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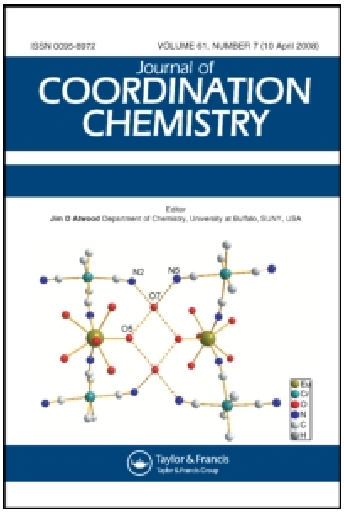

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Emulsion liquid membrane extraction of Ni(II) and Co(II) from acidic chloride solutions using bis-(2-ethylhexyl) phosphoric acid as extractant

Aziza Hachemaoui[a]; Kamel Belhamel[a]; Hans-Jörg Bart[b]
[a] Laboratory of Organic Materials, Process Engineering Department, Faculty of Technology, University of Bejaia, Algeria [b] Institute of Process Engineering, University of Kaiserslautern, Kaiserslautern, Germany

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Emulsion liquid membrane extraction of Ni(II) and Co(II) from acidic chloride solutions using bis-(2-ethylhexyl) phosphoric acid as extractant

AZIZA HACHEMAOUI†, KAMEL BELHAMEL*† and HANS-JÖRG BART‡

†Laboratory of Organic Materials, Process Engineering Department,
Faculty of Technology, University of Bejaia, DZ-06000 Bejaia, Algeria
‡Institute of Process Engineering, University of Kaiserslautern, Kaiserslautern, Germany

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An emulsion liquid membrane process using bis-(2-ethylhexyl) phosphoric acid (D2EHPA) to extract and separate Ni(II) and Co(II) from acidic chloride solutions is described. Liquid membrane consists of a diluent, a surfactant (Span 80), and an extractant (D2EHPA). Hydrochloric acid was used as the stripping solution. The important parameters governing the permeation of nickel and their effect on the separation process have been studied. These parameters are stirring speed, feed phase pH, surfactant concentration, extractant concentration, stripping phase concentration, phase ratio, initial concentration of metal, and treatment ratio. The optimum conditions have been determined. The separation factors of Ni(II) with respect to Co(II), based on initial feed concentration, have been experimentally determined. Furthermore, the extraction selectivity for Co(II) over Ni(II) has been improved by using D2EHPA during the initial minutes.

Keywords: Ni(II); Co(II); Extraction; Emulsion liquid membrane; D2EHPA

1. Introduction

Membrane processes for the separation of chemical species from a mixture are gaining importance and are emerging as viable alternatives to conventional separation processes [1]. The emulsion liquid membrane (ELM) technique was regarded as an emerging separation technology and was extensively examined for potential applications in fields such as hydrometallurgy, environmental engineering, biochemical engineering, pharmaceutical engineering, and food technology [2–15].

Selective separation of metal ions from industrial and waste solutions is frequently required in hydrometallurgical processing. Recently, new applications of solvent extraction processes with organophosphorus extractants for Ni(II) and Co(II) recovery and separation from spent catalysts, batteries, and leach residues have been described. The fact that Ni(II) and Co(II) usually appear together in such waste residues and ores, having similar physical and chemical properties and the high degree of purity required

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*Corresponding author. Email: kbelhamel@yahoo.fr

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in their applications have led to an extensive research on the separation [16] of Ni(II) and Co(II). Most of these studies concerned solvent extraction processes using organophosphorus acid extractants such as bis-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexylphosphoric acid mono-2-ethylhexyl ester (PC-88A), and bis(2,4,4-trimethylpentyl) phosphoric acid (Cyanex 272) [17–19]. Conventional extractants were also used for Co(II) extraction, an area of increasing interest over the last two decades in hydrometallurgy. Many studies are available in which emphasis was placed on the functional group of extractants. Extraction of Co(II) was carried out using bis(2,4,4-trimethylpentyl) phosphinic acid [20], bis(2-ethylhexyl) phosphinic acid (PIA-8) [21], the commercial extractant Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid) [22], tri-*n*-butylphosphate [23], alamine 336 [24], octanal oxime (OCOX) [25], and di-*n*-pentyl sulfoxide [26]. To understand the complexation mechanism in Ni(II) extraction processes, Hyvönen *et al.* [27] studied the complex formation equilibria of Ni(II) with *n*-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid. The subsequent development of phosphonic and phosphinic extractants led to drastic improvements in Ni(II) and Co(II) separation factors. The extraction of Ni(II) was performed using bis(2,4,4-trimethylpentyl)dithiophosphinic acid [28], aloxime 800 [29], mixture of 2-ethylhexanal oxime and D2EPHA [30], 3-mercapto-1,5 diarylformazans in the presence of 2,2′-bipyridine [31]. The organophosphoric acid, D2EHPA, is a very efficient and versatile extraction agent in liquid–liquid extraction processes for purification, enrichment, separation, and recovery of metal salts. D2EHPA replaces carboxylic acids in metal extraction because of its smaller extractant losses, higher metal loadings, and faster equilibrium rates [32].

A limitation in traditional solvent extraction is that a large inventory of solvent is required, especially when processing dilute solutions. Another limitation in traditional solvent extraction is high capital cost. The use of liquid membranes containing specific metal ion carriers offers an alternative method to the solvent extraction processes for selective separation and concentration of metal ions from aqueous dilute solutions [33]. Liquid membranes have shown great potential, especially in cases where solute concentrations are relatively low and other techniques cannot be applied efficiently, since membranes combine the processes of extraction and stripping in a single unit operation [34]. The extraction chemistry is basically the same as that found in solvent extraction, but the transport is governed by kinetic rather than equilibrium parameters [35]. Compared to conventional processes, ELM processes has some attractive features, for example, simple operation, high efficiency, extraction and stripping in one stage, larger interfacial area, and continuous operation. The ELM technique has great potential for the recovery and removal of different metal ions and hydrocarbons from wastewater where conventional methods provide lower separation efficiency [1]. Systems in the form of double emulsions are of two types: water-in-oil emulsion dispersed in an external aqueous phase and oil-in-water emulsion dispersed in an outer organic phase. A thin film of oil is formed between the outer (feed aqueous) phase and inner (stripping aqueous) phase, through which metal ions diffuse. The complex formed with the extractant at the interface of the emulsion globule and the feed phase is then shuttled through the organic phase to the stripping phase, from which it is stripped into the bulk region of the encapsulated phase. The process is completed by the separation of the emulsion [36–45].

In this study, ELM extraction and separation of Ni(II) and Co(II) from acidic chloride solutions using D2EHPA as extractant are reported. The effects of pH, extractant concentration, mixing speed, concentration of stripping solution, phase ratio, treatment ratio, and initial metal concentration on the extraction systems were studied. The optimum conditions of Ni(II) and Co(II) separation have been determined.

2. Experimental

2.1. *Reagents*

The liquid membrane phase is composed of a surfactant, an extractant, and a diluent. The extractant D2EHPA was purchased from Baysolvex BAYER and used without purification. Sorbitane monooleate (Span 80, Sigma–Aldrich) was used as a surfactant for emulsion formulations. Commercial kerosene (density $830\,\mathrm{kg\,m^{-3}}$ and viscosity 1.6 mPa at 20°C) was used as diluent. Hydrochloric acid solution of $0.5\,\mathrm{mol\,L^{-1}}$ was used as an internal phase. Hydrochloric acid and all other chemicals were purchased from Fluka and used as-received from the manufacturer. Ni(II) and Co(II) stock solutions were prepared by dissolving $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ in distilled water in which the pH was adjusted by adding a small amount of HCl.

2.2. *Experimental procedure*

In a 250 mL beaker, a 25 mL portion of D2EHPA and Span 80 in kerosene are emulsified at mixing speed of 2000 rpm using a rotor-stator type high-speed disperser (IKA Ultra Turrax T50). A 25 mL of $0.5\,\mathrm{mol\,L^{-1}}$ hydrochloric acid solution was used as the stripping solution, which was added dropwise to the stirred membrane solution. The solution was stirred continuously for 20 min so that the mixture of the membrane and the stripping solution was emulsified. In 250 mL beakers, the ELM prepared (membrane solution and stripping solution) was dispersed into the feed solutions. The three-phase dispersion was stirred at 25°C with a magnetic stirrer (Variomag Electronic Ruhrer Multipoint HP) at 400 rpm (except when the effect of stirring speed was studied). The uptake of the Co(II) and Ni(II) ions was monitored by removing samples of the feed phase periodically for analysis with an atomic absorption spectrophotometer (AAS). The concentration of solute, in the external aqueous phase, was measured with a Hitachi Z8100 AAS. The pH of the external phase was measured using a Metrohm 632, Bench-model-pH Meter.

3. Results and discussion

3.1. *Effect of pH feed solution on the extraction rate of Ni(II)*

The experiments were performed for different values of pH using small amounts of HCl solution. As shown in figure 1, Ni(II) extraction efficiency increased with increasing pH. The extraction is slower for pH 2.29 because the cationic exchange becomes more difficult when the acidity increases; maximum extraction was achieved at pH 5.62.

3.2. *Effect of stripping solution on the extraction rate of Ni(II)*

The effect of HCl concentration as the internal phase reagent on the extraction rate of nickel is shown in figure 2. An increase in the internal phase reagent concentration

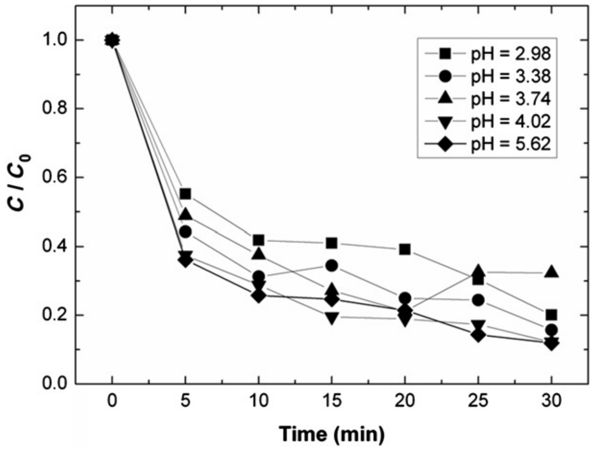

Figure 1. Effect of feed solution pH on the extraction rate of Ni(II): pH, (■) 2.98, (●) 3.38, (▲) 3.74, (▼) 4.02, (◆) 5.62; stirring speed, 400 rpm, surfactant concentration, 2%; extractant concentration, 8%; volume of stripping solution, 25 mL 0.5 mol L^{-1} HCl; treatment ratio, 0.2; phase ratio, 0.5; and initial Ni(II) concentration in the feed solution C_0, 249.6 ppm.

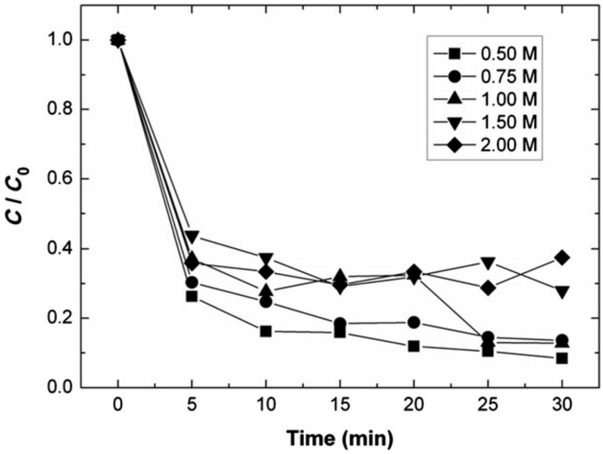

Figure 2. The effect of the HCl concentration as the internal phase reagent on the extraction rate of Ni(II): (■) 0.5 mol L^{-1}, (●) 0.75 mol L^{-1}, (▲) 1 mol L^{-1}, (▼) 1.5 mol L^{-1}, (◆) 2 mol L^{-1}; stirring speed, 400 rpm; surfactant concentration, 2%; extractant concentration, 8%; pH feed solution, 4.02; treatment ratio, 0.2; phase ratio, 0.5; initial Ni concentration in the feed solution C_0, 249.6 ppm.

decreases the ability of the internal phase for stripping Ni(II). However, for HCl concentration greater than 0.5 mol L^{-1}, the emulsion stability is poorer and swells up due to high osmotic pressure gradient between the internal and external phases, resulting in a less effective stripping. The results showed that 0.5 mol L^{-1} HCl is the best concentration as stripping solution for the internal phase.

3.3. *Effect of extractant concentration on the extraction rate of Ni(II)*

Extractant, present in membrane phase as carrier, promotes solute transfer through the ELM. The effect of carrier concentration on the extraction of nickel is

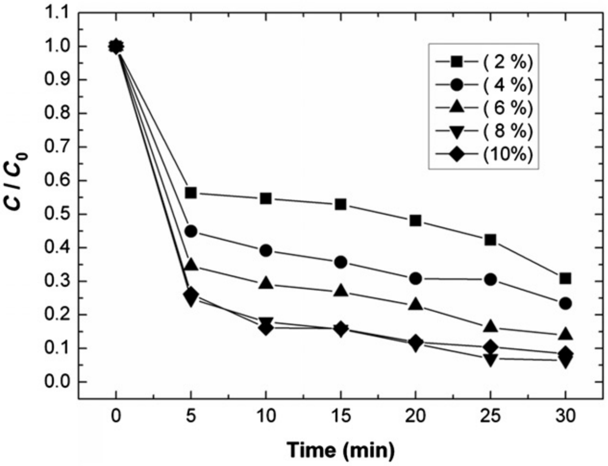

Figure 3. Effect of extractant concentration on the extraction rate of Ni(II): (■) 2%, (●) 4%, (▲) 6%, (▼) 8%, (◆) 10%; stirring speed, 400 rpm; pH feed solution, 4.02; treatment ratio, 0.2; phase ratio, 0.5; volume of stripping solution, 25 mL 0.5 mol L^{-1} HCl; initial Ni concentration in the feed solution C_0, 249.6 ppm.

shown in figure 3. The extraction efficiency increased with increase in the concentration of extractant from 2% to 8% because the carrier concentration in the membrane phase phenomenologically increases the interfacial solute concentration, and hence the driving force for extraction providing an increased extraction rate. Therefore, extractant concentration of 8% was selected as the best concentration. At very high carrier contents in the membrane, there is a decrease in the extraction rate and increase in viscosity, which leads to the formation of larger globules. The stability of the emulsion depends on the ratio of surfactant to extractant concentration. On the other hand, an increase in the surfactant concentration decreases the extraction efficiency of Ni(II) due to mass transfer resistance caused by the surfactant film. This phenomenon was observed by Sabry *et al.* [46].

3.4. *Effect of surfactant concentration on the extraction rate of Ni(II)*

Surfactant is used in ELM to reduce the interfacial tension between oil and water by adsorbing at the liquid–liquid interface. Surfactant concentration is an important factor as it directly affects the stability, swelling, and break up of ELM. Figure 4 shows the variation of extraction efficiency of Ni(II) for various Span 80 concentrations. Emulsion stability improves and the viscosity of the organic phase increases when the surfactant concentration increases due to the addition of more surfactants lowering the surface tension and resulting in smaller droplet size of the emulsion, which gives a larger mass transfer area and thus more efficient solute extraction [47]. Hence, the optimum value of Span 80 concentration was 2%.

3.5. *Effect of stirring speed on the extraction rate of Ni(II)*

The efficiency of ELM extraction increases with increase in stirring speed. Figure 5 shows the effect of stirring speed on the extraction rate of Ni(II). At higher mixing

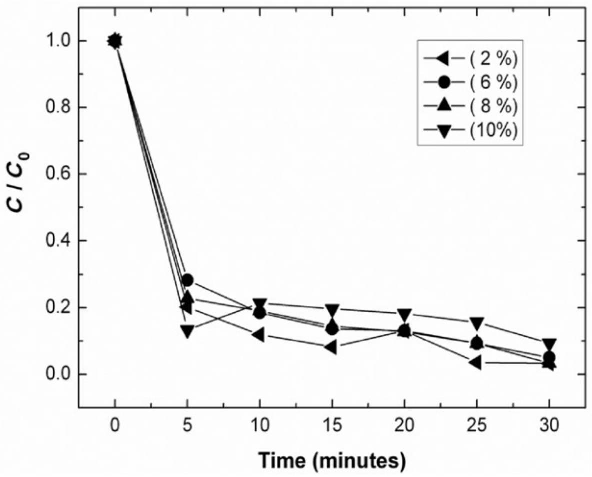

Figure 4. Effect of surfactant concentration on the extraction rate of Ni(II): (◀) 2%, (●) 6%, (▲) 8%, (▼) 10%; stirring speed, 400 rpm; pH feed solution, 4.02; extractant concentration, 8%; treatment ratio, 0.2; phase ratio, 0.5; volume of stripping solution, 25 mL 0.5 mol L^{-1} HCl; initial Ni(II) concentration in the feed solution C_0, 249.6 ppm.

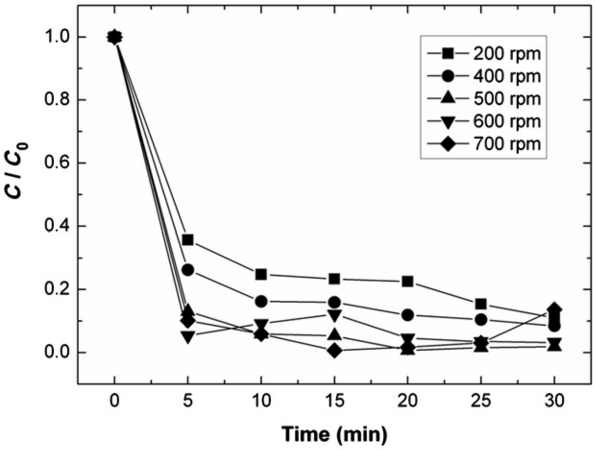

Figure 5. Effect of stirring speed on the extraction rate of Ni (II): stirring speed, (■) 200 rpm, (●) 400 rpm, (▲) 500 rpm, (▼) 600 rpm, (◆) 700; surfactant concentration, 2%; extractant concentration, 8%; pH feed solution, 4.02; treatment ratio, 0.2; phase ratio, 0.5; volume of stripping solution, 25 mL 0.5 mol L^{-1} HCl; initial Ni concentration in the feed solution C_0, 249.6 ppm.

speeds, smaller sized emulsion droplets were formed leading to more surface area for mass transfer. However, as the stirring rate is increased beyond 700 rpm, the emulsion droplets become more unstable and significant breaking of emulsion at the end of operation was observed, resulting in reduction of extraction.

3.6. *Effect of phase ratio on the extraction rate of Ni(II)*

Despite many advantages, the major reason that ELMs are not often used in a large scale in industries is due to their emulsion stability and lifetime, which are mostly too

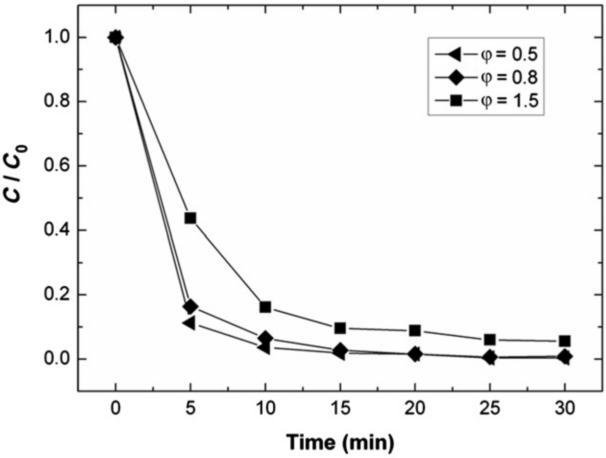

Figure 6. Effect of phase ratio on the extraction rate of Ni: phase ratio φ (V_s/V_m), (◀) 0.5, (◆) 0.8, (■) 1.5; stirring speed, 400 rpm; surfactant concentration, 2%; extractant concentration, 8%; pH feed solution, 4.02; treatment ratio, 0.2; volume of stripping solution, 25 mL 0.5 mol L^{-1} HCl; initial Ni concentration in the feed solution C_0, 249.6 ppm.

low to assure good commercial usage. The phase ratio plays an important role in determining the effectiveness of ELMs. The effect of phase ratio (V_s/V_m), where V_s and V_m are the volumes of the stripping and membrane solutions, respectively, is illustrated in figure 6. Further increase in the phase ratio to 1.5 decreases extraction efficiency of Ni(II) as the stability of emulsion deteriorates. When phase ratio is large, the emulsion globules are more densely packed with internal stripping phase droplets resulting in a decrease of the diffusion path length for Ni(II) extractant complex within the emulsion globule prior to getting stripped. Therefore, the stripping solution volume fraction of the emulsion has a profound influence on extraction using ELMs.

3.7. *Effect of treatment ratio on the extraction rate of Ni(II)*

Regarding the treatment ratio (V_e/V_f), where V_e and V_f are the volumes of emulsion and feed solutions, respectively, the extraction efficiency increases with increase in the treatment ratio. This can be explained by lowering the volume ratio leading to a thinner membrane thickness and hence a greater permeation rate. Figure 7 shows the influence of treatment ratio (V_e/V_f) on the extraction of Ni(II). When the emulsion phase holdup was 0.1, the rate of extraction was the least. Increasing emulsion holdup to 0.2 slightly increased the extraction efficiency. Therefore, the treatment ratio of 0.2 was used at optimum conditions.

3.8. *Effect of initial Ni(II) concentration in the external phase on the extraction rate of Ni(II)*

The effect of the initial Ni(II) concentration in the external phase C_0 was investigated by varying the concentration of Ni(II) from 100 to 600 ppm, where C denotes the concentration in the external continuous phase. Extraction rate of Ni(II) decreases

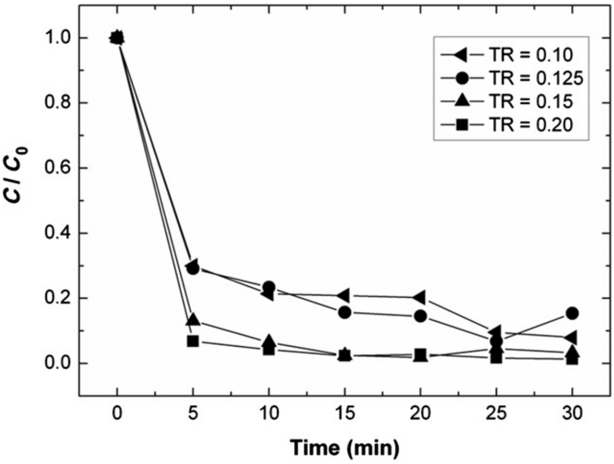

Figure 7. Effect of treatment ratio on the extraction rate of Ni(II): TR, treatment ratio (V_e/V_f) (◀) 0.1, (●) 0.125, (▲) 0.15, (■) 0.2; stirring speed, 400 rpm; surfactant concentration, 2%; extractant concentration, 8%; pH feed solution, 4.02; phase ratio, 0.5; volume of stripping solution, 25 mL 0.5 mol L^{-1} HCl; initial Ni concentration in the feed solution C_0, 249.6 ppm.

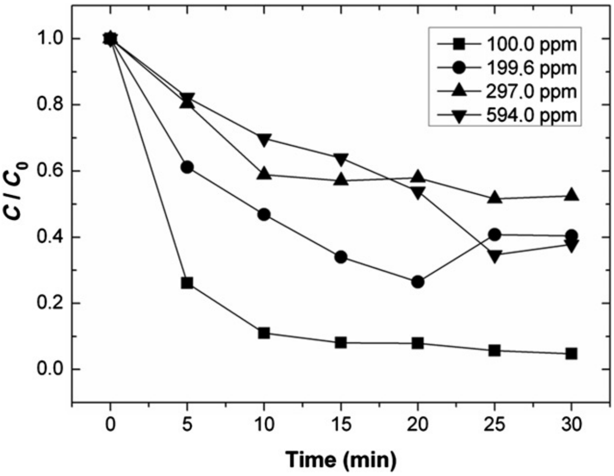

Figure 8. Effect of initial nickel concentration in the feed solution on the extraction rate of Ni(II): C_0, initial nickel concentration, (■) 100 ppm, (●) 199.6 ppm, (▲) 297 ppm, (▼) 594 ppm; stirring speed, 400 rpm; surfactant concentration, 2%; extractant concentration, 8%; pH feed solution, 4.02; phase ratio, 0.5; treatment ratio, 0.2; volume of stripping solution, 25 mL 0.5 mol L^{-1} HCl.

by increasing C_0. When the Ni(II) concentration is low, external mass transfer is under control and the extraction rate is higher than that at high Ni(II) concentration. Therefore, an increase in C_0 also corresponds to an increase in path length diffusion [48]. The effect of initial Ni(II) concentration in the external phase on the extraction rate of Ni(II) is shown in figure 8. The process of separation representing the flow diagram of ELM is shown in figure 9.

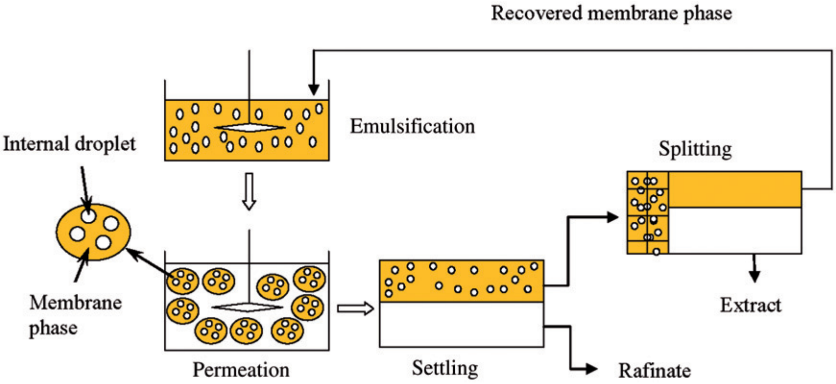

Figure 9. Flow diagram of ELM process.

Table 1. Separation factors of nickel over cobalt from feed mixture solutions.

	$\beta_{Ni/Co}$			
Feed mixture solution	5 min	10 min	20 min	30 min
100 mg L^{-1} Ni + 100 mg L^{-1} Co	0.67	0.81	0.92	0.99
200 mg L^{-1} Ni + 200 mg L^{-1} Co	0.58	0.76	0.79	0.96
50 mg L^{-1} Ni + 500 mg L^{-1} Co	0.35	0.52	0.66	0.69
100 mg L^{-1} Ni + 500 mg L^{-1} Co	0.38	0.87	0.89	0.75

Stirring speed, 400 rpm; surfactant concentration, 2%; extractant concentration, 8%; pH feed solution, 4.02; treatment ratio, 0.2; phase ratio, 0.5; and initial Ni concentration in the feed solution, 249.6 ppm.

3.9. *Optimum conditions*

The optimum conditions were experimentally determined from the effects of the parameters studied as follows:

- Feed solution, pH 4.02–5.62
- Stripping speed, 400 rpm
- Surfactant (Span80) concentration, 2%
- Extractant (D2EHPA) concentration, 8%
- Stripping solution, HCl concentration, 0.5 mol L^{-1}
- Treatment ratio (volume ratio of emulsion phase to feed phase), 0.2
- Phase ratio (volume ratio of strip phase to membrane phase), 0.5

3.10. *Membrane selectivity*

Under optimum conditions, the separation factors, extraction efficiencies and concentrations of metal ions in the strip solution are indicated in tables 1–3, respectively. The separation factor, $\beta_{Ni/Co}$, was calculated using equation (1)

$$\beta_{Ni/Co} = \frac{(C_{Ni(II)}/C_{Co(II)})_{strip}}{(C_{Ni(II)}/C_{Co(II)})_{feed}} \tag{1}$$

Table 2. Percentage extraction of nickel and cobalt from feed mixture solutions.

	Extraction from feed solution (%)							
	Ni				Co			
Feed mixture solution	5 min	10 min	20 min	30 min	5 min	10 min	20 min	30 min
100 mg L^{-1}Ni + 100 mg L^{-1} Co	60.16	76.66	89.19	97.22	88.94	94.61	97.75	98.24
200 mg L^{-1} Ni + 200 mg L^{-1} Co	43.46	70.83	75	90.86	74.822	93.26	94.73	94.37
50 mg L^{-1} Ni + 500 mg L^{-1} Co	17.69	38.48	58.84	65.45	50.49	74.06	88.74	94.63
100 mg L^{-1} Ni + 500 mg L^{-1} Co	20.98	41.82	68.26	67.8	55.22	89.92	75.65	91.49

Stirring speed, 400 rpm; extractant concentration, 8%; pH feed solution, 4.02; treatment ratio, 0.2; phase ratio, 0.5; volume of stripping solution, 25 mL 0.5 mol L^{-1} HCl; and initial Ni(II) concentration in the feed solution, 249.6 ppm.

Table 3. Variation of nickel and cobalt concentration in strip solutions.

	Concentration in strip solution (mg L^{-1})							
	Ni				Co			
Feed mixture solution	5 min	10 min	20 min	30 min	5 min	10 min	20 min	30 min
100 mg L^{-1}Ni + 100 mg L^{-1} Co	96.256	122.656	142.704	155.552	142.304	151.376	156.4	157.184
200 mg L^{-1} Ni + 200 mg L^{-1} Co	139.072	226.656	240	290.752	239.43	298.432	303.136	301.984
50 mg L^{-1}Ni + 500 mg L^{-1} Co	14.152	30.784	47.072	52.36	403.92	592.48	709.92	757.04
100 mg L^{-1} Ni + 500 mg L^{-1} Co	33.568	66.912	108.48	109.216	441.76	719.36	605.2	731.92

Stirring speed, 400 rpm; extractant concentration, 8%; pH feed solution, 4.02; treatment ratio, 0.2; phase ratio, 0.5; volume of stripping solution, 25 mL 0.5 mol L^{-1} HCl; and initial Ni(II) concentration in the feed solution, 249.6 ppm.

where $C_{\mathrm{Ni(II)}}$ and $C_{\mathrm{Co(II)}}$ are the concentrations of Ni(II) and Co(II), respectively, in stripping and initial feed phases. Clearly, D2EHPA extracts both Ni(II) and Co(II) with selectivity for Co(II) over Ni(II), especially at the beginning of extraction and at the higher starting concentration. Further, the separation of Ni(II) and Co(II) could be achieved by increasing the number of extraction stages.

4. Conclusion

An ELM process using D2EHPA to extract and separate Ni(II) from chloride solution has been investigated. From this study, the following conclusions can be drawn: (1) The optimum conditions have been determined experimentally. (2) D2EHPA exhibited poor selectivity of Ni(II) over Co(II) within the first minutes of the extraction process. Further separation of Ni(II) and Co(II) could be achieved by increasing the number of extraction stages. (3) At optimum conditions, the separation factors of Co(II) decrease in time for various Ni(II) and Co(II) mixtures. (4) For equimolar Ni(II) and Co(II) mixtures, when the Co(II) concentration in the feed solution increases, the separation factor of Co(II) also increases. However, for non-equimolar feed mixtures, the separation factor of Co(II) decreases as the Ni(II) concentration increases. (5) Reduced solvent amount required for the extraction and separation of Ni(II) and Co(II) is a promising feature of this technology for practical applications. (6) Experimental results showed the validity of ELM for purification of a solution containing Ni(II) and Co(II) mixtures.

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