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Preparation and Application of Inorganic Microballoons Membrane

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Abstract: The primary emulsification to form the microballoons was studied. The effects of preparation conditions against the formation of microballoons were examined. The factors examined were metal species in the external aqueous phase, the concentrations of sodium silicate in the internal phase and Cyanex 923 as carrier. The particle size and shell thickness were found 10 μm and 2 μm, respectively. Since the penetration of metal species through the oil phase was promoted by the increase of carrier concentration. The formation of microballoons was completed in a short time of less than 30 min. The formation of microballoons of Co(II), Ni(II), Zn(II), Sr(II), and Cu(II) were used for removal of these metal ions.

Keywords: Microballoon, sodium silicate, Cyanex 923 carrier, Co(II), Ni(II), Zn(II), Sr(II), Cu(II)

INTRODUCTION

Although liquid-liquid extraction is presently one of the major techniques for the separation and recovery of metals in many industrial fields (1–5), it has been used in new developing commercial processes because of inherent disadvantages. One disadvantage is the need for an organic solvent, which can be lost in the aqueous phase due to its solubility in the feed. A method to overcome this disadvantage involves immobilizing the extractant through microballoons. Compared to conventional liquid-liquid extraction, there are several advantages with solvent microballoons as separation agent, including large specific interfacial area, high selectivity, minimal use of

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organic solvents and ease of phase separation. Most of the microparticles studied so far are concerned with organic polymers, whereas the application of inorganic microparticles to optical sensor (6) or flocculant (7) has become of interest in recent years. Not a few methods have been reported to prepare micron-sized monodispersed inorganic particles. They include spray-drying (8), pyrolysis (9), sol-gel process (10), coating (11), and template technique (12).

Therefore, microballoons can address the problems of phase separation, phase mixing and leakage of extractant. Several methods have been proposed so far to prepare inorganic microballoons, but the interfacial reaction method developed by Nakahara (13) is considered to be most favorable in that a wide variety of inorganic reactions can be used to form an insoluble shell (14). This method is based on the transport of metal ions through oil phase between internal and external aqueous phases of (W/O)/W emulsion, therefore it is quite similar for separation processes with liquid surfactant membranes. The extent of spherical balloons formation is influenced with preparing conditions of W/O and (W/O)/W emulsions.

In the present study, the primary emulsification to form the microballoons was studied based on Cyanex-923 as extractant and sodium silicate as internal phase using SPAN 80 as emulsifying agent was prepared. The effects of preparation conditions on the prepared inorganic microballoons were examined for various metal silicates microballoons to establish the stability of the formed microballoons and to find the optimum preparation conditions. The prepared microballoons were used for the extraction of some metal ions from aqueous solutions. Advanced studies will examine a secondary emulsification to use the microballoons formed in the recovery of the metal ions.

EXPERIMENTAL

Materials

Metal chlorides used were of analytical reagent grade (AR) and were supplied by Fluka while cyclohexane and sodium silicate were AR grade and obtained from Merck Company (Germany). The used extractant, CYANEX 923, was kindly supplied by Cytec Inc., USA, and it contains a mixture different phosphine oxides extractants (15).

Preparation of Silicate Membrane

An internal aqueous solution, prepared by dissolving sodium silicate in deionized water and organic solution prepared by dissolving SPAN 80 as a surfactant and Cyanex 923 as a carrier in cyclohexane, were mixed in a homogenizer at 3000 to 9000 rpm. W/O emulsion prepared was added to an external aqueous solution containing $CoCl_2$ and stirred gently at 300 rpm. Figure 1 shows the schematic of the preparation procedure of silicate microballoons. Also, Ni(II) chloride were used to extract Ni(II) as Ni silicate microballoons.

Membrane Analysis

The morphology of microballoon was evaluated by scanning electron microscopy (SEM) using a Joel JSM-6060 scanning electron microscope. The FTIR spectroscopy was carried out in the reflectance mode, using a Perkin Elmer Model 1725 X instrument equipped with a horizontal attenuated total reflectance accessory (ZnSe reflecting crystal). Infrared spectra were measured against a background of n-hexane and were scanned across the wave number from 4000 to 400 cm^{-1}.

Membrane Stability

A known volume of membrane was left for one week and the volume of the membrane was released and measured. Then, this membrane was used for the extraction of Co(II).

The stability of the membrane in acid and base was studied. Both strong acid and alkaline solutions were added to known volume of the membrane. The volume released from the membrane was measured from the difference in the volume.

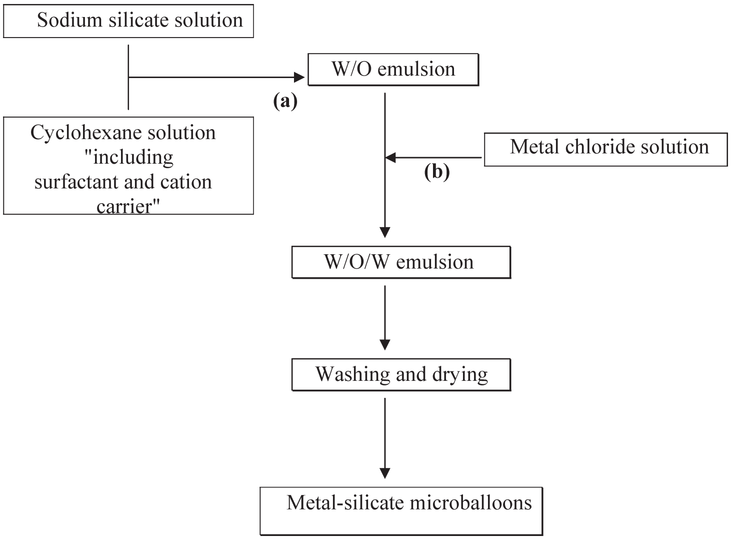

Figure 1. Schematic of process to prepare microballoons: (a) Primary emulsification at 5000 rpm for 5 min. (b) Secondary emulsification at 300 rpm 60 min.

Extraction Experiments

Co(II) forms a blue colored complex with CYANEX 923 in the organic phase. A stock solution of 1 M Co(II) prepared. Extraction experiments were performed with 10 ml of solution in 25 ml polypropylene bottles. 1 ml membrane were added to Co(II) solution. The mixtures were placed on a magnetic stirrer (MIRAK^{TM}, made in USA) set at 300 rpm. After 30 min, the samples were filtered and the filtrate was analyzed spectrophotometrically (16) to determine the Co(II) content. Some factors that affect the extraction were studied. The organic phase was 10% CYANEX 923/cyclohexane solution. Also, the effect of pH was studied. Co(II) solution was adjusted to a desired pH by using 0.1 N HCl or dilute NaOH solutions. The extracted metal ion can be recovered via the stripping solution by stirring the membrane after extraction with 0.3 M H_2SO_4.

RESULTS AND DISCUSSION

Membrane Characterization

The scanning electron microscopy SEM image of silicate micro-balloons is shown in Fig. 2. where almost completely spherical balloons with smooth surface were prepared at high yield. The particle size and shell thickness were found 10 μm and 2 μm, respectively. The cross-section of the particles had a hollow structure with an homogeneous shell, Fig. 1(a, b).

To learn about the types of interactions of the transport of metal ions through the microballoons, the IR spectrum of sodium silicate, cobalt chloride, and sodium silicate mixture, and the microballoons containing cobalt were measured, Fig. 3(a,b,c). The sodium silicate IR spectrum showed a broad absorption band at 3475 cm^{-1} which is assigned to OH stretching and molecular water. This position of this band was decreased to 3289 cm^{-1} (17) as well as its relative absorbance with the generation of two sharp band at 2856 and 2929 cm^{-1} for the $CoCl_2$ and Na-silicate mixture. This indicates that hydrogen bonding between the silicate and Co(II) increased with a decrease in water in the matrix. For the membrane system similar results were observed, however the amount of water released is less than that observed for the $CoCl_2$ and silicate system. This is expected since in the microballoons system the water is contained within the balloons. In the wave length range of 500–2000 cm^{-1}, sodium silicate showed a main sharp band at 1641 cm^{-1}, small band at 1383 cm^{-1} and a medium band at 997 cm^{-1} assigned to OH bending (molecular water) (11), carbonate impurities, and Si-OH band stretching (18–24), respectively. For $CoCl_2$ and Na-silicate mixture the band at 1641 cm^{-1} in the Na-silicate displaced with the generation of a new band at 1739 cm^{-1} which can be related to the formation of hydrated cobalt. Further the band at 1455 cm^{-1}

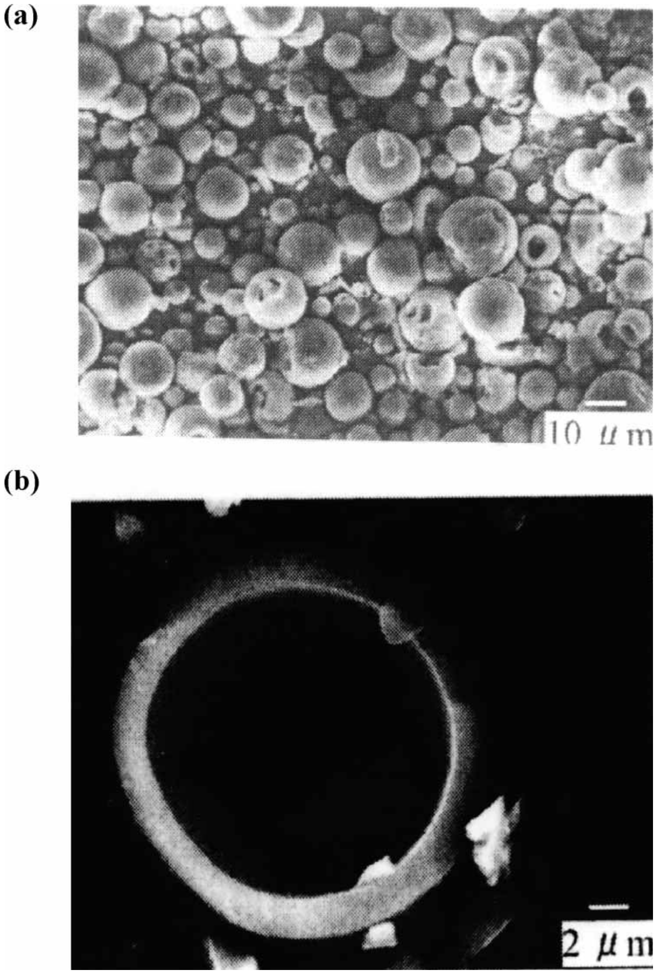

Figure 2. Scanning electronic microscope image of surface and cross-section of Co(II) microballoons.

can be assigned as overtone for the band at 724 cm^{-1} assigned to the $CoCl_2$. The band at 1151 cm^{-1} in the mixture of $CoCl_2$ and silicate is assigned to asymmetric Si-O-Si stretching in $Si\text{-}O_4$ tetrahedron. The band at 806 cm^{-1} is assigned to OH bending (silanol). In the membrane system, the bands at 662, 1460, and 1637 cm^{-1} are assigned to Si-O-Co, overtone for $CoCl_2$ and OH bending (molecular water) (18), respectively. While the bands in the range 2850–3600 cm^{-1} assigned to OH-stretching (water) (12, 13). The band at 1739 cm^{-1} which can be related to the formation of hydrated cobalt as mentioned before.

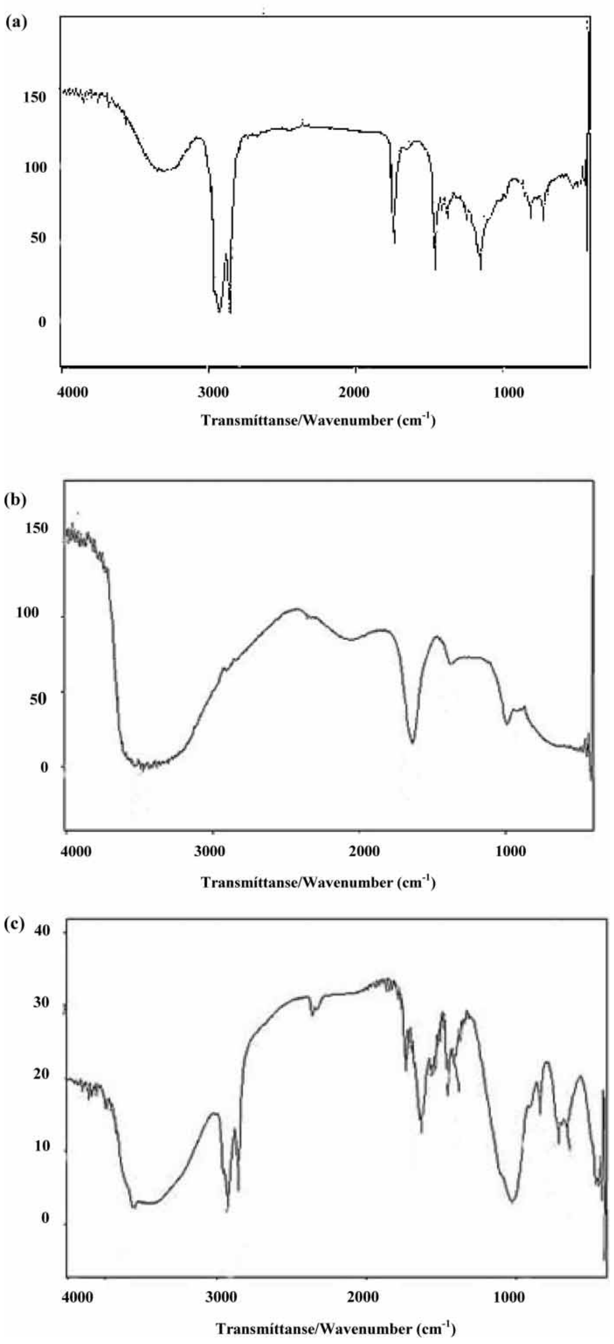

Figure 3. Infrared spectra of inorganic membrane before and after membrane extraction. Before: (a) Co-Na-Silicate mixture (b) (Na-Silicate); After: (c) Microballoons containing Co.

The ability of the membrane to remain stable under continued exposure to different solutions containing defined volume of membrane and having pH values from acidic to alkaline solutions is of great importance. In HNO_3 and NaOH in the range (0.1–1) M the stability of membrane is very high (95%) after one day. The microballoons presented good stability in neutral, acidic, and alkaline medium with no noticeable loss of volume was found. The stability of the membrane in the natural medium reach to one week and the membrane can be used after this time as efficient membrane for Co(II) removal.

Preparation of Inorganic Microballoons Inorganic Emulsion Membrane

The effects of the operating conditions on the preparation of microballoons were studied with the extraction of Co(II) to form spherical balloons which considered the secondary emulsification.

When the W/O emulsion is dispersed by stirring in the continuous aqueous solution, the emulsion must be sufficiently stable in order to extract metal ions into the internal aqueous droplets. Different factors affects of preparation conditions were examined in order to prepare the optimum emulsion membranes for these conflicting requirements.

Effect of Emulsification Rotating Speed

Table 1 shows the effects of homogenizer speed in W/O emulsion. An efficient emulsification rotating speed gives a good dispersion of internal phase drops into the organic phase. The optimal emulsification speed was found to reach a value of 5000 rpm with high Co(II) balloons.

Effect of Emulsification Time

The extraction percent of membrane increase with the increase of mixing time, since the short mixing time is insufficient for microballoons formation. As shown in Table 1, the higher Co(II) extraction is obtained for emulsion time of 5 minutes.

Effect of Sodium Silicate Concentration in Internal Aqueous Solution

The increase in sodium silicate concentration increases the Co(II) which form the balloons as shown in Table 1. However, too high a concentration of sodium silicate (>1.5 M) caused coagulation because of viscosity increase in the inner phase.

Table 1. Effect of different parameters on the preparation of Co(II) microballoons

Investigated parameters	Extraction percent (%)
Emulsification rotating speed, rpm	
3000	80
4000	90
5000	98
7000	89
8000	85
Emulsification time, min.	
2	75
5	98
7	96
10	97
Stirring speed (rpm)	
200	70
250	84
300	98
350	97
400	95
Cyanex 923, M	
0.025	—
0.076	—
0.13	80
0.18	93
0.25	98
0.38	99
Na-silicate concentration, M	
0.5	—
0.6	—
0.8	62
1	70
1.1	87
1.2	98
1.5	99
2	—
SPAN 80 (%)	
1	85
2	98
3	97
4	98

Effect of Surfactant Concentration

Table 1 indicates the effect of SPAN 80 concentration. The increase of surfactant concentration was most effective to elevate the formation of spherical microballoons, but the differences are limited showing that 2% of SPAN80 is a convenient concentration.

The working conditions are summarized as follows: [Co(II)] = 0.15 M, emulsification rotating speed = 5000 rpm, emulsification time = 5 min, stirring speed = 300 rpm, Cyanex-923 = 0.25 M, Na-silicate concentration = 1.1 M, pH = 5.5 ± 0.1, SPAN 80 (%) = 2% and membrane phase/external phase = 1:10.

Effects of Operating Conditions on the Formation Rate of Microballoons

Based on the results obtained, the formation of inorganic microballoons proceeds by the ion transport between the inner and external aqueous solutions through the oil membrane. Therefore, the formation rate of microballoons may be controlled by the operating conditions, which influence the ion penetration. In this study, the rate of transport of metal species was regarded as the formation rate of microballoons and the effects of the operating conditions were studied for the Co silicate microballoons. The formation rate of microballoons increased with the increase in the stirring speed of the mixture solution, and the extractant concentration and sodium silicate concentration may be due to the decrease in size of dispersed emulsion drops and the increase in the specific surface area, Figs.(4–6). The formation of microballoons proceeded just after introducing the emulsion into external aqueous solution and it took fairly long time to reach the steady state when the salt and extractant concentrations were low. The

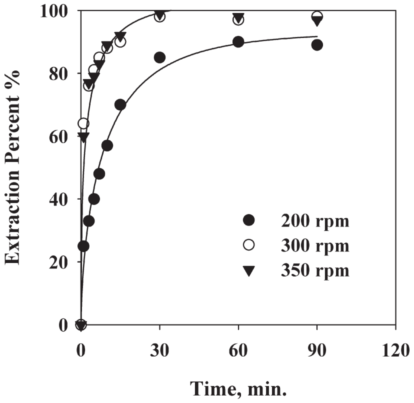

Figure 4. Effect of stirring speed of the external phase ($CoCl_2$) (2nd emulsification) on the Co(II) extraction percent. [Co(II)] = 0.15 M; pH = 5.5 ± 0.1; SPAN 80 (%) = 2%; [Cyanex-923] = 0.25 M; pH = 5.5 ± 0.1; T = 25°C ± 0.1; Membrane phase/external phase =1:10; Emulsification rotating speed = 5000 rpm; Na-silicate concentration = 1.1:M; Emulsification time = 5 min.

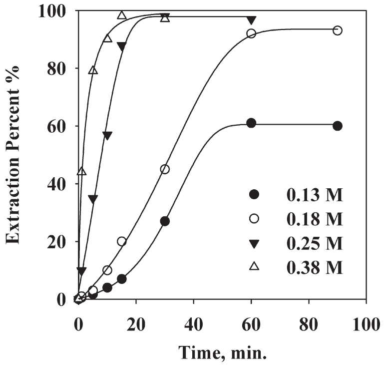

Figure 5. Effect of Cyanex-923 concentration in the internal membrane phase (in 1st emulsification) on the Co(II) extraction percent. [Co(II)] = 0.15 M; pH = 5.5 ± 0.1; pH = 5.5 ± 0.1; T = 25°C ±0.1; SPAN 80 (%) = 2%; Emulsification time = 5 min; Stirring speed of external phase = 300 rpm; Membrane phase/external phase = 1:10; Emulsification rotating speed = 5000 rpm; Na-silicate concentration = 1.1:M.

obtained results indicated that the transfer of ions may control the overall process and the growth of shell proceeds may be from the inside of core initially formed toward the outside.

The balloons are effective for removal of the metal ion over the pH range 1–5 and the extraction percent is 97%, while Co(II) at high pH cobalt precipitated.

For the recovery of extracted metals, on the contrary, the emulsion must be readily broken by the use of demulsification techniques such as heating, applying

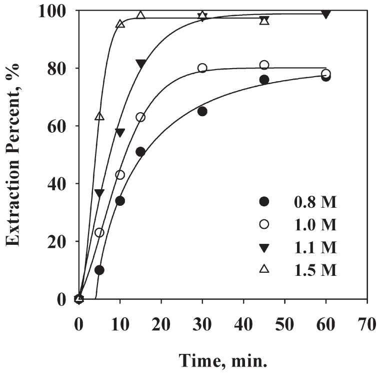

Figure 6. Effect of Na-silicate concentration in the membrane phase (in 1st emulsification) on the Co(II) extraction percent. [Co(II)] = 0.15 M; pH = 5.5 ± 0.1; SPAN 80 (%)= 2%; pH = 5.5 ± 0.1; T= 25°C ±0.1; Emulsification time = 5 min; Stirring speed of external phase = 300 rpm; Membrane phase/external phase =1:10; Emulsification rotating speed = 5000 rpm; Cyanex-923 concentration = 0.25 M.

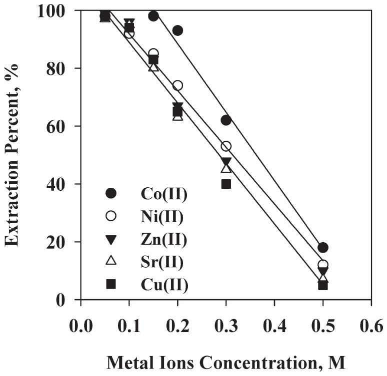

Figure 7. The extraction of different metal ions using inorganic liquid emulsion membrane. pH = 5.5 ± 0.1; SPAN 80 (%)= 2%; pH = 5.5 ± 0.1; T= 25°C ± 0.1; Emulsification time = 5 min; Stirring speed of external phase = 300 rpm; Membrane phase/external phase =1:10; Emulsification rotating speed = 5000 rpm; Cyanex-923 concentration = 0.25 M.

a high voltage electrostatic field, and chemical additives. But in this study the extracted metal ion was recovered via stripping solution with 0.3 M H_2SO_4.

Application of the Use Inorganic Microballoons

To assess the possible use of this technique investigated for the extraction of Co(II), Ni(II), Zn(II), Sr(II), and Cu(II) from the aqueous solution, the extraction of these elements was studied. The extraction of different metal ions concentration ranging 0.05 to 0.5 M was investigated using the same conditions used for maximum extraction of Co(II). The extraction percent increased with the decrease in the metal ions concentration as shown in Fig. 7 this may be due to the increase of the particle diameter and the shell thickness of microballoons. The extraction percent of Co(II) > Ni(II), but the extraction percent of Zn(II), Sr(II) and Cu(II) is more less similar.

CONCLUSIONS

Microballooons newly developed and containing Cyanex-923 and Na-silicate have been prepared successfully. The particle size and shell thickness were found 10 μm and 2 μm, respectively. The optimum conditions for the extraction and the formation of metal ions are summarized as follows: emulsification rotating speed = 5000 rpm, emulsification time = 5 min, stirring speed = 300 rpm, Cyanex-923 = 0.25 M, Na-silicate concentration = 1.1 M, pH = 5.5 ± 0.1 and SPAN 80 (%) = 2%. The microballoons show very good extraction performance and high stability. The extraction percent and stability to acids are enough high. After 2 weeks the microballoons kept almost the same extraction ability as the first time of preparation. Also the metal ions can be stripped from the membrane. The formation of microballoons of Co(II), Ni(II), Zn(II), Sr(II), and Cu(II) were used for removal of these metal ions.

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