Encapsulation of PC-88A in microcapsules of cross-linked gel of poly(vinyl alcohol)/ alginic acid and its extraction property of Co(II)

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2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), which is an effective extractant of Co(II), was microencapusulated by two step crosslinking of sodium alginate by Ca^{2+} ion and polyvinylalcohol by glutaralde. Globular microcapsules containing PC88-A droplets with the diameter around 4 mm were successfully prepared and had a relatively high strength. The microcapsules had smooth surface with large pores and many droplets of PC-88A in their inner side. The percentage content of PC-88A in the microcapsules was 18 % for wet sate of the microcapsule. The extraction of Co(II) using the microcapsules containing PC-88A sharply increased at pH values greater than 5. Zn(II) extracted in the microcapsules was successfully back-extracted at pH values less than 4. No destruction of the microcapsules was observed during the repeated use of several times.

Introduction

The process of solvent extraction has been used for separation and recovery of various substances such as metal ions, organic acids, antibiotics, amino acids and proteins [1]. Solvent extraction sometimes has some problems in that the phase separation of organic and aqueous phases is difficult in some cases and extractants and/or organic solvents are lost by being dissolved in the aqueous phase. To solve these problems, the immobilization of the extractant [2, 3] and microencapsulation [4, 5] of the extractant have been investigated. Microencapsulation of extractants for metal ions, organic acids, amino acids and various compounds is one of effective methods to overcome some disadvantages on the liquid-liquid extraction process. The wall material of microcapsules is important to determine the characteristic of microcapsules. Calcium alginate is often used for a wall material of microcapsules due to easy preparation, especially for the microencapsulation of enzymes and microorganisms. However, the microcapsules prepared from calcium alginate have not so high durability. Therefore, mixed gels with calcium alginate and other polymers, chitosan, polyvinyl alcohol and so on, have been used to enhance strength and durability of microcapsules.

In this study, microencapsulation of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) in a microcapsules with hydrophilic wall were investigated using two step crosslinking of sodium alginate by Ca^{2+} ion and polyvinyl alcohol by glutaraldehyde. The morphologies of the microcapsules prepared and during the preparation were investigated. The extraction properties of Co(II) in ammonium sulfate solution using the microcapsules were also investigated under various conditions.

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Experimental

Reagents

2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A, Daihachi Chemicalindustry Co., Ltd.) was used as the extractant. Sodium alginate and polyvinyl alcohol as a wall material, calcium chloride, glutaraldehyde, ammonium sulfate, cobalt (II) sulfate heptahydrate were purchased from Wako Pure Chemicals Co.

Preparation of microcapsules containing PC-88A

The preparation scheme of the microcapsules containing PC-88A is shown Fig.1. An aqueous solution containing poly vinyl alcohol (PVA) and sodium alginate (Na-Alg) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) as an organic phase were mixed to form O/W emulsion at 5,000 rpm for 5 min. at room temperature. In some cases, the O/W emulsion was treated by ultrasonic irradiation to reduce the droplet diameter. The O/W emulsion was extruded from a glass needle to a calcium chloride aqueous solution to form microcapsules and immersed for 30 min with gentle stirring for crosslinking of Na-Alg by Ca^{2+} ion. The microcapsules were then transferred to hydrochloric acid aqueous solution dissolving glutaraldehyde, and immersed for 2 h with gentle stirring for crosslinking of PVA by glutaraldehyde. The microcapsules prepared were washed with distilled water and stored in water until use.

The morphologies of the microcapsules were observed by scanning electron microscopy (Hitachi S-4100M and TM-1000, SEM) and a digital microscope (KEYENCE VH-8000). The internal structure of the microcapsules was examined by cross-sectioning of the microcapsules. The diameter of the microcapsules was measured from the digital microscope images.

The amount of PC-88A entrapped in the microcapsules was determined by the titration of ethanol solution eluted PC-88A from the microcapsules with 0.01 $mol \cdot dm^{-3}$ KOH/MeOH-BuOH using bromocresol green as the indicator.

Extraction of Co(II) with the microcapsules

The extraction of Co(II) from aqueous solution with the microcapsules containing PC-88A was carried out in a batch wise by contacting 1.0 g of the microcapsules and

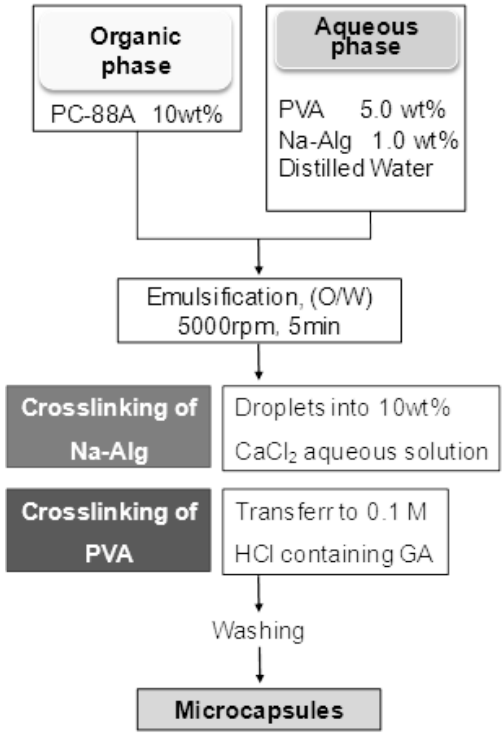

Fig. 1 The preparation scheme of the microcapsules containing PC-88A.

15 dm^3 of the aqueous solution containing Co(II) at given time on several hours. After extraction, the microcapsules were filtrated from the raffinate. The Co(II) concentration in the raffinate and feed solutions were measured by ICP-AES (Shimadzu, ICPS-8100). The amount of Co(II) adsorbed on to the microcapsules was calculated from the mass balance between the initial and the equilibrium metal concentrations in the aqueous solutions.

Results and discussion

Preparation of microcapsules containing PC-88A

The microscope photographs of O/W emulsion and the microcapsules are shown in Fig. 2. The diameters of O/W emulsion and the surface of the microcapsules measured from the photographs are shown in Table. 1. PC-88A was dispersed well in the aqueous solution of the polymers with the diameter around 2 μm. Spherical and oval microcapsules containing PC88-A droplets with the diameter around 4mm were successfully prepared. The inside of the microcapsule was observed darkly by a lot of small droplets of PC-88A. The microcapsules shrank by the crosslinking of PVA with glutaraldehyde. The percentage content of PC-88A in the microcapsules was 18 %. The SEM images of the surface and the inside of the microcapsules are shown in Fig. 3. The microcapsules had dimpling pores on their

Table 1 The diameters of O/W emulsion and microcapsules.

	O/W emulsion [μm] microcapsules [mm]
O/W emulsion	2.01±0.19
before crosslinking of PVA	4.27±0.19
after crosslinking of PVA	4.00±0.19

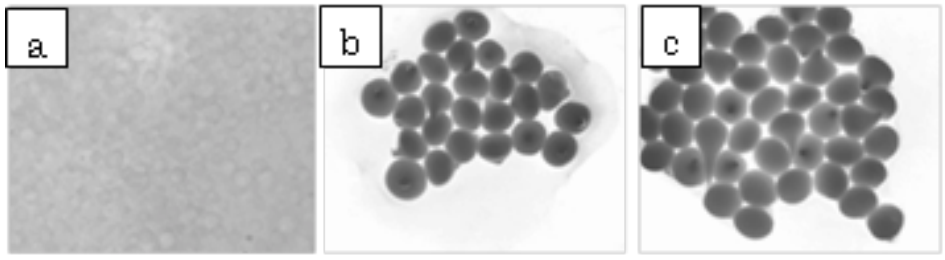

Fig. 2 The digital microscope images of O/W emulsion (a) and the microcapsules before crosslinking of PVA (b), and after crosslinking of PVA (c).

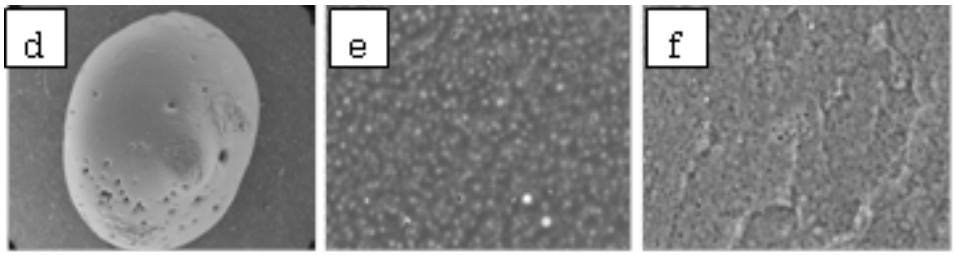

Fig. 3 The SEM images of the microcapsules. (d) : surface ×50; (e) : surface ×1000; (f) : cross-section ×1000

surface. These pores would be traces of the droplets of PC-88A which were released from the surface in the first crosslinking of alginate. A lot of small pimples, which were frequently observed as bright spots by SEM, were observed on the surface and inside of the microcapsules. These would be caused by the existence of the droplets of PC-88A in the gel wall.

Extraction properties of Co(II) using the microcapsules containing PC-88A

The effect of the pH in the aqueous phase on the forward and back extraction of Co(II) is shown in Fig. 4. The extraction of Co(II) increased sharply above pH 5. This result was almost the same pH dependence as reported for the solvent extraction system using PC-88A [6]. Therefore, PC-88A encapsulated into the microcapsules shows the same extraction properties as in the solvent extraction system. The back extraction of the Co(II) extracted into the microcapsules was successfully carried out by using a sulfuric acid solution at a pH value lower than 4.

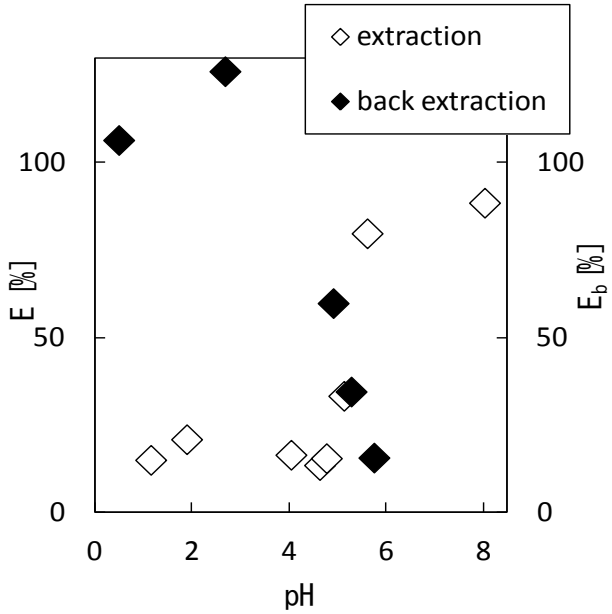

Fig. 4 Effect of the aqueous pH on the extraction of Co(II) by the microcapsules. $E_{PC\text{-}88A}$=18 wt%, M_{MC}=0.20 g, $C_{Co,aq,ini}$ = 200 mg·dm^{-3}, aqueous solution =15x10^{-3} dm^3

The extraction of Co(II) was carried out using the microcapsules prepared with and without ultrasonic treatment of O/W emulsion as shown in Fig. 5. The amount of Co(II) extracted to the microcapsules gradually increased with time and reached equilibrium values. The extraction properties of Co(II) using the microcapsules prepared with and without the ultrasonic treatment were almost same. The droplets of PC-88A became small and their surface area increased by the ultrasonic treatment, however the effect of ultrasonic treatment was not observed on the extraction rate. This suggests that the diffusion of Co(II) in the wall of the microcapsules is the rate determining step of the extraction of Co(II) with the microcapsules prepared in this study.

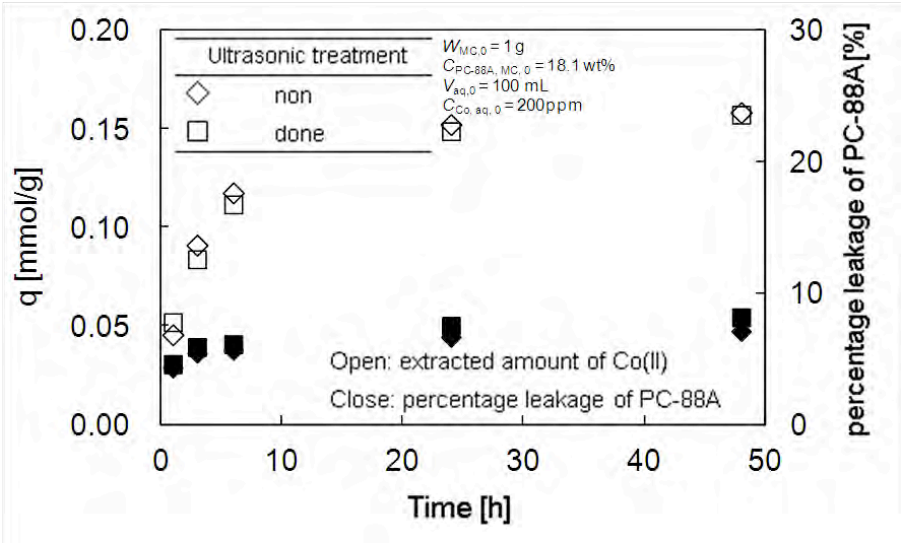

Fig. 5 Effect of time on the extraction of Co(II) by the microcapsules prepared with and without ultrasonic treatment of O/W emulsion. E_{PC-88A}=18 wt%, M_{MC}=1.0 g, $C_{Co,aq,ini}$ = 200 mg·dm^{-3}, aqueous solution =100x10^{-3} dm^3

Conclusion

Microcapsules containing PC-88A were successfully prepared by crosslinking of Na-Alg by Ca^{2+} ion and crosslinking of PVA by glutaraldehyde. The diameter of the microcapsules was around 4 mm and the percentage content of PC-88A in the microcapsules was 18 %. The extraction of Co (II) increased sharply above pH 5. The back extraction of Co (II) extracted into the microcapsules was successfully carried out by using the sulfuric acid solution at pH lower than 4. The diffusion of Co(II) in the wall of the microcapsules was suggested to be the rate determining step of the extraction of Co(II) with the microcapsules.

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