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Extraction Properties of Nickel (II) with Polymeric Particles with Interconnected Spherical Pores Impregnating with LIX84-I

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1-(2-hydroxyl-5-nonyphenyl)ethanone oxime (LIX84-I) was impregnated into polymeric particles with interconnected spherical pores by the solvent evaporation method. Divinylbenzene was used as a wall material and polymerized in the organic phase of a (W/O/W) emulsion by free radical polymerization. The diameter of the polymeric particles was almost constant at around 208 ± 26μm. The impregnated yield of LIX84-I in the polymeric particles was higher than 80% in all preparation conditions. The extraction of Ni(II) with the polymeric particles impregnated with LIX84-I sharply increased at pH values higher than 6. It is confirmed that three molecules of LIX84-I reacted with one Ni(II) ion by quantitative analysis of the relationship between the maximum amounts of Ni(II) extracted and the amount of LIX84-I impregnated in the polymeric particles. The extraction rate of Ni(II) was effectively accelerated by the presence of the interconnected-spherical pores in the inside of the polymeric particles.

1. Introduction

Solvent extraction has been used for separation and recovery of various substances such as metal ions, organic acids, antibiotics, amino acids and proteins, due to its relatively high selectivity for target substances, simplicity of equipment and operation, and facility of scale-up and application [1]. However, it uses large amounts of organic solvents which may adversely affect the environment and the human body.

Solvent extraction also has some problems in that the phase separation of organic and aqueous phases is difficult and extractants and/or organic solvents are lost by being dissolved in the aqueous phase. To solve these problems, the immobilization of the extractant [2-8] and microencapsulation [9-22] of the extractant have been investigated. The immobilization of the extractant is achieved using porous polymer particles [2-6] and in some cases using fibers [7, 8]. Porous polymer particles impregnated with the extractant are called solvent impregnated resins (SIRs). Solvent impregnated resins are simply prepared by immobilization of the extractants within the matrix structure of the polymer particles by physical contact. Hence, SIRs containing various extractants have been prepared and investigated for a variety of applications [23].

In our previous work, we reported that the extraction rate significantly increased when the diameter of the microcapsules containing tri-*n*-octylamine decreased to less than 20μm [16]. However, small microcapsules are difficult to use in the industrial field due to handling difficulties. If large size microcapsules are used for extraction, it is important to shorten the diffusion distance and to increase the surface area. We also have prepared microcapsules with large interconnected spherical pores prepared from a (W/O/W) emulsion by an *in situ* polymerization method. These are (W/O/W) type microcapsules [24]. The interconnected spherical pores are open to the outside of the microcapsules and can be freely accessed by water from outside the microcapsules. The (W/O/W) type microcapsules are considered to be an effective material for the microencapsulation of extractants thus providing a large surface area through the many interconnected pores. Actually, the extraction rate was accelerated by the formation of the interconnected spherical pores in the inside of the microcapsules [25, 26].

Hydroxyoximes are chelating type extractants and can extract many useful metals from aqueous solution. When 1-(2-hydroxyl-5-nonylphenyl)ethanone oxime (LIX84-I), which is an effective extractant for Ni(II), was used for microencapsulation by *in situ* polymerization, no microcapsules could be prepared due to the inhibition of the polymerization by LIX84-I which has a chemical structure similar to polymerization inhibitors. In this study, polymeric particles with interconnected spherical pores were firstly prepared from a (W/O/W) emulsion by *in situ* polymerization [25], and then the obtained polymeric particles were impregnated with LIX84-I by the solvent evaporation method. The effects of the preparation conditions on the impregnation of LIX84-I within the polymeric particles and the extraction properties of Ni(II) with the LIX84-I impregnated polymeric particles has been investigated under various conditions.

2. Experimental

2.1 Reagents

1-(2-hydroxy-5-nonylphenyl)ethanone oxime (LIX84-I, Cognis Co. , Ltd.) was used as the extractant. The chemical structure of LIX84-I is shown in Figure 1. Monomeric divinylbenzene (DVB) were purchased from Wako Pure Chemicals Co. and washed with 10 wt% NaOH aqueous solution to remove the polymerization inhibitor. The monomers were stored in a refrigerator until use. Trioctylamine (TOA), toluene, 2,2'-Azobis (4-methoxy-2,4-dimethylvaleronitrile)

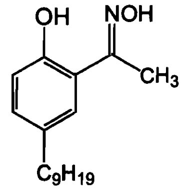

Figure 1. Chemical structure of LIX84-I.

(ADVN), polyvinyl alcohol (PVA, Polymerization Degree about 500), sodium dodecylsulfate (SDS), ammonium sulfate, nickel sulfate hexahydrate was purchased from Wako Pure Chemical Co. The hexaglycerin ricinoleic acid (818SX) was purchased from Taiyo Kagaku Co.

2.2 Preparation of polymeric particles impregnated with LIX84-I

The preparation scheme of polymeric particles impregnated with LIX84-I is shown in Figure 2. An aqueous solution containing NaCl at 4.5 mol/dm^3 was used as the inner aqueous phase (8 mL). The organic phase (72 mL) was prepared by dissolving the extractant, TOA (20 wt%), the surfactant, 818SX (10 wt%), the initiator, ADVN (1 wt%), and the wall material DVB (80 wt%) in toluene (10 wt%). The (W/O) emulsion was prepared by adding the inner aqueous phase to the organic phase and agitating at 3,000 rpm for 10 min. The (W/O) emulsion was added to the outer aqueous phase (720 mL), which was a mixture of PVA (2 wt%) and the SDS aqueous solutions (0.25wt%), to make the (W/O/W) emulsion at 343 K with stirring at 250 rpm. The solution was agitated at 250 rpm and 343 K for 5 hr. The polymeric particles obtained were washed with water and were dried under vacuum overnight. The polymeric particles obtained were immersed in ethanol to remove TOA. The polymeric particles were collected after filtration and drying under vacuum. The polymeric particles were immersed in a hexane solution of LIX84-I overnight. The hexane was removed from the particles with a rotary evaporator and the polymeric particles impregnated with LIX84-I were obtained after drying under vacuum.

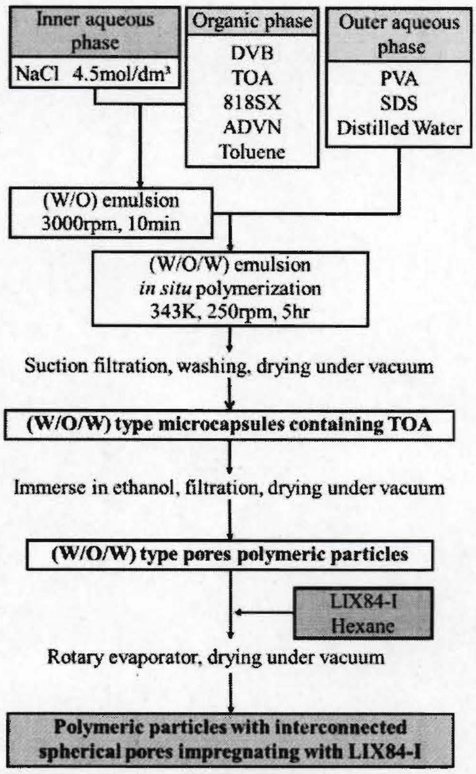

Figure 2. The preparation scheme for polymeric particles impregnated with LIX84-I with interconnected spherical pores.

2.3 Observation of polymeric particles impregnated with LIX84-I with interconnected spherical pores

The morphologies of the polymeric particles impregnated with LIX84-I and (W/O/W) type polymeric particles were observed by scanning electron microscopy (Hitachi, TM-1000, SEM) and a digital microscope (KEYENCE, VHX-600 system). The diameter of the polymeric particles was measured from the digital microscope images.

2.4 Measurement the degree of impregnation of the polymeric particles impregnated with LIX84-I

In order to determine the amount of LIX84-I impregnated in the polymeric particles, the polymeric particles were added to ethanol to elute LIX84-I from the polymeric particles, and the concentration of LIX84-I in the ethanol solution was measured by gas chromatography with FID (Shimadzu GC-17A). The percentage content of LIX84-I in the polymeric particles, *E*, the impregnated yield of

LIX84-I, E^* and the molar content of LIX84-I, E' were calculated using the following Eqs. (1), (2) and (3), respectively;

$$E = \frac{c_{\mathrm{LIX84-I}} \cdot M_{\mathrm{LIX84-I}} \cdot V_{\mathrm{ethanol}}}{W_{\mathrm{pp}}} \cdot 100 \quad [\%] \qquad (1)$$

$$E^* = \frac{E(W_{\mathrm{pp,add}} + W_{\mathrm{LIX84-I,add}})}{100 \cdot W_{\mathrm{LIX84-I,add}}} \cdot 100 \quad [\%] \qquad (2)$$

$$E' = \frac{E}{100 \cdot M_{\mathrm{LIX84-I}}} \quad [\mathrm{mol/kg}] \qquad (3)$$

where $C_{\mathrm{LIX84\text{-}I}}$, $M_{\mathrm{LIX84\text{-}I}}$, V_{ethanol}, W_{pp}, $W_{\mathrm{PP,add}}$, and $W_{\mathrm{LIX84\text{-}I,add}}$ are the molar concentration of LIX84-I in the ethanol solution, the molecular weight of LIX84-I, the volume of the ethanol solution, the weight of the polymeric particles used for the elution, and the weights of the polymeric particles and LIX84-I used for the preparation, respectively.

2.5 Extraction of Ni(II) from aqueous solutions

The extraction of Ni(II) into the polymeric particles was carried out batch wise. The prepared polymeric particles impregnated with LIX84-I (0.1 g) were added to 10×10^{-3} dm^3 of the 0.5 mol/dm^3 $(NH_4)_2SO_4$ aqueous solution containing Ni(II) and were shaken for 12 hr. at 303 K. After extraction, the polymeric particles were removed from the raffinate by filtration. The concentrations of Ni(II) in the raffinate and the feed solutions were measured by ICP-AES (Shimadzu, ICPS-8100). The amount of Ni(II) extracted into the polymeric particles, q_{eq}, and the forward extraction ratio, E_{e}, were calculated from Eqs. (4) and (5);

$$q_{\mathrm{eq}} = \frac{(c_{\mathrm{Ni,aq,ini}} - c_{\mathrm{Ni,aq}}) \cdot V_{\mathrm{aq}}}{W_{\mathrm{pp}} \cdot M_{\mathrm{Ni}}} \quad [\mathrm{mol/kg}] \qquad (4)$$

$$E_{\mathrm{e}} = \frac{c_{\mathrm{Ni,aq,ini}} - c_{\mathrm{Ni.aq}}}{c_{\mathrm{Ni,aq,ini}}} \cdot 100 \quad [\%] \qquad (5)$$

where $C_{\mathrm{Ni,aq,ini}}$, $C_{\mathrm{Ni,aq}}$, V_{aq} , M_{Ni} and W_{pp} are the initial concentration of Ni(II) in the aqueous phase, the equilibrium concentration of Ni(II) in the aqueous solution after extraction, the volume of the aqueous phase, the atomic weight of Ni(II) and the weight of the polymeric particles used for the extraction, respectively.

2.6 Extraction rate of Ni(II) into the polymeric particles

An aqueous solution containing at 100 mg/dm^3 Ni(II) was prepared by using the 0.5 mol/dm^3 $(NH_4)_2SO_4$ solution and adjusted to pH 7.5. The polymeric particles classified at 200 - 450 μm by sieving (0.50 g) were added to the Ni(II) solution adjusted to 303 K. The Ni(II) solution was collected at the prescribed time. When the sample was taken, the Ni(II) solution was filtered using a membrane filter (0.45 μm) and diluted using distilled water. The Ni(II) concentrations in the collected solution and the feed solution were measured by ICP-AES (Shimadzu, ICPS-8100). The amount of Ni(II) extracted into the polymeric particles was calculated from Eq.(4).

2.7 Back-extraction of Ni(II) extracted in the polymeric particles

The back-extraction of Ni(II) extracted in the polymeric particles to a new aqueous phase was carried out batch wise. The polymeric particles impregnated with LIX84-I (0.10 g) were added to 10×10^{-3} dm^3 of the 0.5 mol/dm^3 $(NH_4)_2SO_4$ aqueous solution containing excess Ni(II) and were shaken for 12 hr. at 303K. After extraction, the polymeric particles were recovered from the raffinate by filtration and were dried. Then the impregnated polymeric particles loaded with Ni(II) were placed in 10×10^{-3} dm^3 of an aqueous H_2SO_4 solution adjusted to pH 1 - 9 for 24 hr. at 303 K. After back-extraction, the polymeric particles were recovered from the raffinate by filtration. The Ni(II) concentration in the raffinate solution was measured by ICP-AES (Shimadzu, ICPS-8100). The back-extraction ratio of Ni(II) to the aqueous phase, E_b, was calculated using Eq. (6);

$$E_b = \frac{C_{Ni,aq,eluted} \cdot V_{aq} \cdot 100}{q_{eq} \cdot W_{pp}} \quad [\%] \tag{6}$$

where $C_{Ni,aq,eluted}$ is the concentration of Ni(II) in the aqueous solution after back-extraction.

3. Results and Discussion

3.1 Preparation of polymeric particles impregnated with LIX84-I with interconnected spherical pores

The SEM images of the surface and the cross sectioning of the prepared (W/O/W) type polymeric particles are shown in Figure 3. The polymeric particles had a porous and rough surface and many large interconnecting spherical pores in their inner side. These pores are formed by the inner aqueous phase. The average diameter of the polymeric particles was 208±26μm.

The SEM images of the surface and the cross section of the polymeric particles impregnated with LIX84-I are shown in Figure 4. No change of the morphologies of the polymeric particles by the impregnation of the LIX84-I was observed. It is considered that LIX84-I exists as a concentrated liquid in small pores and surface of the polymer wall of the polymeric particles.

The SEM images of the surface and the cross section of the (O/W) type polymeric particles prepared without the inner aqueous phase are shown in Figure 5. The (O/W) type polymeric particles were used for the extraction rate experiments of Ni(II). There are small spherical pores in the surface and inside of the polymeric particles, but they are densely packed inside. The average diameter of the polymeric

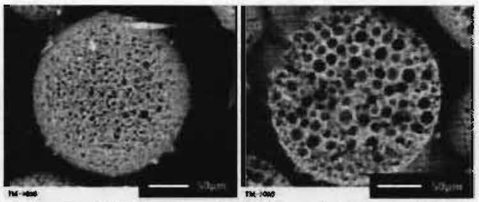

Figure 3. The SEM images of the (W/O/W) type polymeric particles (Left: surface, Right: cross-section).

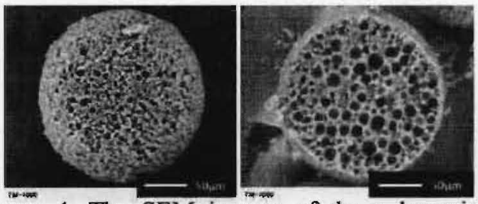

Figure 4. The SEM images of the polymeric particles impregnated with LIX84-I.
(Left: surface, Right: cross-section) $W_{LIX84-I}$ = 10 wt%.

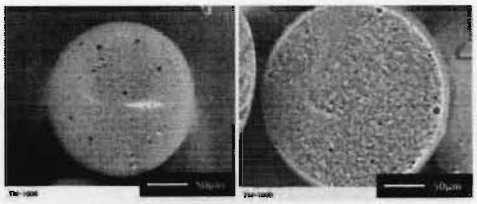

Figure 5. The SEM images of the (O/W) type polymeric particles.
(Left: surface, Right: cross-section).

particles was 207±47μm.

The effect of the added amount of LIX84-I on the percentage content, *E* and the impregnated yield, *E** of LIX84-I in the preparation of the polymeric particles impregnated with LIX84-I is shown in Figure 6. The percentage content gradually increased with the amount of LIX84-I added, and reached about 60%. Meanwhile, the impregnated yield was almost constant at about 80% regardless of the added amount of LIX84-I. The curve in Figure 6 is the theoretical quantity of the impregnated yield at 100%. Thus this method can achieve a high content of LIX84-I compared with the general result for the microcapsulation method for the extractant which usually achieved an extractant content of up to 30 wt%. However, at LIX84-I contents higher than 50%, the particles became sticky through leakage of LIX84-I.

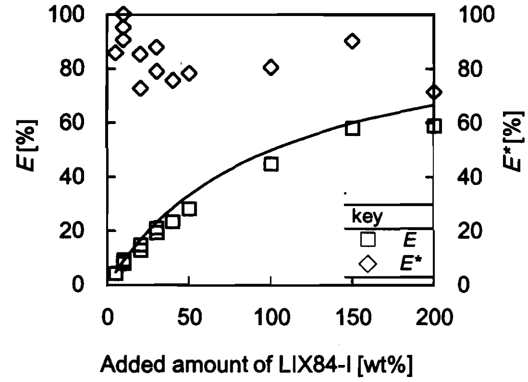

Figure 6. Effect of the concentration of LIX84-I on the percentage content and the impregnated yield of LIX84-I.

3.2 Extraction properties of Ni(II) using the polymeric particles impregnated with LIX84-I

The effect of the pH in the aqueous phase on the extraction of Ni(II) with the polymeric particles impregnated with LIX84-I is shown in Figure 7. *E*' in figure 7 is the molar content of LIX84-I per 1.0 g of the polymeric particles. In the acidic range, no Ni(II) was extracted. The extraction of Ni(II) increased with increasing pH. With an increase in the content of LIX84-I impregnated in the polymeric particles, the extraction pH range is shifted to lower pH values. The lines in figure 7 are the calculated results using the equilibrium constant for the extraction reaction determined as described later.

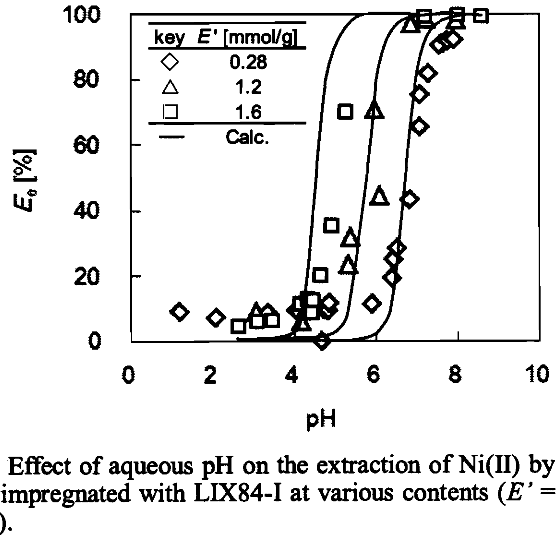

Figure 7. Effect of aqueous pH on the extraction of Ni(II) by polymeric particles impregnated with LIX84-I at various contents (*E*' = *E*, 10, 70, 100 wt%).

The effect of the initial concentration of Ni(II) on the extraction using the polymeric particles prepared with various LIX84-I contents is shown in Figure 8. The amount of Ni(II) extracted into the polymeric particles, q_{eq}, increased with an increase in the concentration of Ni(II) in the aqueous phase and reached a constant value at high Ni(II) concentration. When the content of LIX84-I in the polymeric particles was changed as shown in Figure 8, the molar quantity of Ni(II) extracted in the polymeric particles increased with an increase in the content of LIX84-I in the polymeric particles.

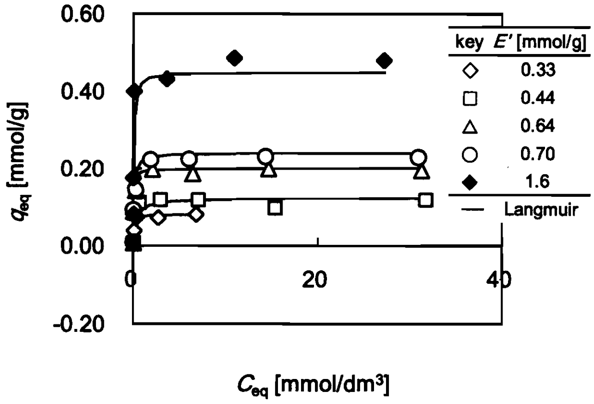

Figure 8. Effect of the initial concentration of Ni(II) on the extraction of Ni(II) with the polymeric particles prepared at various concentrations of LIX84-I.

The extraction behavior of Ni(II) into the polymeric particles conformed well to a Langmuir type adsorption as shown in Eq. (7) where q_{eq}, q_{max}, K, and C_{eq} are the molar equilibrium amount of Ni(II) extracted in the polymeric particles, the maximum molar amount of Ni(II) in the polymeric particles, and the equilibrium concentration of Ni(II) in the aqueous phase. The values of q_{max} and K were calculated from the results in Figure 8 using Eq. (8).

$$q_{eq} = \frac{q_{max} K C_{eq}}{(1+K C_{eq})} \tag{7}$$

$$\frac{1}{q_{eq}} = \frac{1}{q_{max}} + \left(\frac{1}{K q_{max}}\right)\left(\frac{1}{C_{eq}}\right) \tag{8}$$

The relationship between the molar content of LIX84-I per g of the polymeric particles, E', and the maximum molar amount of Ni(II) extracted in the polymeric particles, q_{max}, is shown in Figure 9. The plotted values of q_{max} gave straight line having a slope of 1/3. This result means that three molecules of LIX84-I react with each nickel ion and the extraction equilibrium is as shown in Eq. (9). In the solvent extraction system, it has been reported that two molecules of LIX84-I react with one nickel ion on extraction into the organic phase [27]. However molecules of LIX84-I impregnated in the polymeric particles would exist under conditions of no free movement and no solvent molecules around them. Therefore, the extraction conditions would be quite different from the solvent extraction system. Hence, one molecule of LIX84-I would act as a solvent to stabilize the extraction complex between two LIX84-I and one nickel ion. The detail of the extraction mechanism is not still clear. More investigation will be needed to understand the properties of the impregnated LIX84-I in the polymeric particles.

$$\mathrm{Ni^{2+} + 3HR \rightleftharpoons NiR_2(HR) + 2H^+} \quad \mathrm{HR~;~LIX84\text{-}I} \tag{9}$$

The extraction of Ni(II) with the polymeric particles impregnated with LIX84-I was analyzed using the extraction equilibrium results. From the extraction reaction shown in Eq. (9), the equilibrium constant, K_{eq}, of the extraction can be represented as in Eq. (10). The distribution coefficient, D, of Ni(II) is written as in Eq. (11). The logarithm of Eq. (10) wherein D is substituted is shown in Eq. (12).

$$K_{eq} = \frac{[\mathrm{NiR_2(HR)}][\mathrm{H^+}]^2}{[\mathrm{Ni^{2+}}][\mathrm{HR}]^3} \qquad [\mathrm{kg^2/(mol\cdot dm^3)}] \tag{10}$$

$$D = \frac{[\mathrm{NiR_2(HR)}]}{[\mathrm{Ni^{2+}}]} \qquad [\mathrm{dm^3/kg}] \tag{11}$$

$$\log\left(\frac{D}{[\mathrm{H^+}]}\right) = 3\log\left(\frac{[\mathrm{HR}]}{[\mathrm{H^+}]}\right) + \log K_{eq} \tag{12}$$

The value of log (D/[H$^+$]) was plotted against log ([HR]/[H$^+$]) in Figure 10. All results lay on a straight line whose slope was about 3. Hence, the extraction equilibrium reaction of Ni(II) proposed in Eq. (9) is also validated. From the intercept of the plot in Figure 10, the equilibrium constant, K_{eq} was determined as $2.13\mathrm{x}10^{-7}$ kg^2/(mol·dm^3).

The extraction of Ni(II) was calculated using the K_{eq} value obtained as shown in Figures 7 and 11, respectively. The extraction behavior calculated almost conformed to the measured values in Figures 7 and 8, respectively. From those results, the extraction equilibrium reaction of Ni(II) proposed in Eq.(9) is also validated.

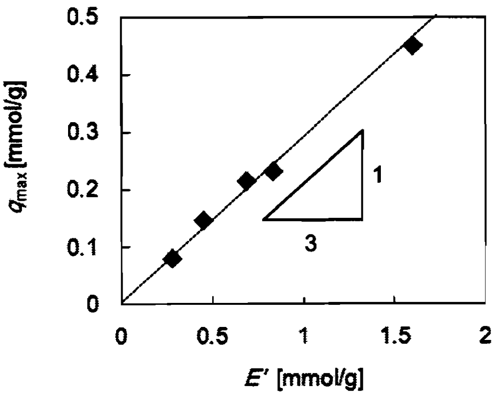

Figure 9. The relationship between the molar content of LIX84-I in the polymeric particles and the maximum quantity of extraction of Ni(II).

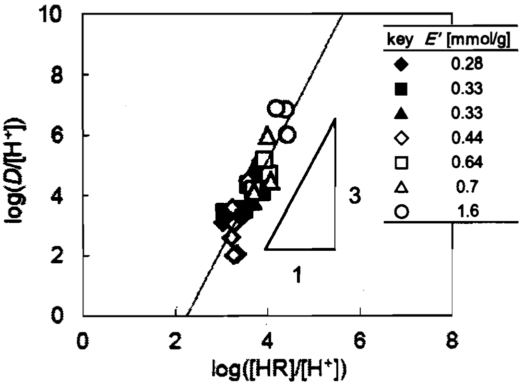

Figure 10. The relationship between log(D/[H$^+$]) and log([HR]/[H$^+$]).

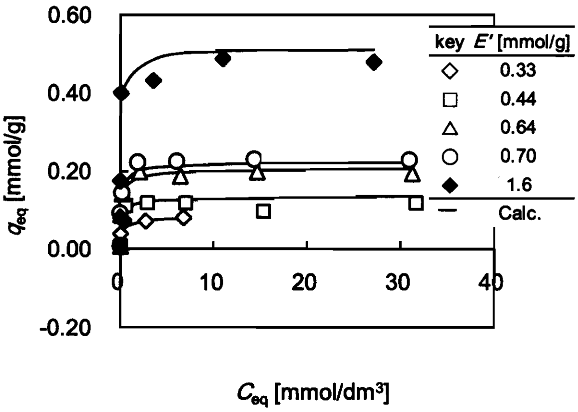

Figure 11. Effect of the equilibrium concentration of Ni(II) on the extraction of Ni(II) from the experimental results and by calculation.

The rates of Ni(II) extraction with the polymeric particles prepared with the inner aqueous phase at 4.5 mol/dm^3 NaCl and without the inner aqueous phase are shown in Figure 12. When the polymeric particles prepared with the 4.5 mol/dm^3 NaCl aqueous solution in the inner aqueous phase was used, the extraction of Ni(II) increased sharply with time and reached a constant value within 4 hr. denoting extraction equilibrium. On the other hand, the extraction with the polymeric particles prepared without the inner aqueous phase was slower than that of the polymeric particles prepared with the 4.5 mol/dm^3 NaCl aqueous solution in the inner aqueous phase. From these results, it is found that the interconnected spherical pores are very favorably for the extraction of Ni(II). This acceleration would be caused by the increase in the interfacial area of the polymeric particles and in the diffusion of Ni(II) to the inner space of the polymeric particles through the pores from the particles surfaces.

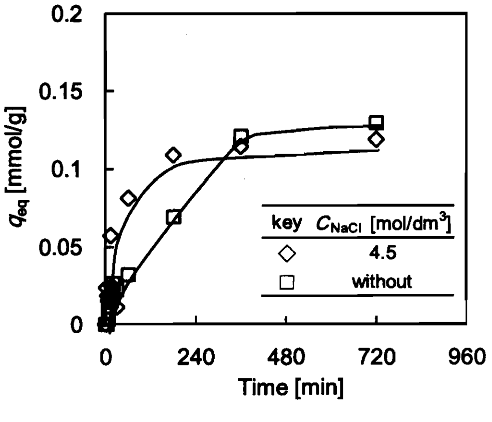

Figure 12. Effect of extraction time on the extraction of Ni(II) using the polymeric particles impregnated with LIX84-I prepared with and without the inner aqueous phase (E' = 0.44 mmol/g).

3.3 The back-extraction of Ni(II) extracted in the polymeric particles with various concentrations of an aqueous H_2SO_4 solution

The effect of the pH in the aqueous phase on the back-extraction of Ni(II) is shown in Figure 13. Ni(II) extracted into the polymeric particles could be back-extracted by using sulfuric acid solutions at pH values lower than 5. From this result, it was found that the reaction between LIX84-I and nickel ion proceeds reversibly.

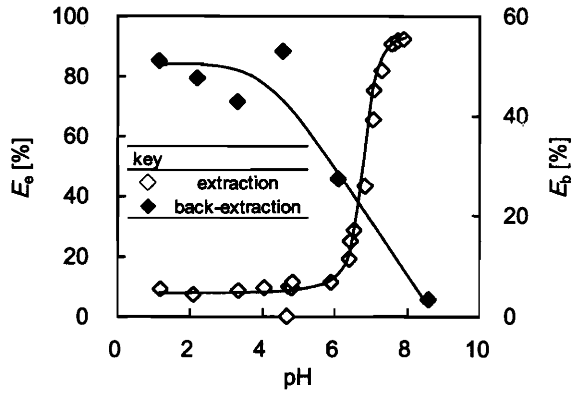

Figure 13. Effect of the aqueous pH on the extraction and back-extraction of Ni(II) extracted in the polymeric particles impregnated with LIX84-I (E' = 0.28 mmol/g).

4. Conclusion

Polymeric particles impregnated with LIX84-I were successfully prepared. The polymeric particles had a porous and rough surface and interconnecting-spherical pores inside the particles. The impregnation efficiency of LIX84-I was over 80% for all polymeric particles. The extraction of Ni(II) with the polymeric particles was successfully achieved and conformed well to the Langmuir type adsorption isotherm. Moreover, the back-extraction of Ni(II) from the polymeric particles was successfully achieved using H_2SO_4 aqueous solutions. It is confirmed that three molecules of LIX84-I reacted with one Ni(II) ion from the quantitative analysis of the relationship between the amount of Ni(II) extracted and the amount of LIX84-I impregnated in the polymeric particles. The extraction rate of Ni(II) was accelerated by the formation of the interconnected spherical pores in the inside of the polymeric particles.

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