

Loading time and channeling effect in removing copper ions from sand surface by surfactin solution in flushing column

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Abstract. The variations of loading time (t) were used to indicate the channeling effect of in removing copper ions from sand surface by surfactin solution in continuous flushing column technique. Results trend shows that by increasing loading time will increase the interaction with the contaminant on sand surface. In shorter time showed that the removal efficiency of water was higher than surfactin if flushing without foam. The micelle structure within the surfactin solution has ability to move into intra particle and tend to flow down which decrease the loading time in comparing with water molecule. Flushing with foam, the bubbles gas penetrates and spreads the surfactin micelles to the whole sand surface and spend shorter time in loading the sand column. Types of flushing with and without foam with the removal efficiency result are possible to predict the channeling affect.

1. Introduction

Flushing technique was used to remove metal ion from contaminated sand in column remediation. Flushing approaches with surfactant solution with and without foam were applied. Flushing without foam made the solution difficult to search the surface area uniformly in the packed column. The formations of channels provide low contact areas between the solution and the contaminated material. The solution has tendency to flow through certain channels [1,2].

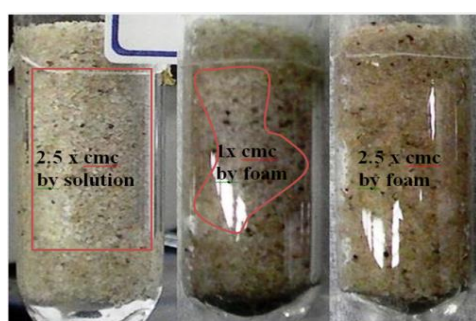


Figure 1. The foam inhibits the channeling effect [3].

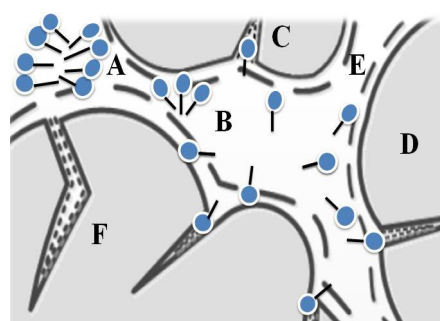


Figure 2. Illustration of the sand particles with inter and intra particle area [4].

Figure 1 shows flushing the solution without foam and with foam. The sand-packed column was mostly composed of dry sands. Flushing without foam, demonstrating the pronounced channeling effect (Fig.1, left). Flushing with foam could improve the solution movement in the sand column and then flow more evenly through the column medium (Fig. 1, center). Increasing the surfactant concentration is possible to wet all sand surfaces and this significantly reduced channeling effect (Fig. 1, right). With the inhibition of the channeling effect, it has been reported that the removal efficiency was apparently increased.

As shown in the illustration, flushing with foam is possible to spread the surfactant molecules to intra particle areas. Without foam within the micelle structure, it is difficult to reach the intra particle area that impacts metal ions removal from the contaminated sand medium. In Figure 2 is shown that flushing with foam enhanced solution technique in the inside of the sand-packed column. A is the foam lamella; B is monomers spread onto inter-particle sand pores; C is penetration into the intra-particle sands pores. D is sand particle, E is inter-particle pores and F is intra particle pores [4].

The objective of this study is to observe the time needed between the first drops of solution into the column, until the first drop left the column (t). The loading time of water and surfactin solution was investigated and then compared with surfactin solution with foam flushing the column. Adsorbed metal ions in sands were prepared by an adsorption process and by putting them in oven to get the residual type. The loading time with the removal efficiency was used to indicate the channeling effect.

2. Experimental Method

Surfactant was produced from *Bacillus subtilis* ATCC 21332 with purity about 90%, [5]. Surfactin solution was dissolved in a 10^{-3} M phosphate buffer with a pH value of 8.0 [4,6]. Copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was chosen as the model metal ion contaminant and was purchased from Showa Chemical Co., Ltd., Japan. Purified water with a resistivity of $18.2 \text{ M}\Omega\text{-cm}$ was produced by Milli-Q plus purification system, Millipore, USA and was used in all experiments. Contaminated sands were provided by mixing the sands and the copper ion-containing solution for 24 hours at a rate of 150 rotations per minute. 24 hours waiting period of was allowed for the system to reach adsorption equilibrium, there after the sands were collected. An atomic absorption spectrometer (Sens AA Dual, GBC, Australia) was used to analyze the metal ion concentration in the solution, and then dried by putting it in oven at 50°C . As the residual type, the adsorption density of metal ions on sands with the inner-sphere interaction and precipitation were then evaluated.

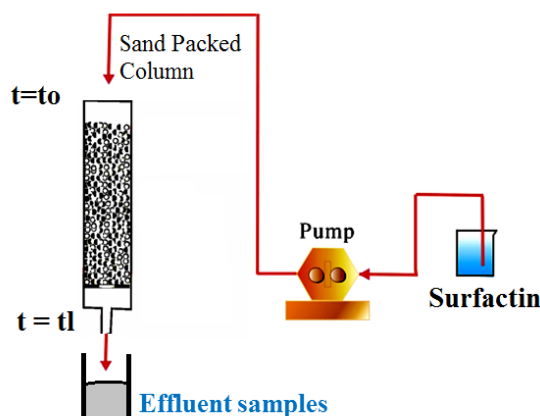


Figure 3. Illustration of instrument used for surfactant solution flushing operation without foam [4]

The instrument used for surfactant solution flushing operation without foam is as shown in Figure 3. The loading time was measured by timer for $t=t_0$ to $t=t_1$ as shown at the sand column. Contaminated sand of 10.15 g was put to the column. A glass column with a length of 7.5 cm and with outside diameter of 1.5 cm was used in the column experiments. The pore volume was about 2.2 ml and the

sand height is about 3.8 cm. Solution was pumped by peristaltic pump 2 ml/min into the column. Flushing solution was collected after 4 pore volume. A peristaltic pump (Masterflex, Model 7518-10, Cole-Parmer Instrument Company, Barrington, USA) was used to create continuous flow of surfactin solution [7,8]. The instrument used for surfactant solution flushing operation with foam is similar as to that been used by Huang and Chang, 2000 and Haryanto et al. 2014 [7,9]. AAS was used to analyze metal ions removal from the concentration in the effluent solution.

3. Results

Flushing with water only was used in comparing with surfactin solution. The impact of surface properties of Surfactin with ability to decrease the air water surface tension till 29mN/m, provides shorter loading time in comparing to water with surface tension 72mN/m. Increasing the flow rate will decrease the loading time needed. The volume of solution to flow through the column decreases the time needed when increasing the rate as shown in Figure 4. The surfactin micelles at 5x cmc in solution tend to flow out than to interact with sand interface then produce channeling effect. Water molecule is possible to wet the sand surface then interact with the chemical compound on sand surface which tend to delay the loading time.

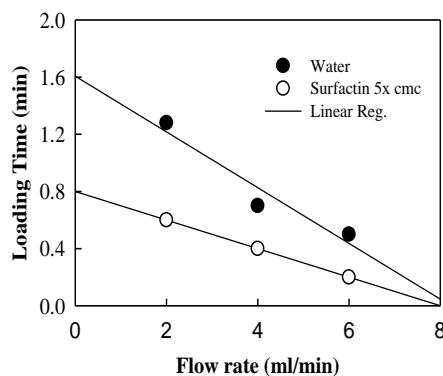


Figure 4. Time loading at different water flow rates and surfactin solution

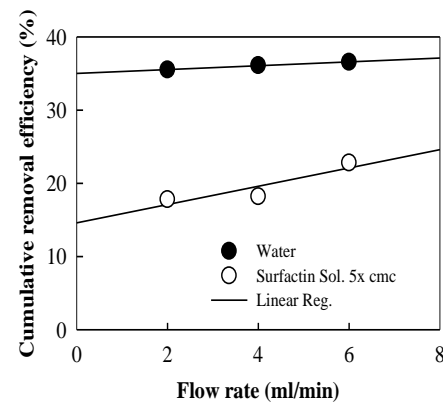


Figure 5. Removal efficiency at different water flow rate and surfactin solution of sand with residual type.

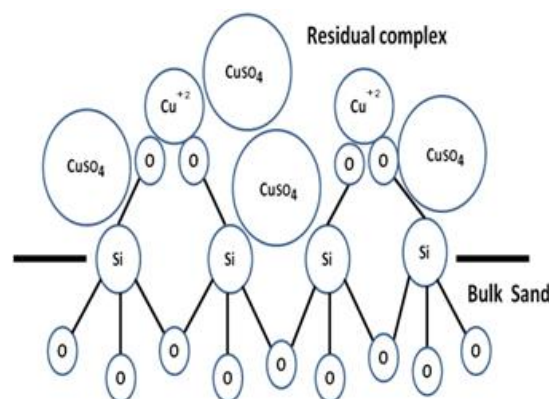


Figure 6. The residual sand type [4,10]

The removal efficiency of the flushing operation with, flowrate variation is shown in Figure 5. Sand with residual type model was used to confirm the flushing with surfactin solution, in comparing with water. Water with longer loading time was possible to remove the copper ion contaminant from

sand surface. The trend removal efficiency of surfactin solution is also possible to increase the copper ion removal as increasing the flow rates. Surfactin molecules in micelles structure may be more affected by increasing the flow rate rather than by decreasing the loading time. Residual type of contaminant occupied the inter particle sand surface area (Figure 6). In the presence of water molecule, it is possible to desorb the adsorbed then the Surfactin molecule was trapped in their micelle. The micelle have to break then interact with adsorbed on sand surface and desorb the adsorbed to solution phase. The ability of Surfactin to decrease interface tension of water and solution was limited by sand surface areas which tend to create channeling effect.

Flushing characteristic by water is shown in Figure 7. The removal efficiency at each 4 pore volume flushing solution was collected in the flushing column with flow rate variations. The removal efficiency of adsorbed was not impacted by the variation of flow rate. It tends that water molecules have the same way to interact on sand surface. The loading time impacts to wet the sand surface with the longer loading time make it possible to desorb the adsorbed but with limited surface area interaction as shown at the first 4 pore volume result. The removal efficiency each of 4 pore volume has the same result even by increasing the flow rate.

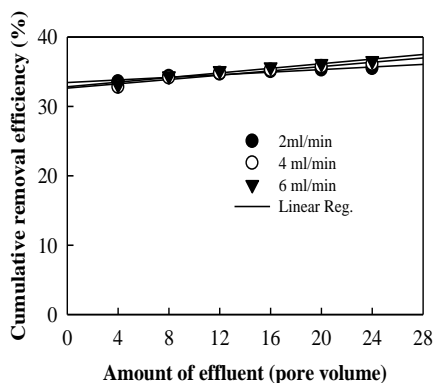


Figure 7. Effects of flow rates variation to the removal efficiency of sand with residual type by flushing with water

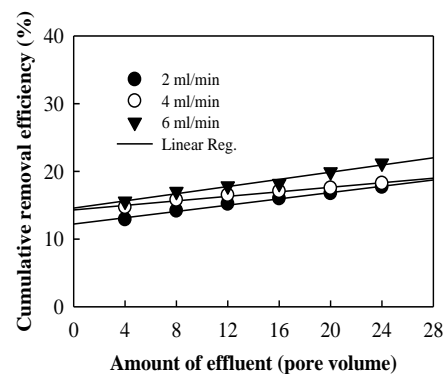


Figure 8. Effects of flow rates variation to the removal efficiency of sand with residual type by flushing with Surfactin 5x cmc

Flushing by 5x cmc surfactin is shown in Figure 8. The removal efficiency at each 4 pore volume flushing solution was increased with the increasing of flow rate. The removal efficiency of adsorbed was impacted by the variation of flow rate. The surfactin molecules in the micelles with higher flow rate are possible to increase interaction in the surface area then increased the adsorbed to desorb. The shorter loading time but with higher flow rate was possible to desorb continuously with different higher removal efficiency. The removal efficiency is tending to increase for each 4 pore volume by adding the flushing pore volume.

Flushing column with foam possible to increase the removal efficiency of the copper ion as shown in Figure 9 with the flow rate was 2 ml/min. Surfactin foam with variation concentrations are possible to spread within the surfactin molecules in the foam structure to interact with copper ion at sand surface. The foam is possible to spread within the surfactin molecule into the intra particle on sand then increases the removal efficiency of the adsorbed. The loading time with foam flushing is relatively shorter but with foam surfactin, it is more possible to reach surface area of sand then increases the removal efficiency.

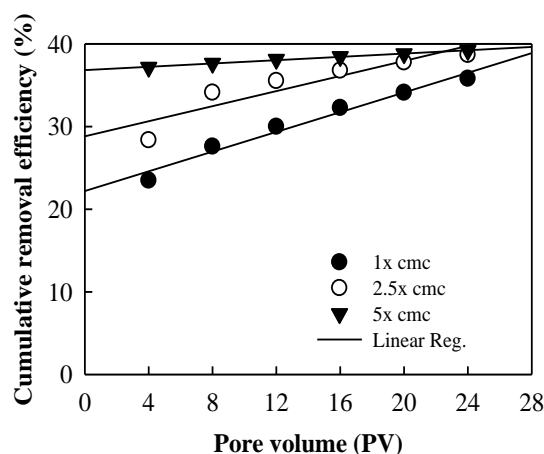


Figure 9. Effects of Surfactin concentration variation to the removal efficiency of sand with residual type by flushing with foam solution with flow rate 2 ml/min.

4. Conclusions

Loading time was impacted by flow rate variation. For surfactin molecule with micelles structure in solution tend to flow out faster in comparing with water molecule. The removal efficiency was influenced by at least 3 factors: flow rate variation, concentration and flushing by surfactin solution or foam. The channeling effect was occurred and influenced by at least 3 factors flow rate, concentration and flushing type.

References

- [1] Chowdiah P, Misra B R, Kilbane J J, Srivastava V J, Hayes T D 1998 *Journal of Hazardous Materials* **62** 265-280
- [2] RK Rothmel, RW Peters, E S Martin E S and MF Deflaun 1998 *Environ. Sci. Technol.* **32** 1667-1675
- [3] B Haryanto and CH Chang 2015 *Journal of Oleo Science* **64** 2 161-168
- [4] B Haryanto 2014 PhD Thesis Chem. Eng. Department, NCKU Taiwan
- [5] MS Yeh, YH Wei and JS Chang 2005 *Biotechnol. Prog.* **21** 1329-1334
- [6] CN Mulligan, RN Yong, BF Gibbs, J Susan, and HP Bennett 1999 *Environ. Sci. Technol.* **33** 3812-3820
- [7] B Haryanto and CH Chang 2014 *Journal of the Taiwan Institute of Chemical Engineers* **45** 2170 -2175
- [8] B Haryanto, JS Chang, and CH Chang 2014 *Tenside Surf. Det.* **5** 1-5
- [9] CW Huang, and CH Chang 2000 *Colloids and Surfaces A: Physicochemical and Engineering Aspect* **173** 171-179
- [10] C Koretsky 2000 *Journal of Hydrology* **230** 127-171