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EMULSION LIQUID MEMBRANE EXTRACTION OF CERIUM IONS FROM ACIDIC SOLUTION USING CYANEX 301

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Abstract: Membrane processes for separation of chemical species from a mixture are gaining in importance and are emerging as a viable alternative to conventional separation processes. The emulsion liquid membrane (ELM) technique was regarded as an emerging separation technology and was extensively examined for potential applications in such fields as hydrometallurgy, environmental engineering, biochemical engineering, pharmaceutical engineering, and food technology. In the present work, the removal of Cerium ions from acidic solution by using an emulsion liquid membrane (ELM) technique was investigated and we obtained > 98% efficiency with the treatment. For the transport of Ce(III) ions using Cyanex 301 as extractant, the effects of extractant and surfactant concentrations, mixing speed, concentration and type of stripping solution, phase ratio, treatment ratio, and nature of diluent on the extraction rate were studies. Under the optimum conditions, solvent extraction and stripping of Ce(III) ions were investigated.

Keywords: *Ce(III) ions; Extraction; Emulsion liquid membrane; Cyanex 301*

I. Introduction

Membrane processes for separation of chemical species from a mixture are gaining in importance and are emerging as a viable alternative to conventional separation processes. The emulsion liquid membrane (ELM) technique was regarded as an emerging separation technology and was extensively examined for potential applications in such fields as hydrometallurgy, environmental engineering, biochemical engineering, pharmaceutical engineering, and food technology [1-3]. Due to large throughput, fast reaction, and easy phase separation, the major method used in the rare earth element separation industry is solvent extraction with mixer settler. However, this traditional equipment has many drawbacks, such as: large equipment area occupation, high energy consumption, and large solvent holdup [4]. To solve the problems, many types of methods and equipment are devised, such as hollow fiber contactor [5], impregnated polymer beads and resin [6-9], ionic liquid [10-13], magnetic absorption [14], and polymer sorbent [15], etc. Emulsion liquid membranes (ELM) separation technique [16] has been regarded as an emerging technology with considerable potential for a variety of applications such as recovery and concentration of metal ions and biochemical products and the removal of pollutants from waste waters. ELMs exhibit several attractive features in comparison with solvent extraction. These include a large specific surface area for extraction, simultaneous extraction and re-extraction in a single stage, and the requirement only

small quantities of an expensive carrier [17-19]. In view of all these advantages, the separation of metals by the ELM techniques has drawn considerable attention [20].

In the present work, Emulsion liquid membrane is investigated to select the suitable conditions for extraction of Ce (III) ions from acidic chloride solutions using Cyanex 301 as extractant. The effects of extractant and surfactant concentrations, mixing speed, concentration and type of stripping solution, phase ratio, treatment ratio, and nature of diluent on the extraction rate were studies. Under the optimum conditions, extraction of Ce(III) ions has been also studied for different feed mixture solution. Solvent extraction and stripping of Ce(III) ions were carried out in order to study the influence of the pH of the aqueous solution, the concentration of Cyanex 301, the equilibrium time on the extraction percent of Ce(III) ions and stripping percent of this metal ions from loaded organic phase by hydrochloric acid solution.

II. Material and methods
II.1. Reagents

Cyanex 301 and Sorbitane monooleate (Span 80) were supplied by Cytec Inc and sigma-Aldrich respectively. Commercial kerosene (density 830 kg m^{-3} and viscosity 1. 6 mPa at 20 °C), hydrochloric acid were obtained from Fluka. Cerium solutions were prepared by dissolving $Ce(NO_3)_3.6 H_2O$ and in distilled water. All this reagents were used as received.

II.2. Experimental Procedures
II.2.1. General extraction procedure

A suitable aqueous solution (10 mL) containing metal ions was equilibrated with an equal volume of Cyanex 301 diluted in kerosene in stoppered glass tubes using a mechanical shaker. Extraction experiments were carried out at the desired equilibrium pH values of the aqueous phase by adding dilute HCl. After phase disengagement, the aqueous phase was separated and metal concentrations were analyzed with a Hitachi Z8100 atomic absorption spectrophotometer (AAS). The concentration of metal ions in the organic phase was calculated from the difference between the metal ion concentration in the aqueous phase before and after extraction. The loaded organic phases were stripped with HCl. Stripping efficiency (% S) was calculated as the concentration of metal present in stripping phase after stripping to that part in organic phase at equilibrium. The distribution ratio, D was calculated as the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. All the experiments were carried out at room temperature (25°C). The pH value of the external phase was measured on a Metrohm 632, Bench-model-pH Meter.

II.2.2. Emulsion liquid membrane (ELM) procedure

In 250 mL beaker, a 25 mL portion of Cyanex 301 and Span 80 in kerosene are emulsified at mixing speed of 10000 rpm during 5 minute using a rotor-stator type high-speed disperser (IKA Ultra Turrax T 25). 25 mL of 0.5 M hydrochloric acid solution was used as stripping solution. Stripping solution was added dropwise to the stirred membrane solution. The solution was stirred continuously for 5 min, so that the mixture of the membrane and the stripping solutions were 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 stirred (Variomag Electronic Ruhrer Multipoint HP) at 500 rpm (except when the effect of stirring speed was studied). The uptake of the Ce(III) ions was monitored by removing samples of the feed phase periodically for analysis with an AAS.

III. Results and discussion
3.1 Solvent extraction
3.1.1 Effect of the pH equilibrium of the aqueous phase

In order to study the effect of equilibrium pH on the extraction of Ce(III) with Cyanex 301, experiments were conducted in the equilibrium pH range 1–6. The results, presented in fig.1, show that Cyanex 301 can efficiently extract Ce(III) (up to 99%) at pH above 3, i.e. this extracting agent does not requires very strict pH control.
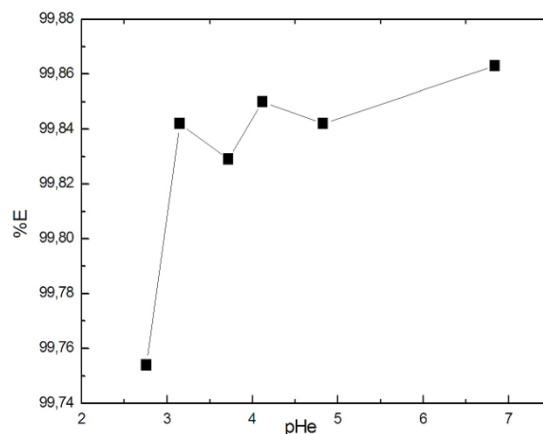

Figure1: Effect of feed solution pH on the extraction percentage of Ce(III). (Stirring speed: 500 rpm, surfactant conc.:2%, extractant conc.: 8%, stripping solution: 25mL 0.5 M HCl, treatment ratio: 1/5; phase ratio:0,5 ; initial Ce(III) concentration in the feed solution : 327 ppm

III.1.2 Effect of equilibrium time

The effect of equilibrium time on the extraction of Ce(III) ions from chloride solution is presented in Fig.2. It was observed that more than 99% of Ce(III) ions was achieved within 15 min.
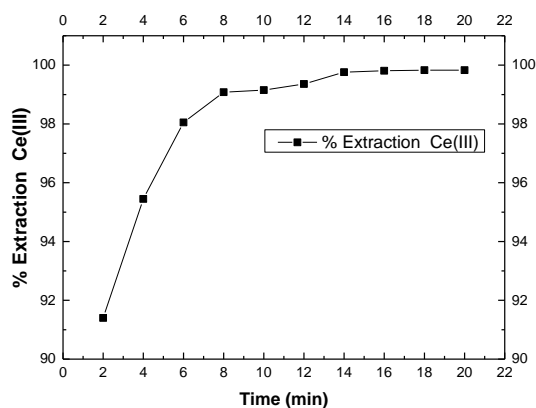

Figure 2: Effect of strip phase concentration on the extraction percentage of Ce(III), (stirring speed: 500 rpm, surfactant conc.: 2%, extractant conc.: 8%, pH feed solution: 4.02, treatment ratio: 1/5; phase ratio: 0.5 M; initial Ce(III) concentration in the feed solution: 327 ppm).

III.1.3 Effect of Cyanex 301 concentration

The effect of Cyanex 301 concentration on the extraction *percentage* of Ce(III) ions was studied in the range 0.01– 0.5 M is show in Fig.3. It was observed that more than 99% of Ce(III) ions recovery was achieved within 12 minute with optimum concentration 0.1M of Cyanex 301.
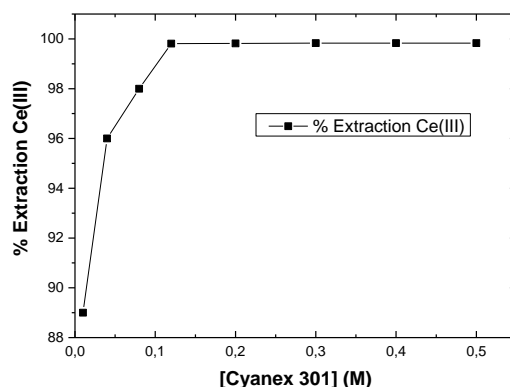
Figure 3: Effect of extractant concentration on the extraction percentage of Ce(III), (stirring speed: 500 rpm, surfactant concentration: 2%, pH feed solution: 4.02 , treatment ratio: 1/5; phase ratio: 0.5M ; stripping solution: 25mL 0.5 M HCl, initial Ce(III) concentration in the feed solution: 327 ppm).

III.2. Emulsion liquid membrane (ELM)
III.2.1 Effect of stripping phase concentration

Fig. 4 shows that during the first minute the extraction rate slightly increased with the increase in HCl concentration from 0.5 to 2 M because the capacity of the receiving phase increased, but this increase is not significant and the three curves converge at the end of run time indicates that the Ce(III) ions extraction took place in all three cases. In addition, emulsion stability not affected by the variation of stripping phase concentration.
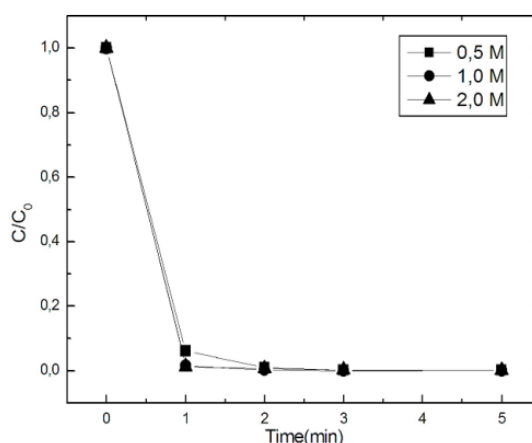

Fig. 4: Effect of stripping phase concentration on the extraction rate of Ce(III):
[SPAN 80]: 3.0%, [Cyanex 301]:0.05M, stirring speed: 500 rpm, treatment ratio: 1:5, phase ratio: 1, pH feed solution: 4.02, initial Ce(III) concentration in the feed solution: 327 ppm

III.2.2 Effect of stripping solution type

The selection of suitable stripping solution is considered to be one of the key factors for an effective ELM system. Here we examined the availability of stripping solutions for the ELM, which were commonly used in ELM process: HCl, H_2SO_4, and HNO_3. The results were shown in fig.5. It was found that stripping solution with 0.5 M HCl solution gave slightly higher Ce(III) extraction. Therefore, 0.5 M hydrochlorid acid was selected as the best stripping solution. As seen from this figure, the stability of emulsion not affected for all three stripping solution type.
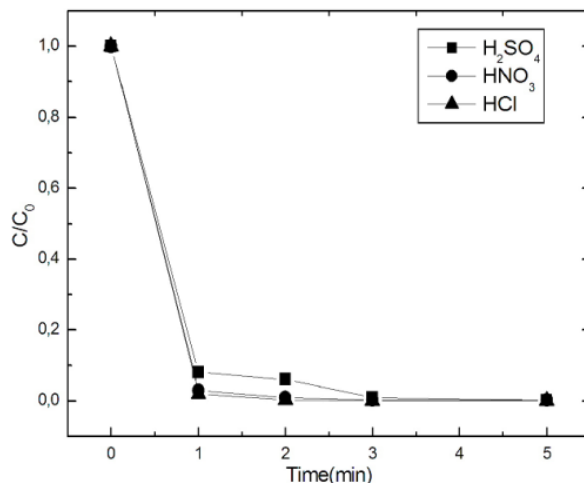
Fig. 5: Effect of stripping phase type on the extraction rate of Ce(III): [SPAN 80]: 3.0%, [Cyanex 301]:0.05M, concentration of stripping solution: 0.5M, stirring speed: 500 rpm,   treatment ratio: 1:5, phase ratio: 1, pH feed solution: 4.02, initial Ce(III) concentration in the feed solution: 327 ppm

III.2.4 Effect of surfactant concentration

Fig.6 represents the variation of extraction efficiency of Ce(III) for various surfactant concentrations. It was observed that extraction efficiency of cobalt up to two minute decrease for surfactant concentration of 1% and 7%. Because after this period the extraction efficiency of Ce(III) decreased due to deterioration of stability of emulsions to be formed with 7% and 1% concentrations. Additionally, it is known that the increase of surfactant concentration leads to a higher viscosity of the W/O emulsion and does not favour for the extraction kinetics [21]. Hence, the optimum Span 80 concentration was taken as 3%.
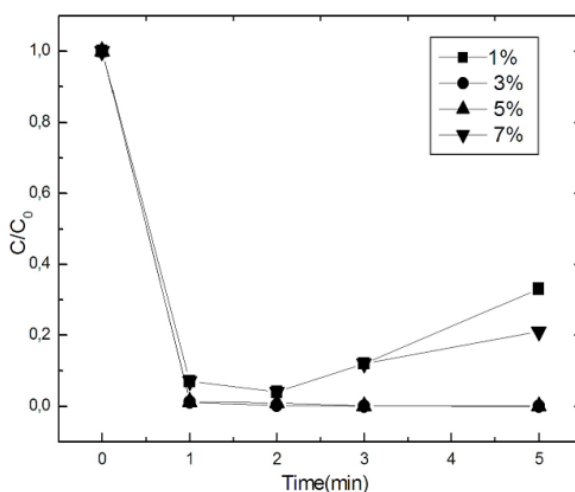

Fig. 6: Effect of surfactant concentration on the extraction rate of Ce(III):
[SPAN 80]: (1%-7%), [Cyanex 301]:0.05M, [HCl]: 0.5M, stirring speed: 500 rpm, treatment ratio: 1:5, pH feed solution: 4.02, phase ratio: 1, initial Ce(III) concentration in the feed solution: 327 ppm

III.2.5 Effect of stirring speed

Effects of stirring speed on the extraction of Ce(III) are studies in the range of 300 through 700 rpm are shown in Fig.7. At higher mixing speed, smaller sized emulsion droplets were formed leading to more surface area for mass transfer. However, it is not possible to increase the rotating speed over 700 rpm without having breaking of emulsion and leakage of the stripping solution. Hence, the stirring speed was taken as 500 rpm to ensure a good stability of the W/O emulsions and to enhance the interfacial area available for mass transfer.
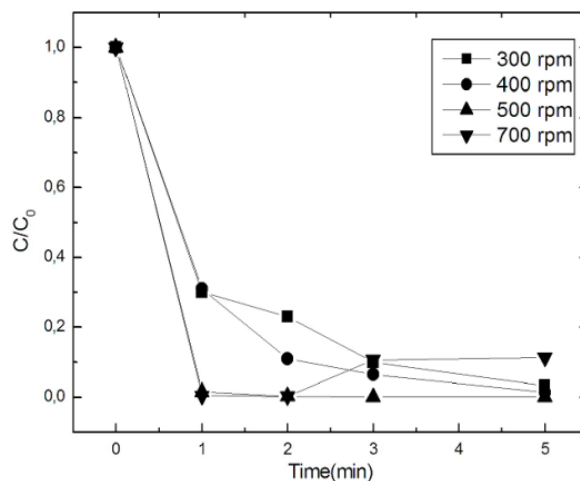

Fig. 7: Effect of stirring speed on the extraction rate of Ce(III):[SPAN 80]: 3.0%, [Cyanex 301]:0.05M, [HCl]:0,5M, treatment ratio: 1:5, phase ratio: 1, pH feed solution: 4.02, initial Ce(III) concentration in the feed solution: 327 ppm

III.2.6 Effect of phase ratio

The phase ratio, defined as the ratio of strip phase volume (Vs) to the membrane phase volume (Vm), showed an increase in the rates of extraction of Ce(III) when the volume ratio of the stripping solution to the membrane solution change from 0.5 to 1.5 because when phase ratio is large, the emulsion globules are more densely packed with the internal stripping phase droplets, this results in a decrease of the diffusion path length for the Ce(III)-extractant complex within the emulsion globule prior to getting stripped. It was also seen from fig.8 that phase ratio of 1.5 and 1 are comparable. Therefore, phase ratio: 1 was used at optimum condition.
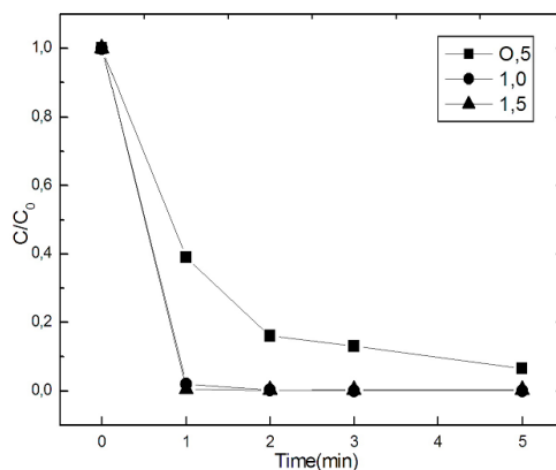

Fig. 8: Effect of phase ratio on the extraction rate of Ce(III):
[SPAN 80]: 3.0%, [Cyanex 301]:0.05 M, [HCl]: 0.5M, stirring speed: 500rpm, treatment ratio: 1:5, pH feed solution: 4,02, initial Ce(III) concentration in the feed solution: 327 ppm

III.2.7 Effect of treatment ratio

Treatment ratio defined as the ratio of emulsion phase volume (VE) to the feed phase (VF), plays an important role in determining effectiveness of ELM. As seen from fig.9, it is evident that an increase in treatment ratio, leads to an increase in the extraction efficiency especially at the beginning of extraction process, because with an increase in the treatment ratio, the volume of both the carrier and stripping reagent, i.e. the volume of emulsion as whole increased. Therefore, the surface area for mass transfer owing to the formation of a large number of emulsion globules increased. Additionally, the influence of the volume ratio of emulsion to the feed solution on the stability was not significant, because the breakage decreases very slightly with a decrease of this volume ratio. Therefore, treatment ratio: 0.2 was used at optimum condition.
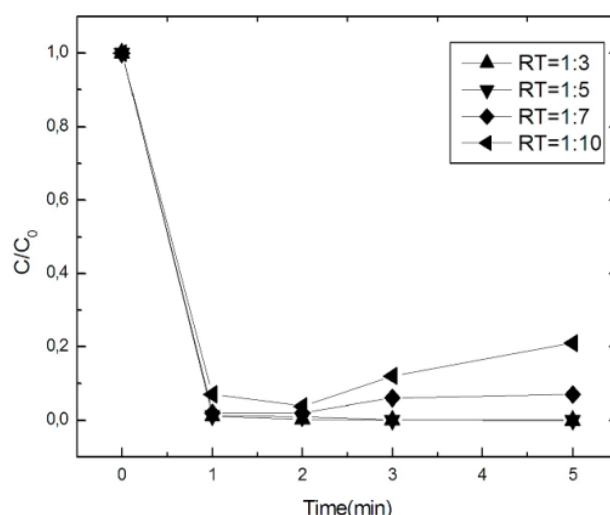

Fig. 9: Effect of treatment ratio on the extraction rate of Ce(III):[SPAN 80]: 3.0%, [Cyanex 301]:0.05M, [HCl]: 0.5M, stirring speed: 500rpm, pH feed solution: 4.02, phase ratio: 1, initial Ce(III) concentration in the feed solution: 327 ppm

III.2.8 Effect of nature of diluent

The diluent is an important factor as it directly affects the stability of ELM. It is observed from fig.10 that extraction efficiency of cobalt is better than that obtained with toluene because toluene has higher viscosity than kerosene. Therefore, kerosene is the best choice of diluent.
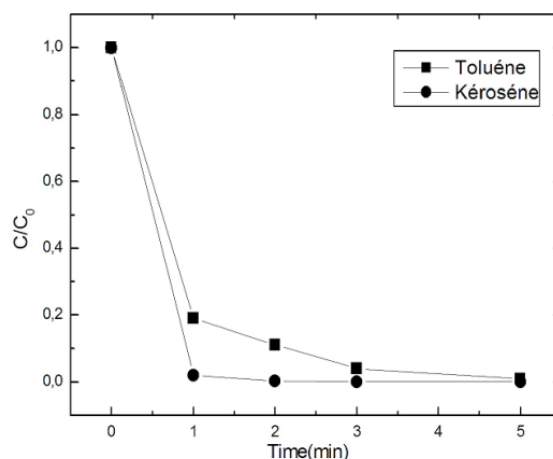

Fig. 10: Effect of nature diluent on the extraction rate of Ce(III): [SPAN 80]: 3.0%, [Cyanex 301]:0.05M, [HCl]: 0,5M, stirring speed: 500rpm, pH feed solution: 4.02, treatment ratio: 1:5, phase ratio: 1, initial Ce(III) concentration in the feed solution: 327 ppm

IV. Conclusion

An emulsion liquid membrane process using Cyanex 301 as extractant to extract Ce(III) ions from the chloride solution has been investigated. From this study the following conclusions can be drawn:

- The optimum conditions have been determined experimentally as stated above (table 1).
- Cyanex 301 exhibited a quantitative Ce(III) extraction.
- ELM using Cyanex 301 as extractant and HCl as stripping phase at low concentration allows extraction of Ce(III).
- The reduced of solvent and extractant concentration amount required for extraction Ce(III) ions for the promising performance of this technology in practical applications.
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Table 1 Optimum conditions for the extraction of Ce(III) ions with ELM

Parameter	Value
Surfactant (Span 80)	3%
Extractant (Cyanex 301)	0.1 M
Stripping solution type	0.5 HCl
Mixing speed	500 rpm
Phase ratio	1
Treatment ratio	1:5
Diluent	Kerosene

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