the complexes with the inner-sphere interaction is a coordinate-covalent bonding in contrast to the electrostatic bonding in the complexes with the

outer-sphere interaction. The complexes with the inner-sphere interaction are, in general, more stable than those with the outer-sphere interaction[1, 3, 4].

Sand possesses natural macro-pore and meso-pore structures[7]. The porosity of soil is mostly influenced by particle size, uniformity, and rock type[8]. Pores not only create large surface area, but also provide high selectivity in reaction and adsorption[9]. The interactions between metal ions and sand surfaces affect the desorption behavior of the metal ions from sands in a remediation process. Adsorbents with porous characteristics exhibit kinetic limitations which prevent ion desorption from porous sites[10].

A number of remediation processes have been developed for removing heavy metal ions from contaminated soils[11, 12], for example, the surfactant solution flushing process. In the surfactant solution flushing process, sand contaminated

by metal ions is washed by surfactant or biosurfactant solution. Flushing sand with foam (foam-enhanced approach) tends to improve the migration of surfactants[11−13] by increasing the ability of surfactants to spread and penetrate into the pore regions of sand even in a heterogeneous porous medium[11, 14], thus enhancing the removal efficiency for adsorbed metal ions. It also improves wettability and contaminant desorption[15]. This technique is very efficient due to the low usage of surfactants[11, 12].

Biosurfactants have received a lot of attention with the consideration of the environmental protection issue. Biosurfactants are biodegradable and are effective in enhancing the biodegradation of hydrophobic compounds[16−19]. Biosurfactants also have low critical micelle concentration (cmc) values[20, 21]. Rhamnolipid is one kind of biosurfactants and is produced by various strains of *Pseudomonas aeruginosa*[20, 22]. It have been reported that rhamnolipid has excellent stability and can produce high quality foams with high dynamic capacity[23]. In addition, rhamnolipid possesses a negatively charged characteristic and may be particularly effective in remediating soils contaminated with metal ions that are less sensitive to ion exchange processes[22]. The reported cmc value of a pure rhamnolipid is about 10-30 mg/L, depending on the pH value and characteristics of the salt[24−26].

The objective of this study is to take the advantages of interfacial properties of biosurfactant rhamnolipid to remove heavy metal ions with a low adsorption density from sand surfaces by a flushing approach.

2 EXPERIMENTAL

Rhamnolipids are a class of glycolipids produced from *P. aeruginosa J4*. The rhamnolipids have been purified to a confirmed 62.75% using the purification method reported by Wei *et al.*[20]. Research-grade copper (II) sulfate pentahydrate ($Cu_2SO_4 \cdot 5H_2O$) was purchased from Showa Chemical Co., Ltd., Japan and was used as the model metal ion contaminant. Purified water with a resistivity of 18.2 MΩ-cm (Milli-Q plus purification system, Millipore, USA) was used in all experiments.

The information on the morphology and composition of the sand surface was obtained with scanning electron microscope (SEM) (JSM-6700F, JOEL, Japan) and energy dispersive spectrometer (EDS) (INCA 400, Oxford Instruments, UK). The surface tension of the rhamnolipid solution was measured using the Wilhelmy plate method with a surface tensiometer (CBVP-A3, FACE, Kyowa Interface Co., Ltd., Japan). The zeta potential of rhamnolipid micelles or aggregates was measured with a commercial zeta potential analyzer (Zetasizer Nano, Malvern, UK).

Cleansed sands were adsorbed with copper ions by mixing 100 g of sands with 100 ml 0.05 M Tris HCl solution containing 50-ppm copper ion. An orbital shaker was used to mix the sands and the copper ion-containing solution for 24 hours at a rate of 150 rotations per minute. After the shaking procedure, a waiting period of 24 hours was allowed for the system to reach adsorption equilibrium[27]. Then the sands were collected and dried using nitrogen gas. The metal ion concentration in the solution was analyzed using an atomic absorption spectrometer (Sens AA Dual, GBC, Australia), and the adsorption density of copper ions with the inner-sphere interaction was evaluated. For adsorbed copper ions with the residual type, the sands were collected from the solution and dried in an oven. The adsorption density of metal ions on sands with the inner-sphere interaction and precipitation as the residual type was then evaluated.

Batch washing experiments were performed using pure water and rhamnolipid solutions with concentrations of 40, 100, and 200 mg/L. One gram of metal ion-adsorbed sand (inner-sphere interaction type or residual type) was mixed with 10 ml of rhamnolipid solution, and the sand/solution mixture was shaken for 24 hours at 150 rotations per minute with an orbital shaker, after which the metal ion concentration in the solution was determined using an atomic absorption spectrometer and the removal efficiency was evaluated.

The apparatus used for the foam-enhanced surfactant solution flushing operation is similar to that used by Huang and Chang[13]. The foam was generated in a glass column (h = 5 cm, ø = 3.5 cm) with two inlets for rhamnolipid solution and N_2 gas, respectively. The foaming abilities of rhamnolipid solutions with concentrations of 40, 100, and 200 mg/L were evaluated[27, 28] prior to the flushing operation. In the flushing operation, the foam was introduced into a second glass column (h = 7.5 cm, ø = 1.5 cm) containing the packed sands. A peristaltic pump (Masterflex, Model 7518-10, Cole-Parmer Instrument Company, Barrington, USA) was used to create continuous flow of rhamnolipid solution into the foam generator. Sand with an average grain diameter of 320 μm was used as the porous medium.

All experiments were performed at room temperature. The rhamnolipid solutions were prepared with pure water[29] at a pH of 5.6. The flow rates of the rhamnolipid solution and N_2 gas were fixed to be 2 ml/min and 20 ml/min, respectively. Rhamnolipid solutions with concentrations of 40, 100, and 200 mg/L were used to flush the copper ion-adsorbed sands in packed columns. The flushing effluent was collected every 4 pore volumes (PVs, one PV is 2.2 ml) and was analyzed using an atomic absorption spectrometer to evaluate the removal efficiency for the copper ions.

3 RESULTS AND DISCUSSION

3.1 Metal ion adsorption

With the adsorption process described in the previous section, the sands were collected and dried with N_2 gas and an oven, respectively. It is known that adsorption equilibrium could be reached more rapidly when a shaking approach was adopted[30]. With a shaking approach, copper ions could penetrate into the intra-particle pore regions of the sands and adsorb on the surfaces.

For the sands dried with N_2 gas, the adsorption density of copper ions was found to be 13.45 mg/kg. Drying with N_2 gas could remove most of the aqueous phase in pore regions. One would expect that the N_2 stream would remove the copper ions not bound to the sand surfaces via the inner sphere interaction[3, 4]. When an oven was applied to dry the sands, the copper ions in the solution phase of the pore regions and adsorbing with the outer-sphere interaction would not be removed, and an adsorption density of copper ions with the residual type was found to be 26.78 mg/kg. With an oven-drying approach, the copper ion adsorption with the outer-sphere interaction might be converted to that with the inner-sphere interaction when the water was evaporated.

The surface morphology of the sands was analyzed with SEM, and the rough characteristic of the sand surfaces was identified. The sands with porous characteristics possessed the intra-particle pore regions[8]. The sand particles were crushed and the surfaces were analyzed with EDS to identify the composition of the surfaces. It was found that the sand surfaces were mainly composed of Si and O. The adsorbed copper ions were also detected in the EDS analysis.

3.2 Interfacial properties of rhamnolipid

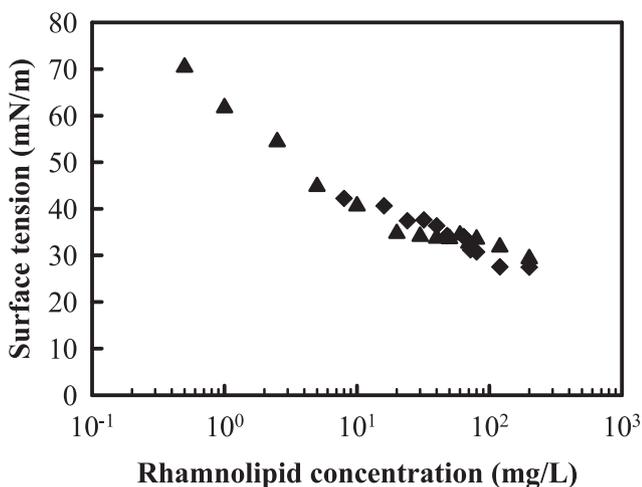The surface tension-lowering ability of rhamnolipid is

demonstrated in Fig. 1. When the rhamnolipid concentration was increased from zero to 40 mg/L, the surface tension of water was decreased from 72 to 35 mN/m. With a further increase in the rhamnolipid concentration to 200 mg/L, the surface tension was reduced to 28 mN/m.

Rhamnolipid is an anionic glycolipid surfactant, and negative zeta potentials were found for rhamnolipid micelles or aggregates in aqueous phase (Fig. 2). With a concentration of 200 mg/L, the average zeta potential of rhamnolipid micelles or aggregates was −37mV. The zeta potential of rhamnolipid aggregates would affect the interaction between the rhamnolipid aggregates and adsorbed metal ions on sand surfaces and thus the removal efficiency for the adsorbed metal ions. The micelle or aggregate proper-
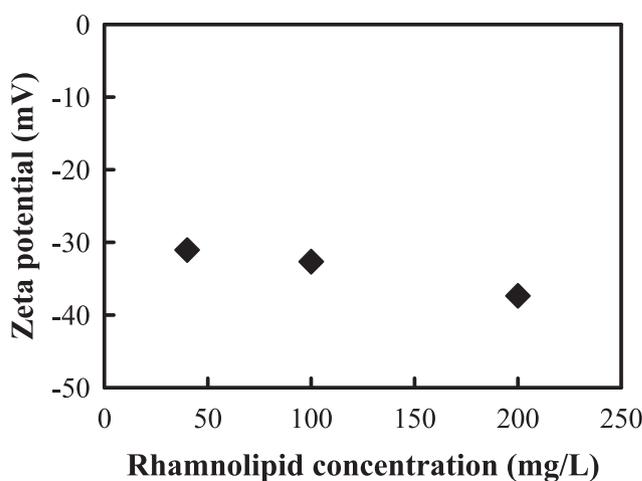

Fig. 2 Zeta potentials of rhamnolipid micelles or aggregates in aqueous solutions with different rhamnolipid concentrations.
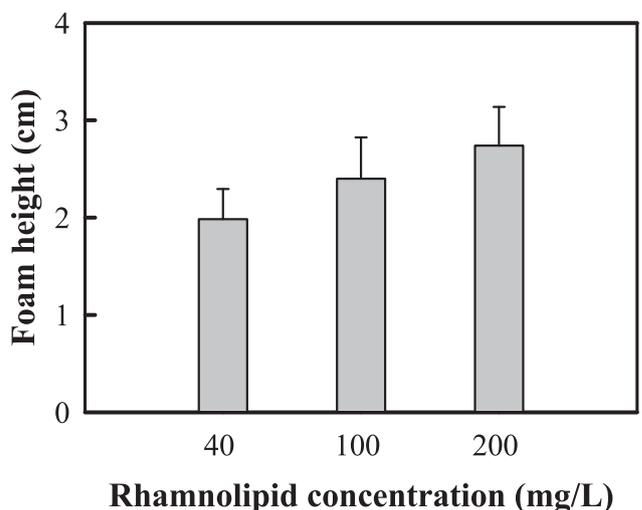

Fig. 3 Foam heights of rhamnolipid solutions with different concentrations. The flow rates of rhamnolipid solution and N_2 gas were kept at 2 ml/min and 20 ml/min, respectively.

Fig. 1 Surface tensions of rhamnolipid aqueous solutions. Two kinds of symbols are indicative of two individual data sets.

ties are also related to the ability of providing monomers when the micelles or aggregates are applied to remove adsorbed metal ions from sand surfaces[31].

The foaming ability is determined by the foam height. Figure 3 shows the foam height as a function of rhamnolipid concentration. The mean foam height was slightly increased with the increase in the rhamnolipid concentration. During foam generation, surfactant monomers were supplied from surfactant micelles and adsorbed onto the newly created air/water interfaces[32]. Increasing the rhamnolipid concentration, or the number of rhamnolipid micelles or aggregates, would enhance the foam production[33, 34].

3.3 Batch washing

The removal efficiencies of rhamnolipid solutions with various concentrations for adsorbed copper ions from the sand surfaces by a batch washing approach are shown in Fig. 4. It was noted that some adsorbed copper ions might be removed by water alone but only with limited removal efficiency. With the presence of rhamnolipid micelles or aggregates in the solutions, the removal efficiency for the adsorbed copper ions was generally improved. In addition, the removal efficiency was increased with the increase in the rhamnolipid concentration. For the adsorbed copper ions of the inner-sphere interaction type, the average cumulative removal efficiencies were 15%, 24%, and 32% for rhamnolipid solutions with concentrations of 40, 100, and 200 mg/L, correspondingly（Fig. 4a）. For the adsorbed copper ions of the residual type, the removal efficiencies were 26%, 36%, and 45% for rhamnolipid solutions with concentrations of 40, 100, and 200 mg/L, correspondingly （Fig. 4b）. The results reflected that the concentration of rhamnolipid is a key parameter in the removal efficiency for adsorbed copper ions from sand surfaces. Increasing the concentration of rhamnolipid would increase the number of negatively charged micelles or aggregates, which could interact with adsorbed metal ions.

3.4 Rhamnolipid solution flushing

Flushing with rhamnolipid solutions in order to remove adsorbed copper ions from packed sand surfaces was then investigated. The efficiencies of rhamnolipid aqueous solutions with various concentrations for removing adsorbed copper ions of the inner-sphere interaction type are shown in Fig. 5a. The average cumulative removal efficiencies were gradually increased up to 5%, 6%, and 12% with 24-PV effluent for rhamnolipid solutions with concentrations of 40, 100, and 200 mg/L, correspondingly. For the adsorbed copper ions of the residual type, higher removal efficiencies were found with 19%, 21%, and 23 %, correspondingly（Fig. 5b）. However, the pronounced fluctuation of the removal efficiency, which was apparently associated with the significant channeling effect in the solution flushing operations, suggested that the rhamnolipid concentra-
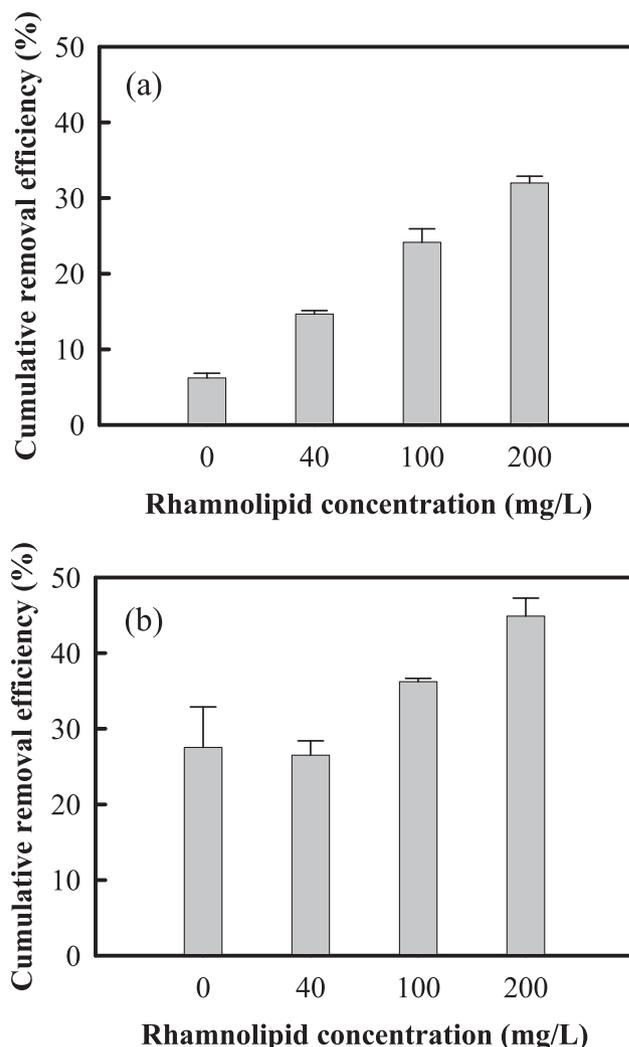

Fig. 4 Removal efficiencies of rhamnolipid solutions with different concentrations for adsorbed copper ions of (a) the inner-sphere interaction type and (b) the residual type by a batch washing approach.

tion effect on the removal efficiency seemed indeterminate in the concentration range, except for the case of 200 mg/L solution in Fig. 5a.

In the presence of rhamnolipid micelles or aggregates, with the surface tension lowering ability and negatively charged characteristic, rhamnolipid would interact and then remove the adsorbed copper ions from the sand surfaces[21]. For the adsorbed copper ions of the residual type, the ions located in the inter-particle pore regions could be removed more efficiently by interacting with rhamnolipid micelles or monomers, and the continuous solution flushing would increase the removal efficiency for the adsorbed copper ions. The apparently lower removal efficiency obtained for the adsorbed copper ions with the inner-sphere interaction type in comparison with the residual type was
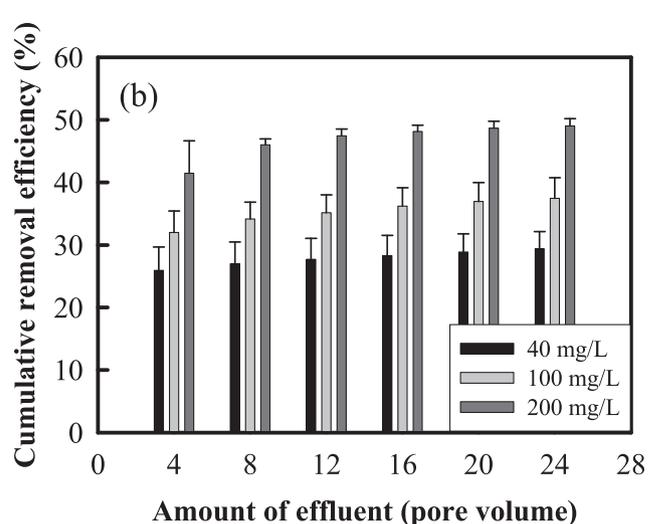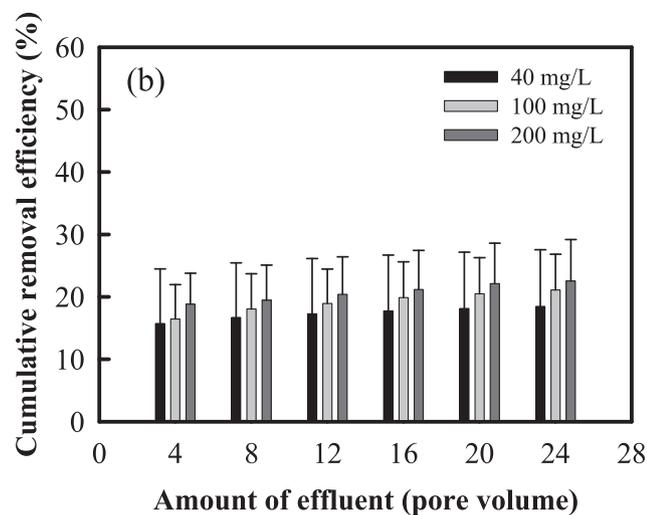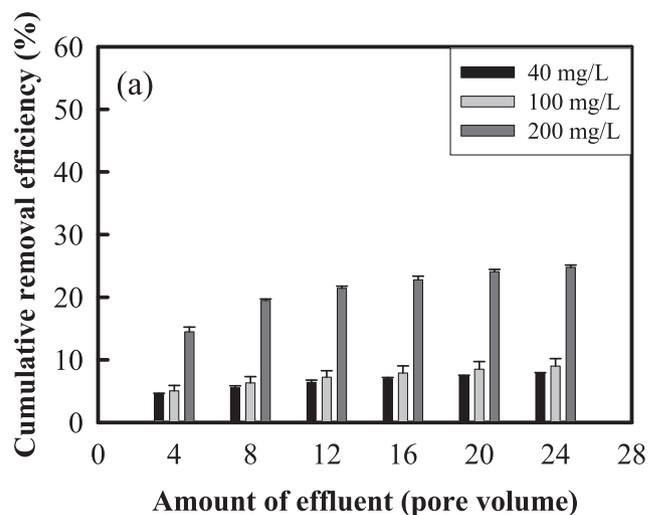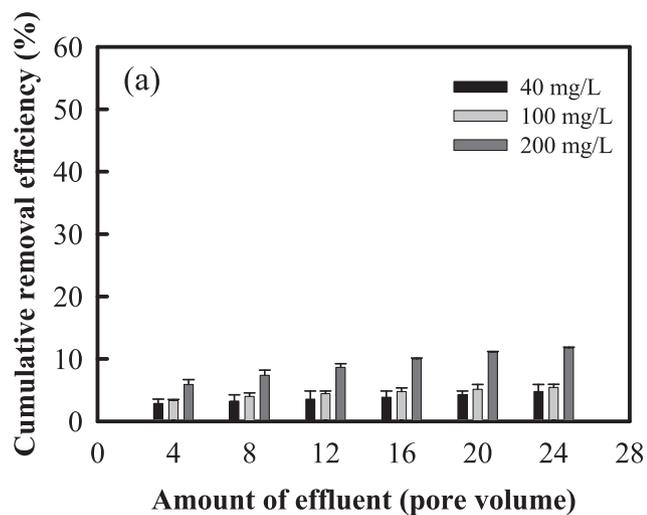
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Fig. 5 Cumulative removal efficiencies of the rhamno-lipid solution flushing operations with various concentrations for adsorbed copper ions of (a) the inner-sphere interaction type and (b) the residual type.

Fig. 6 Cumulative removal efficiencies of the foam-enhanced rhamnolipid solution flushing operations with various concentrations for adsorbed copper ions of (a) the inner-sphere interaction type and (b) the residual type.

due to the strong interaction between the adsorbed ions and the sand surfaces.

The channeling effect is a key limitation for the removal efficiency of the solution flushing approach. The channeling effect of solution flow in a packed medium would result in a low contact area between the solution and the sand surface. As a result, the rhamnolipid micelles or aggregates could only interact with few adsorbed copper ions, resulting in the low removal efficiency.

3.5 Solution Flushing with Foam

The packed sands with adsorbed copper ions were flushed by using rhamnolipid solution with foam in order to overcome the channeling effect and to improve the removal efficiency for the adsorbed ions[11, 13, 15, 33]. The efficiencies of

the foam-enhanced rhamnolipid solution flushing operations for removing adsorbed copper ions from the packed sand surfaces are shown in Fig. 6. For the foam-enhanced solution flushing operation with a rhamnolipid solution at a concentration of 200 mg/L, the average cumulative removal efficiencies obtained with 24-PV effluent for the adsorbed copper ions of the inner-sphere interaction type and residual type were 25% and 49%, respectively. The removal efficiency of a rhamnolipid solution at a concentration of 200 mg/L was significantly higher than that obtained at a concentration of 40 or 100 mg/L.

It is reasonable to expect that the foam quality of the rhamnolipid solution will affect the removal efficiency in the foam-enhanced solution flushing approach. With a high concentration of rhamnolipid, the increased number of mi-

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celles or aggregates in the solution could enhance the foam production. When injecting the foam with the rhamnolipid solution into the sand-packed column, the mobility of the solution flowing in the packed medium would be significantly affected[33]. For a rhamnolipid solution with a high foam height, the foam lamella could interact with copper ions not only in the inter-particle pore regions but also in the intra-particle pore regions. Thus more copper ions adsorbing in the intra-particle pore regions could be desorbed from the surfaces through the electrostatic interaction between the negatively charged rhamnolipid aggregates and the positively charged copper ions[23].

It was found that the efficiency of removing adsorbed copper ions from packed sand surfaces was improved by the presence of foam in the rhamnolipid solution flushing approach. The foam would increase the resistance of the flowing liquid in the sand-packed medium, helping the solution to flow evenly through the medium and reducing the channeling effect[11, 35]. When flushing the packed sands with a rhamnolipid solution in the presence of foam, the rhamnolipid molecules could penetrate into the inter-particle and intra-particle pore regions to interact with more adsorbed copper ions. The copper ions were then desorbed and transported away from the surfaces into the solution[36]. The complexes of the copper ions and the rhamnolipid micelles or aggregates in the solution could then be flushed from the packed medium, resulting in an increase in the removal efficiency.

With the solution flushing approach without foam, it would be difficult for the solution to spread evenly in the packed column, resulting in the formation of channels with low contact areas between the solution and the sands. That is the solution tended to flow through certain channels[15, 35]. When flushing with a rhamnolipid solution at a concentration of 100 mg/L, one could see that the sand-packed column was mostly composed of dry sands, demonstrating the pronounced channeling effect（Fig. 7, left）. In comparison with the solution flushing without foam, the solution flushing with foam could improve the solution mobility, allowing the solution to flow more evenly through the packed medium. With regard to the effect of rhamnolipid concentration, a portion of the sand was found to remain dry, when the foam-enhanced solution flushing was performed only with a rhamnolipid concentration of 40 mg/L（Fig. 7, center）. Increasing the rhamnolipid concentration to 100 mg/L, all of the visible sands were wetted, suggesting that the channeling effect was significantly inhibited（Fig. 7, right）. The removal efficiency for adsorbed copper ions was apparently increased with the inhibition of the channeling effect.

In order to confirm the association between the negatively charged rhamnolipid aggregates and positively charged copper ions, zeta potential measurements were performed for the effluent collected from the flushing op-
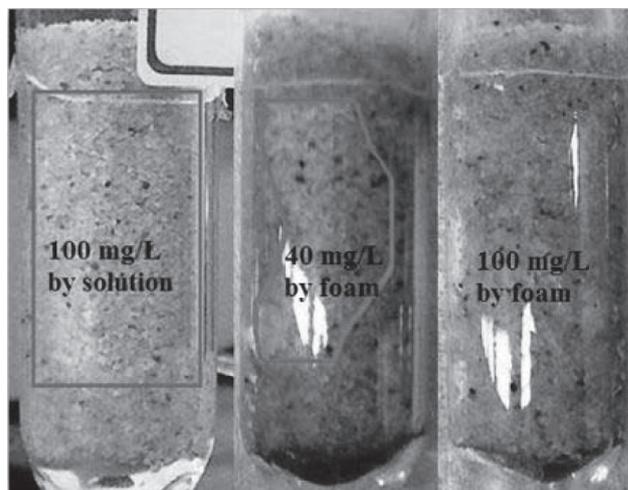

Fig. 7 The inhibited channeling effect of the rhamnolipid solution flow with the presence of foam in the sand-packed medium. From left to right: the sand-packed medium was flushed by a rhamnolipid solution of 100 mg/L without foam, 40 mg/L with foam, and 100 mg/L with foam, correspondingly.

eration. The mean zeta potential obtained for a rhamnolipid solution with a concentration of 100 mg/L was -33 mV. It was noted that mean zeta potentials for the effluent collected after 4-PV flushing by solution only and by solution with foam were -8 and -7 mV, respectively. The results demonstrated the less negatively charged characteristic of the rhamnolipid aggregates in the effluent, which was apparently attributed to the electrostatic interaction of copper ions with rhamnolipid aggregates.

These experiments showed that the removal of the adsorbed copper ions mainly occurred during the first 4-PV flushing. This is probably because when the rhamnolipid solution flowed through the sand-packed medium, the copper ions in the inter-particle pore regions could be removed in the early stage of the flushing operation, resulting in the significant removal efficiency observed with the first 4-PV flushing. Solution flushing with foams was more effective for removing the adsorbed copper ions. The foam-enhanced solution flushing approach is thus attractive with low surfactant usage and short treatment time[11].

Furthermore, using foam-enhanced solution flushing approach with a rhamnolipid concentration of 200 mg/L, the average cumulative removal efficiency was only about 49% with 24-PV flushing. It is evident that during the drying process for adsorbed copper ions of the residue type, the outer-sphere interaction of some ions on the sand surfaces was converted to the inner-sphere interaction, which certainly increased the difficulty of removing the ions from the sand surfaces.

For a popular anionic surfactant, sodium dodecylsulfate

（SDS）, the critical micelle concentration（cmc）at 22℃ is about 8.0 mM. The surface tensions of SDS aqueous solutions are 38 and 32 mN/m at cmc and 5x cmc[37, 38], respectively. The negatively charged characteristic of SDS micelles has been generally accepted[39], and the zeta potential of SDS micelles was about − 18 mV[40]. Apparently, rhamnolipid possessed better tension-lowering activity and more pronounced charge characteristic than SDS. However, SDS solution at 2.5x cmc possessed a better foaming ability than rhamnolipid solution at 5x cmc（200 mg/L）. With the solution flushing operation without foam, the removal efficiencies of SDS solution at 2.5x cmc and rhamnolipid solution at 200 mg/L for adsorbed copper ions of the inner-sphere interaction type were similar. It is interesting to note that with the foam-enhanced solution flushing operation, higher removal efficiency for the adsorbed copper ions was detected for the SDS solution（～30％）than the rhamnolipid solution（～23％）[38]. This could be attributed to the different foaming abilities of the surfactant solutions. Although SDS has the advantage over rhamnolipid of possessing better removal efficiency in the foam-enhanced solution flushing operations, the application of rhamnolipid in the operations would be attractive by taking the biodegradable characteristic and extremely low usage into consideration.

4 CONCLUSIONS

In this study, the interfacial properties of rhamnolipid were investigated and then were applied in flushing operations to remove adsorbed copper ions from sand surfaces. The potential of using rhamnolipid in removing adsorbed copper ions from sand surfaces was demonstrated in a batch washing operation. By using rhamnolipid in solution flushing operation to remove adsorbed copper ions from sand surfaces, low removal efficiency was detected due to the strong inner-sphere interaction of the ions with the sand surfaces and to the pronounced channeling effect of solution flow in the sand-packed medium. By using rhamnolipid solution with foam in the flushing operations, the channeling effect was inhibited with the extent becoming significant with increased rhamnolipid concentration, or with enhanced foaming ability, resulting in improved removal efficiency for the adsorbed copper ions. It appears that the foam-enhanced rhamnolipid solution flushing operation is efficient in terms of surfactant usage and operation time.

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