Application of Liquid Emulsion Membrane Technique for the Removal of Cadmium(II) from Aqueous Solutions Using Aliquat 336 as a Carrier

B. Medjahed, M. A. Didi, B. Guezzen

***Abstract*—In the present work, emulsion liquid membrane (ELM) technique was applied for the extraction of cadmium(II) present in aqueous samples. Aliquat 336 (Chloride tri-N-octylmethylammonium) was used as carrier to extract cadmium(II). The main objective of this work is to investigate the influence of various parameters affected the ELM formation and its stability and testing the performance of the prepared ELM on removal of cadmium by using synthetic solution with different concentrations. Experiments were conducted to optimize pH of the feed solution and it was found that cadmium(II) can be extracted at pH 6.5. The influence of the carrier concentration and treat ratio on the extraction process was investigated. The obtained results showed that the optimal values are respectively 3% (Aliquat 336) and a ratio (feed: emulsion) equal to 1:1.

***Keywords*—Cadmium, carrier, emulsion liquid membrane, surfactant.

I. Introduction

THE continuous use of heavy metals in industrial applications with the production of contaminated waste waters is a serious environmental problem. As heavy metals are not biodegradable, they tend to accumulate in living organisms causing various diseases and disorders [1]. Cd(II) is considered as highly toxic heavy metal, which is commonly used in a number of industrial applications.

ELM is known to be one of the most effective methods for separation and concentration when the material being extracted is present in very low concentration. As a result, the ELM has been considered a promising alternative technology for diverse separation processes including removal and recovery of various heavy metals such as copper, zinc, nickel, Cd, and mercury [2]-[6].

Many successful applications of ELMs for separation processes in general, and especially for removal of heavy metal ions from wastewaters have been reported in the literature [7]–[9]. The objective of this study was to determine the parameters that influence the extraction of Cd(II).

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II. Experimental

A. Reagents

The reagents used in this study were Chloride tri-N-octylmethylammonium (Aliquat336) (Sigma-Aldrich Chemicals Co.) used as a carrier, dichloromethane (Fluka) used as organic solvent, nonionic surfactant (polyoxyethylene sorbitan monolaurate) which is commercially known as Tween 20 (Aldrich). Cd nitrate (tetrahydrate) with a formula $Cd(NO_3)_2{\cdot}4H_2O$ (Aldrich), is used to prepare a stock solution of Cd. Aqueous nitric acid (Fluka) solutions were used as an internal phase. 4-(2-Pyridylazo) resorcinol (PAR) (Fluka) was used as ligand for complexation of Cd(II) in order to be analyzed.

B. Procedure

Stable emulsion liquid is prepared by emulsifying aqueous solution of nitric acid (internal phase) of different concentrations with an organic phase (membrane phase) containing carrier, surfactant and organic solvent, using vortex agitator for 5 min. The emulsion is then immediately dispersed into a glass reactor (10.0 cm diameter) containing aqueous feed phase of Cd ions and continuously stirred with a magnetic stirrer fixed speed for different time intervals. After stirring, phase separated in cylindrical separating funnels and samples of about 8 ml are withdrawn and filtered through a filter paper to separate the remaining emulsion droplets and the aqueous feed phase, and then, are analyzed.

C. Analytical Method

The concentration of Cd(II) was measured by taking samples from batch ELM reactor periodically, and all the Cd(II) samples were then analyzed by Analytik Jena SPECORD 210 Double Beam UV-VIS which was used for spectra recording and absorbance measurements. pH measurements for all solutions were taken on a potentiometer Consort C831, with combined glass electrode, that was calibrated with buffer standards at different pH values. Spectra have been recorded over the range 4000-800 nm [10].

The Cd(II) concentrations in the aqueous phase were determined, before and after extraction by UV-Visible with PAR as ligand for Cd(II) at pH 9. The absorbance of PAR-Cd(II) complex was measured at 520 nm.

The batch ELM experiments were conducted at room temperature of 25 °C. A combined glass electrode was calibrated with pH 4.00, 7.00, and 10.00 buffer standards. The Cd(II) concentrations in the aqueous phase were determined, before and after extraction by UV-Visible with PAR as ligand for Cd(II) at pH 9. The absorbance of PAR-Cd(II) complex was measured at 520 nm. The batch ELM experiments were conducted at room temperature of 25 °C.

D. The Investigated Parameters

The effects of parameters such as contact time, treat ratio, carrier concentration, pH of feed phase and nitric acid concentration in the internal phase were reported with the aim of determining the best conditions of extraction.

III. Results and Discussions

A. Effect of the Contact Time

Study the effect of stirring time on extraction yield is very important as a design parameter. The effect of stirring time on Cd(II) extraction efficiency was examined in the range from 1 to 25 minutes. From the results presented in Fig. 1, it is clear that complexation kinetics is fast, and extraction yield remains about 90% for the studied range of stirring time.

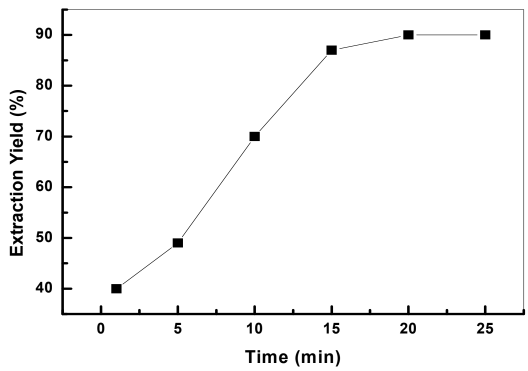

Fig. 1 Effect of contact time

B. Effect of Treat Ration

The effect of ($V_{external}/V_{emulsion}$) ratio on metal extraction is presented in Fig. 2. The results showed that the extraction yield decreases with the increase of the ratio.

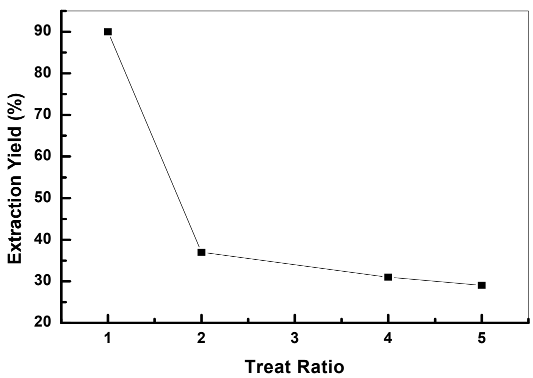

Fig. 2 Effect of treat ratio

The decrease of the yield on extraction between both ratios 1/1 and 2/1 is more important.

Compared to the amount of feed treated, enrichment factor achieved reduction in equipment size and the cost of chemicals, and the reduction of the yield on extraction beyond ratio 4/1 is negligible.

C. Effect of Carrier Concentration

The results presented in Fig. 3 showed that a maximum of extraction yield (90%) is reached for a value equal to 3% of carrier (Aliquat 336).

Higher values of carrier resulted in a decrease of extraction due to increase in the viscosity of the membrane phase.

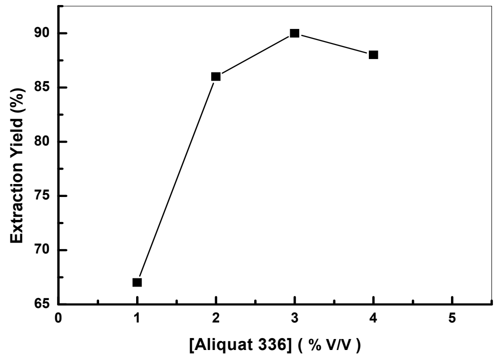

Fig. 3 Effect of carrier concentration

D. Effect of pH of Feed Phase

The effect of pH on stripping is presented in the Fig. 4. As can be seen from the plot, Cd stripping is maximum at pH=6.5 Here stripping phase is HNO_3.

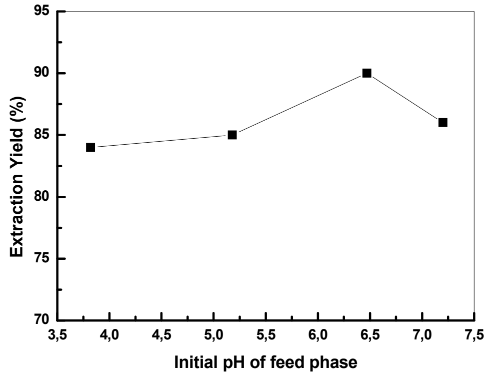

Fig. 4 Effect of pH of feed phase

E. Effect of Nitric Acid Concentration in Internal the Phase

The influence of nitric acid concentrations (0.05–0.5 molar) on the emulsion stability at optimum emulsification speed, at constant surfactant concentration, carrier concentration 3% v/v, organic solvent (dichloromethane) at a mixing speed 250 rpm, O/A ratio 1 and contact time 20 min have been studies. It can be noted from Fig. 5 that when the nitric acid concentration increases from 0.3 to 0.5 M, the extraction yield increases.

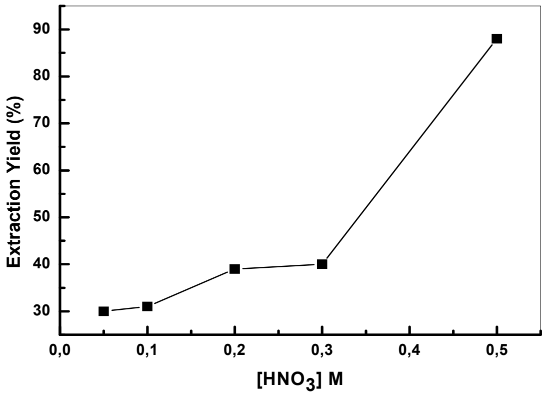

Fig. 5 Effect of nitric acid concentration in the internal phase

F. Effect of Addition of Sodium Nitrate

The influence of the ionic strength on the extraction yields of Cd(II), was studied by adding the salt of sodium nitrate to the aqueous phase.

The results, presented in Fig 6, showed that the addition of amount of the nitrate sodium to the aqueous phase, in the range 0.01-0.5 M, has an antagonistic effect on the yield of extraction.

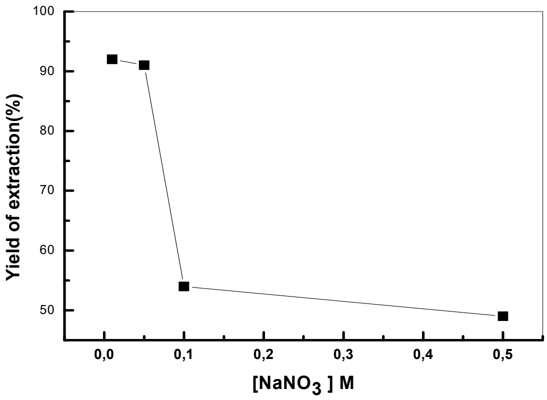

Fig. 6 Effect of the addition of nitrate of sodium V_{aq}/V_{org}= 1, [Cd(II)] = 10^{-3} M, T =20 °C

G. Effects of Potassium Thiocyanate Concentration

The effect of concentration of KSCN on Cd(II) extraction was studied at initial pH equal to 6.47 and fixed initial concentration of Cd ion equal to 10^{-3} M. Results are presented in Fig. 7.

The experimental results showed that the addition of KSCN, at a concentration of 0.1 M, increased the yield of extraction until 94%, and the influence of the KSCN concentration on the extraction of Cd(II) is relatively important.

Changing the ionic strength by the addition of an electrolyte influences the transport of metal ion in at least two ways:

- by affecting interfacial potential and, therefore, the activity of electrolyte ions.
- by affecting the competition of the electrolyte ions [11].

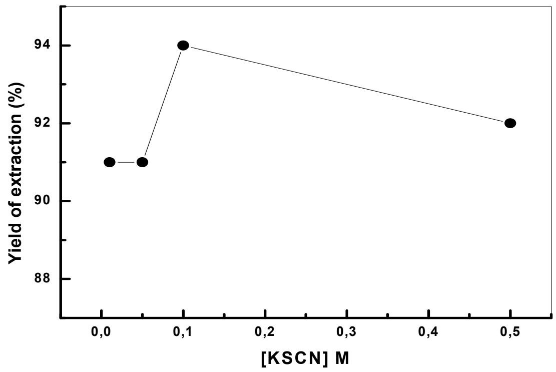

Fig. 7 Effect of addition of potassium thiocyanate Vaq/Vorg= 1, [Cd(II)] = 10^{-3}M, T =20°C

The identification and the quantification of the present chemical species, in aqueous phase, were obtained by the use of a software called Chemical Equilibrium in Aquatic System (CHEAQS) [12].

The results, recapitulated in Table I, showed that the corresponding majority chemical species in the best conditions of extraction (94%) are the $Cd(SCN)^{3-}$ ions and molecules $Cd(SCN)_2$ (aq).

TABLE I
RATE OF THE PRESENT CHEMICAL SPECIES IN THE AQUEOUS PHASE
[KSCN] = 0,1 M, [Cd(II)] = 10^{-3} M, pH = 6,47

Chemical species	Rate of species (%)
$Cd(SCN)^{3-}$	67.14
$Cd(SCN)_2$(aq)	27.10
$Cd(SCN)^{+}$	4.28
$Cd(SCN)^{+}$	1.36

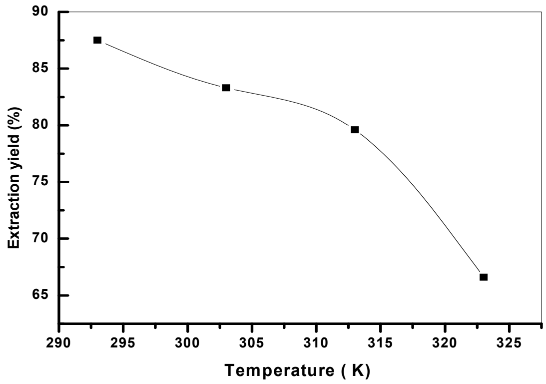

Fig. 8 Variation of extraction yield with temperature Vaq/Vorg= 1, [Cd(II)] = 10^{-3} M, pH= 6.5

H. Effect of Temperature

The effect of temperature on the extraction of the Cd(II) ions was studied under optimum conditions.

The results presented in Fig. 8 showed that the extraction reaction of the Cd(II) is favored by a relative decrease of the temperature.

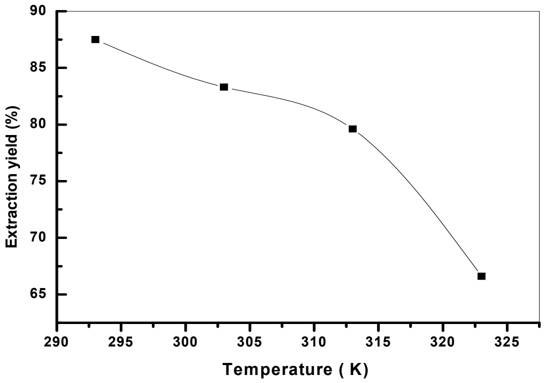

Fig. 8 Variation of extraction yield with temperature Vaq/Vorg= 1, [Cd(II)] = 10^{-3} M, pH= 6.5

Different thermodynamic parameters were computed by using Van't Hoff equation in the form [13], [14]:

$$Ln\,K_C = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

$$\Delta G = -RTLn\,K_C \quad (2)$$

where ΔH, ΔS, ΔG, and T are the enthalpy, entropy, Gibbs free energy, and temperature in Kelvin, respectively.

The values of equilibrium ratio (K_c), were calculated at each temperature using:

$$K_C = \frac{F_e}{1 - F_e} \quad (3)$$

where Fe is the fraction of Cd(II) extracted at equilibrium.

The plot of logK_c vs. $1/T$ is a straight line as shown in Fig. 9 with correlation coefficient r = 0.9831. The numerical values of ΔH, ΔS are computed from the slope.

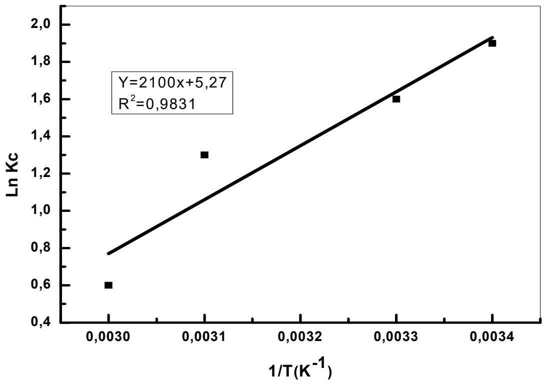

Fig. 9 Variation of logK_c with 1/T for the extraction of Cd(II)

The negative value of Gibbs free energy as shown in Table II indicates the spontaneous nature of extraction, while negative value of ΔH reflects the exothermic extraction behaviour. The negative value of ΔS indicates the complex stability.

TABLE II
THERMODYNAMIC CONSTANTS OF THE EXTRACTION OF Cd(II)

Thermodynamic parameters	Values
ΔH (kJ/mol)	-17.47
ΔS (J/mol.K)	-43.86
ΔG (kJ/mol)	-4.61 (293 K)

IV. CONCLUSION

In this investigation, application of ELMs to metal separation is studied. The best extraction of Cd(II) was obtained at contact time of 25 min, pH of feed phase equal to 6.5, concentration of carrier (Aliquat 336) corresponding to a value of 3% and treat ration ($V_{external}/V_{emulsion}$) of 1:1 (feed: emulsion). Thermodynamic study showed that the reaction of extraction of the Cd(II), using ELM, is spontaneous and exothermic. This process can be used to multicomponent feed systems where the type of the carrier and the experimental conditions depend on nature of pollutants.

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