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Extraction of Cu(II) with microcapsules of cross-linked gel of poly(vinyl alcohol)/alginic acid encapsulating dispersed droplets of phenolic oxime extractant

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Abstract

PVA/Alg-GA crosslinked-gel microcapsules containing phenolic oxime extractant, LIX84-I, were prepared by falling-drop method of O/W emulsion followed by crosslinking of Na-Alg by Ca^{2+} ion and crosslinking of PVA by glutaraldehyde. The small droplets of LIX84-I were observed in the microcapsules. The contents of LIX84-I in the microcapsules increased with the added amounts of LIX84-I to the aqueous polymer solution. The maximum amounts of Cu(II) extracted in the microcapsules increased linearly with the LIX84-I contents with the slope of 1/2 which means two molecules of LIX84-I react with one Cu(II) ion. The high durability of the microcapsules was confirmed by the repeated use for extraction and back-extraction of Cu(II).
Keywords: Gel microcapsules, Cu(II) extraction, Phenolic oxime extractant, Alginic acid, PVA

1. INTRODUCTION

Microencapsulation of extractants for metal ions, organic acids, amino acids and various compounds is one of the effective methods to overcome some disadvantages on the liquid-liquid extraction process, such as the difficulty in phase separation by the formation of stable emulsion or third phase between aqueous and organic phases, and use of a large amount of organic solvent.

In this study, PVA/Alg-GA crosslinked gel microcapsules containing phenolic oxime extractant, 1-(2-hydroxy-5-nonylphenyl) ethanone oxime (LIX84-I) were prepared by crosslinking of Na-Alg by Ca^{2+} ion and crosslinking of PVA by glutaraldehyde. The microcapsules containing LIX84-I have an ability to extract Cu(II) in the aqueous ammonium sulfate solution. The extraction properties of Cu(II) in the solution using the microcapsules were investigated under various conditions, such as effects of LIX84-I contents, Cu(II) concentration and repeated use of the microcapsules.

2. EXPERIMENTAL

2.1 Preparation of microcapsules

The microcapsules containing LIX84-I were prepared by the same procedure as shown in the previous paper (Komatsu *et al.* 2016). An aqueous solution containing poly(vinyl alcohol) and sodium alginate (Na-Alg) and LIX84-I as an organic phase were mixed to form O/W emulsion at room temperature. The O/W emulsion was extruded from a needle to an aqueous calcium chloride solution to form droplets and immersed for 30 min with gentle stirring for crosslinking of Na-Alg by Ca^{2+} ion. The capsules were then transferred to hydrochloric acid aqueous solution dissolving glutaraldehyde and immersed for 2h with gentle stirring for crosslinking of PVA by glutaraldehyde.

2.2 Extraction of Cu (II) from aqueous solutions

The experiments were carried out in a batch-wise by contacting the microcapsules and the aqueous solution containing Cu(II) at given time. After extraction, the

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microcapsules were filtrated from the aqueous phase. The Cu (II) concentration in the filtrate and feed solutions were measured by ICP-AES (Shimadzu, ICPS-8100). The amount of Cu (II) adsorbed on the microcapsules was calculated from the mass balance between the initial and the equilibrium metal concentrations in the aqueous solutions.

3. RESULTS and DISCUSSION

The images of the microcapsules by digital microscope and its cross-section by SEM are shown in Figure 1. The microcapsules were almost spherical shape with 3.6 mm of the average diameter. Many spherical pores and fibrous network were observed in the cross-section of the microcapsules. The spherical pores would be traces of LIX84-I droplets and fibrous structure would be cross-linked polymer network to form the microcapsule wall.

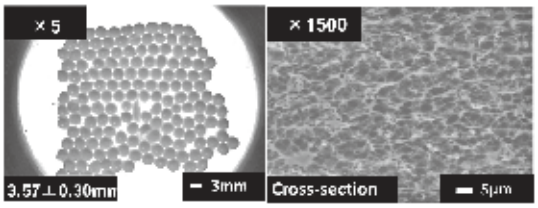

Fig. 1 Observation of the microcapsules containing LIX84-I by digital microscope (left) and its cross-section by SEM (right).

The microcapsules containing LIX84-I successfully extracted Cu(II) from the aqueous solution. The effect of the Cu(II) concentration on the Cu(II) amount extracted in the microcapsules is shown in Figure 2. The Cu(II) amount extracted in the microcapsule increased with the Cu(II) concentration and reached constant values depending on the LIX84-I content. This extraction isotherm fits well with Langmuir type isotherm. The maximum extracted amount at each LIX84-I content was obtained from the plot based on Langmuir isotherm. The maximum amount of Cu(II) was plotted against the LIX84-I content of the microcapsules in Figure 3. The maximum amount increased linearly with the LIX84-I content. The slope of the straight line in Figure 3

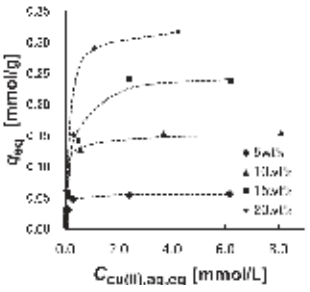

Fig. 2 Effect of the equilibrium concentration of Cu(II), $C_{cu(II),aq,eq}$, on the extracted amount of Cu(II), q_{eq}.

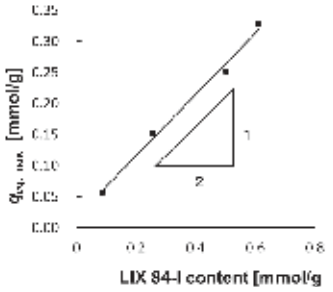

Fig. 3 Effect of the LIX84-I content on the maximum extraction amount $q_{eq,max}$.

was 1/2. This result means two molecules of LIX84-I extracted one Cu(II) ion as shown by the following reaction. This extraction equilibrium is same as that of the microcapsules with interconnected spherical pores using poly divinylbenzene (Inda *et al*. 2016).

$$2HR + Cu^{2+} \rightleftarrows CuR_2 + 2H^+ \quad R:LIX84\text{-}I$$

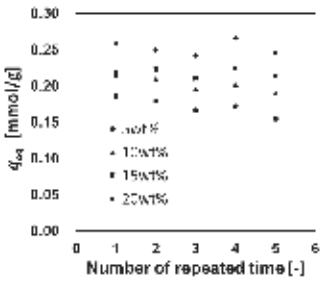

Fig. 4 Effect of the number of repeated time on the extraction amount q_{eq}.

The repeated use of the microcapsules for forward and back extractions was carried out. The extracted amounts of Cu(II) were plotted against the repeated times in Figure 4. The amount was almost constant and showed no significant decrease. This means there is no leakage of the extractant from the microcapsules during the repeated process. After five times of the repeated use, the surface morphology of the microcapsules was observed using SEM after freeze-drying and washing with ethanol to remove the extractant. No significant change on the surface was observed. This result shows the wall of the crosslinked-gel microcapsules used in this study has enough strength for the repeated use.

4. REFERENCES

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