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Emulsion liquid membrane for selective extraction of bismuth from nitrate medium

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Abstract−The novelty of this work is the selective extraction of bismuth ions from nitrate medium by emulsion liquid membrane. Di(2-ethylhexyl)phosphoric acid was used as extractant of bismuth ions from nitrate medium by emulsion liquid membrane, and Triton X-100 was used as the biodegradable surfactant in n-pantanol n-pentanol bulk membrane. The extraction of bismuth ions was evaluated by the yield of extraction. The experimental parameters were evaluated and were optimized. They included the ratio of di(2-ethylhexyl)phosphoric acid concentration to the concentration of /Triton X-100 concentration (1.0 : 0.5% w/w), nature of diluents (n-pentanol), nature and concentration of the stripping solution (sulfuric acid, 0.5 M), stirring speed (1,800 rpm) and equilibrium time of extraction (20 min), initial feed solution of bismuth (350 ppm) and the volume ratio of the internal stripping phase to the membrane phase (14 times). The experimental parameters of kinetic extraction revealed that the bismuth ions were extracted at 100% 97%.

Key words: Nano-emulsion, Surfactant, n-Alcohol, Extraction

INTRODUCTION

In the pharmaceutical industry, for example, bismuth nitrate is used for treating intestinal disorders; in cosmetic products, for the preparation of creams and hair dyes; in the chemical industry, bismuth is used in plastic manufacturing and as a catalyst in the synthesis of methanol, and in the metallurgical process for the production of low melting alloys used in the protective coatings for wood patterns [1-3]. World reserves of bismuth are usually obtained as a sub-product in lead, copper, tin and gold ores. During the industrial metallurgical process of these ores, leaching stages with using H_2SO_4, HCl and HNO_3 are involved, and highly acidic solutions with base metals and bismuth are obtained [4]. For many industrial uses, bismuth is not considered as a toxic metal. Otherwise, it is a curious metal and can be toxic in an unsuitable form [5,6].

Currently, the extraction and recovery of a value metal is an important challenge for both scientific and industrial communities. The technologies of metal extraction from theirs ores are pyrometallurgical or hydrometallurgical processes. Solvent extraction technique is the most widely used in the hydrometallurgical process. Other techniques such as precipitation, ion exchange, adsorption and electrochemical recovery can be used also as the treatment techniques [7-9]. These last may be ineffective because they sometimes fail to meet regulation levels for technical, economical and/or environmental reasons [10,11].

Emulsion liquid membranes (ELM) invented by Li (1968) [12-16] have been widely used for water treatment [17,18] and for removal of toxic organic and inorganic species from aqueous streams and industrial wastewaters [19]. ELM can constitute an attractive technique compared to the common liquid-liquid extraction used in hydrometallurgical process [20,21]. It is present an improvement of kinetics, selectivity of species to be removed and decreasing the necessary volume ratio of organic phase to aqueous feed solution, with respect to the environmental aspect [18]. Furthermore, it is characterized by simplicity and high efficiency. Besides these advantages, ELM processes allow very high mass transfer rates due to a large surface area within the emulsion globules and internal droplets [22,23].

In this technique, extraction and striping processes are carried out in a single step [22]. ELM is a three-phase dispersion system [24-30], where a primary emulsion is dispersed in a continuous effluent phase, which is the phase to be treated [31]. The continuous phase of the emulsion drops consists of low viscosity organic diluents, a surfactant to stabilize the emulsion and sometimes a carrier. This intermediate phase separates the external phase and the emulsified internal phase and behaves like a liquid membrane, allowing the permeation of solutes. For the separation of low concentrations metals, the carrier is a soluble organic extractant, which selectively combines with the solutes that diffuse from the bulk of the effluent aqueous phase to the outer interface. The metal-carrier complex permeates through the membranes from the outer to the inner interface. Fig. 1 shows the graphical implementation of the ELM process.

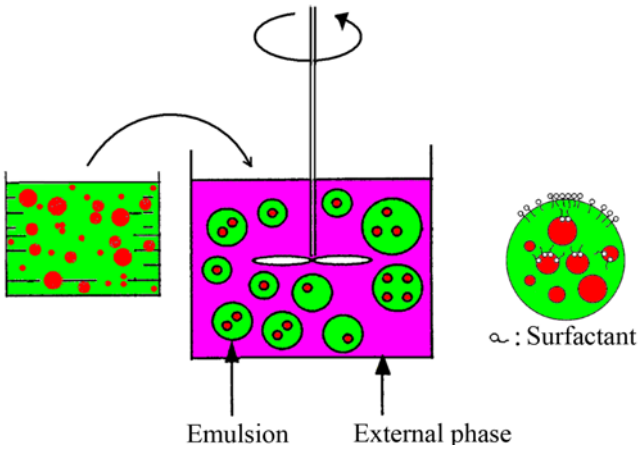

Fig. 1. Graphical implementation of the ELM process.

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At the inner interface, the complex decomposes by the reversal of the equilibrium reaction and the metal ion is liberated into the internal phase [32-35] and the regenerated carrier goes back into the membrane phase [36,37]. The commercial extractants most frequently [38] used are neutral or acidic organophosphorus compounds such as di(2-ethylhexyl)phosphoric acid (D2EHPA). This last extractant can be used in several cycles of the extraction process during several months without risk of decomposition. In solvent extraction processes, D2EHPA interact with metals ions by cation exchange to form the metal complex. From the literature, very few papers deal with the extraction of Bi(III), knowing that until 1982 there was only one patent on Bi(III) [39].

The aim of this first part of the work launched on the Bi(III) is the study of their kinetic extraction, by ELM technique from nitrate medium, based on the optimization of the experimental parameters, while using D2EHPA as carrier and Triton X-100 as biodegradable surfactant.

The aim of this work is optimization and selective extraction of Bi(III) from nitrate medium by ELM technique. The optimal conditions were examined based upon the optimization method of one-at-a-time. The results revealed that ELM process extracts Bi(III) from nitrate medium.

EXPERIMENTAL

1. Reagents

D2EHPA was purchased from Fluka containing 40% of M2EHPA; in mono(2-ethylhexyl)phosphoric acid. The biodegradable non-ionic surfactant; isooctylphenoxypolyethoxyethanol (Triton X-100) with the critical micellar concentration equal to 3.0×10^{-4} M, and the cloud point temperature of 68 °C at 1 wt% in water was supplied by Sigma-Aldrich. Dichoromethane was purchased from Merck. Sulfuric acid (98%) and chloroform were provided from Prolabo. Kerosene was purchased from Riedel de Haen. Heptane was supplied by Fluka where n-pentanol pur was obtained from Reachim. The stock of pure basic bismuth nitrate ($BiONO_3$) was supplied by Reachim, and potassium iodide was obtained from Gerhard Buchmann.

2. Apparatus

Haier mechanical agitator with standard platform was used in extraction experiments; pH measurements were taken with a Consort C831 by a pH-meter (Consort C831) using a combined electrode. The weighing was made with an electronic analytical balance, type (Kern ABS). A mixer type Vortex at 2,500 rpm was used for the emulsion formation. UV-visible absorption spectrophotometer; type spectrophotometer (Lambda 800, Perkin Elmer) was used for Bi(III) analysis.

3. Preparation of Emulsion

First, an organic solution (7.5 mL) was prepared by mixing amounts of TritonX-100 surfactant and D2EHPA extractant in n-pentanol (as diluent). After, the acidic aqueous solution was added drop-wise to the organic solution under great agitation using the Vortex mixer.

4. Extraction and Pre-concentration of Bi(III)

The obtained emulsion was mixed with the 62.5 mL of feed solution (62.5 mL, containing bismuth ions) and all were stirred by Haier mechanical agitator for the reaction time. After the end of the extraction reaction, an aliquot of 10 μL of the feed solution (10 μL) led to the analysis where the quantities of bismuth remaining in feed solution after extraction were determined by atomic absorption spectrometry UV-Visible at 460 nm by iodide method [40-42]. This method is a common test in the world and is used as a standard test method. The analytical response was given by the yield of Bi(III) extraction of Bi(III). All experiments were performed at 20 °C. All aqueous solutions were prepared using demineralized water. Each extraction experiment was repeated three times and then the value is was taken in calculation.

RESULTS AND DISCUSSION

The optimum conditions for the extraction of Bi(III) were determined by the method of one-at-a-time. Table 1 presents all conditions that were tested as well as the optimum conditions in bold.

1. Reaction Stoichiometry

The equilibrium and kinetic studies were carried out in the presence of phosphate as ligand. In acidic feed solution, Bi(III) reacts with phosphate to form $BiPO_4$, which then form complexes with extractant (D2EHPA). The extraction reactions are written as Eq. (1):

$$Bi(PO_4)_{aq} + n\,(D2EHPA)_{org} \rightarrow (\text{metal complex})_{org} \quad (1)$$

The equilibrium constant (K_{eq}) for Eq. (1) is written as Eq. (2):

$$K_{eq} = \frac{[C_{comp.}]_{eq}}{[C_{D2EHPA}]^n [C_{Bi}]_{eq}} = \frac{[C_{Bi}]_{org} - [C_{Bi}]_{eq}}{[C_{D2EHPA}]^n [C_{Bi}]_{eq}} \quad (2)$$

Table 1. The experimental and optimum conditions for the extraction of Bi(III)

Item	Parameter	Level 1	Level 2	Level 3	Level 4	Level 5
1	Extractant/surfactant ratio	0.1	0.5	1.0	1.5	**2.0**
2	Nature of diluents	Dichloromethane	Heptane	Chloroform	Kerosene	**Pentanol**
3	Stirring speed of emulsion formation (rpm)	600	1000	1500	**1800**	2500
4	Stirring time (min)	10	**20**	30	40	-
5	Type of stripping solution	Nitric acid	**Sulfuric acid**	Hydrochloric acid	-	-
6	Concentration of stripping solution (M)	0.1	0.25	**0.5**	1.0	2.0
7	Contact time (min)	10	20	**30**	40	60
8	Stirring speed of ELM extraction (rpm)	0	150	**210**	230	270
9	Feed concentration (M)	**350**	500	650	-	-
10	V_S/V_M ratio	0.5	2	6	10	**14**

The **bold** items were obtained and used as the optimum conditions, M: Mole/Liter

The equilibrium distribution ratio (α) of the metal ion between the membrane phase and the feed solution is written as Eq. (3).

$$\alpha_{Bi}=\left[\frac{C_{comp.}}{C_{Bi}}\right]_{eq}=\frac{[C_{Bi}]_{org}-[C_{Bi}]_{eq}}{[C_{Bi}]_{eq}} \quad (3)$$

Eqs. (2) and (3) may be combined as Eq. (4):

$$\log\alpha_{Bi}=\log K_{eq}+n\log[C_{D2EHPA}]_{eq} \quad (4)$$

In the experiments, the concentration of extractant (D2EHPA, 1% w/w) was in large excess in comparison to the metal ions in the feed solution. Hence, Eq. (5) may be assumed that,

$$[C_{D2EHPA}]_{eq}=[C_{D2EHPA}]_{org} \quad (5)$$

Then, Eq. (5) becomes as Eq. (6)

$$\log\alpha_{Bi}=\log K_{eq}+n\log[C_{D2EHPA}]_{org} \quad (6)$$

Equilibrium experiments were conducted at different concentrations of extractant (0.1, 0.4, 0.7, 1.0, 1.3, 1.6 mM) keeping the feed pH at 1.0 and phosphate (500 ppm) constant to find the values of equilibrium distribution ratios. The logarithmic plot of α_e *vs.* $[C_{D2EHPA}]_{org}$ gives a straight line with slope n=1.36. The plot is shown in Fig. 2.

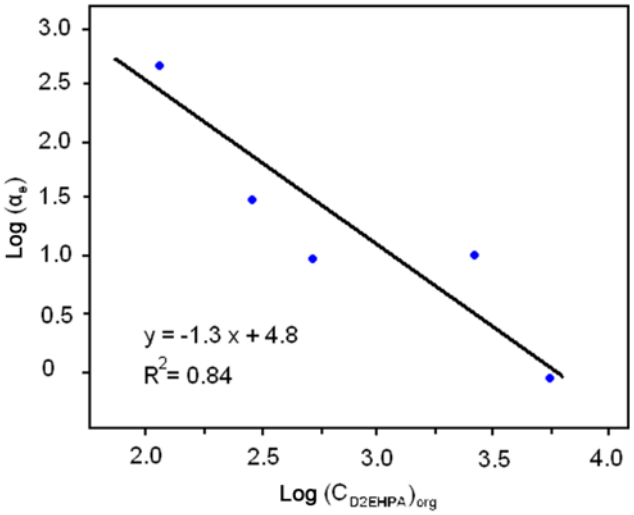

Fig. 2. Plot of log (α_e) *vs.* log $(C_{D2EHPA})_{org}$ from batch equilibrium studies (pH=1.0).

The reaction order is determined from the kinetic experiments, with different stirring speed (600-2,500 rpm) and D2EHPA concentration (0.1, 0.4, 0.7, 1.0, 1.3, 1.6 mM). To determine the reaction order, Eq. (7) is assumed:

$$-r=-\frac{dC_{Bi}}{dt}=K_r\ C_{D2EHPA}^{m_1}\ C_{Bi}^{m_2} \quad (7)$$

Kinetic experiments were conducted over the period of 5 h. Attempts were first made to fit the data for the entire period with one reaction order, but it failed. When the data was divided into parts, suggesting a change of reaction order with concentration, better fits to the reaction models were obtained. According to the plots, the transition occurred between the first 10 and 20 min of extraction time, which corresponds to 500 ppm of Bi(III) concentration. The experimental data was divided into two parts, from starting up to 10 min and the rest of the time, to fit the models separately. Integrating Eq. (7) for individual components, Eq. (8) is obtained.

$$C_{Bi(zero)}^{1-N}-C_{Bi}^{1-N}=(1-N)K_r t \quad (8)$$

Experimental data were fitted to the equation by varying the value of N until the best fit was obtained. The results led to the extraction Eq. (9)

$$\begin{cases} -r=K_r\ C_{D2EHPA}^{3}\ C_{Bi}^{3} & \text{at higher concentrations} \\ -r=K_r\ C_{D2EHPA}^{1.5}\ C_{Bi}^{1} & \text{at lower concentrations} \end{cases} \quad (9)$$

2. Effect of Extractant/Surfactant Ratio on Bi(III) Extraction

A study of the influence of the D2EHPA/TritonX-100 ratio on Bi(III) extraction was carried out. First, we fixed the concentration of extractant and varied the concentration of surfactant and screws to it (see Fig. 3). The liquid membrane was based on dichloromethane as diluent. From Fig. 3, the extraction yield of Bi(III) increased in both cases by increasing the ratio D2EHPA/TritonX-100. The extraction yield of Bi(III) reached 89% at D2EHPA/TritonX-100 ratio equal to 2. After this value, the extraction yield of Bi(III) decreased

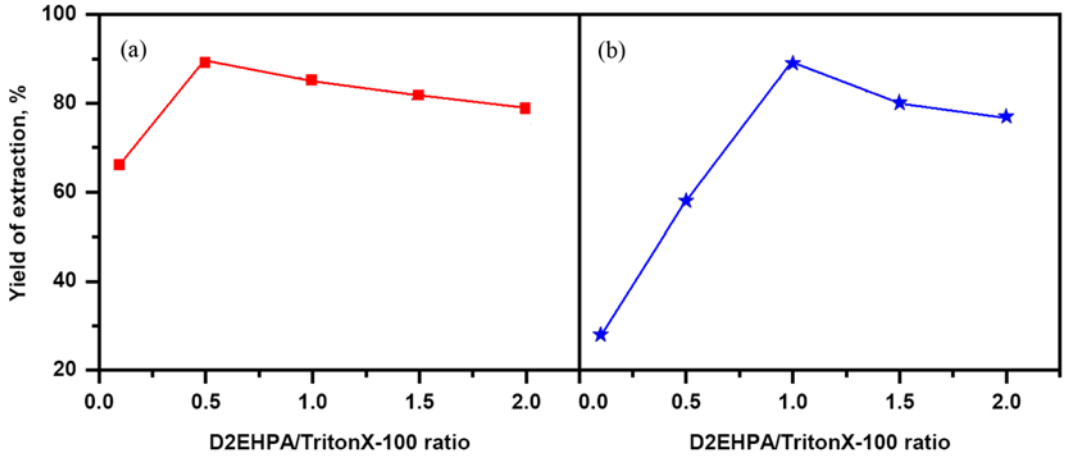

Fig. 3. Effect of D2EHPA/TritonX-100 ratio on the extraction of Bi(III). (a) At constant concentration of D2EHPA=1% w/w, (b) at constant concentration of TritonX-100=0.5% w/w. Stripping solution: 4.5 mL of H_2SO_4 (0.5 M); reaction stirring: 210 rpm; $[Bi^{3+}]$=500 ppm (pH=1).

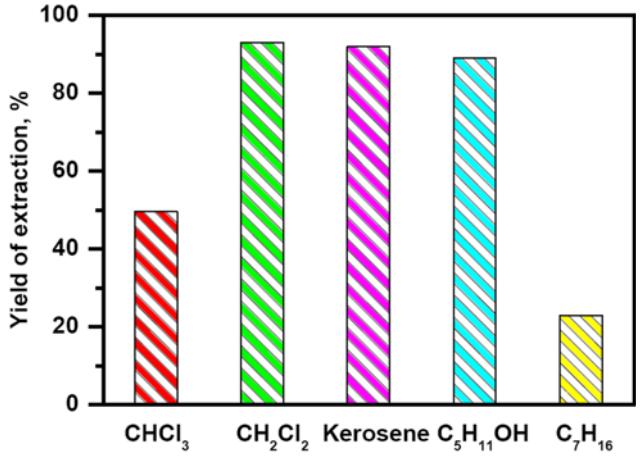

Fig. 4. Effect of the nature of diluents on the extraction yield of Bi (III). Stripping solution: 4.5 mL of H_2SO_4 (0.5 M); reaction stirring: 210 rpm; [Bi^{3+}]=500 ppm (pH=1); D2EHPA/TritonX-100=2.

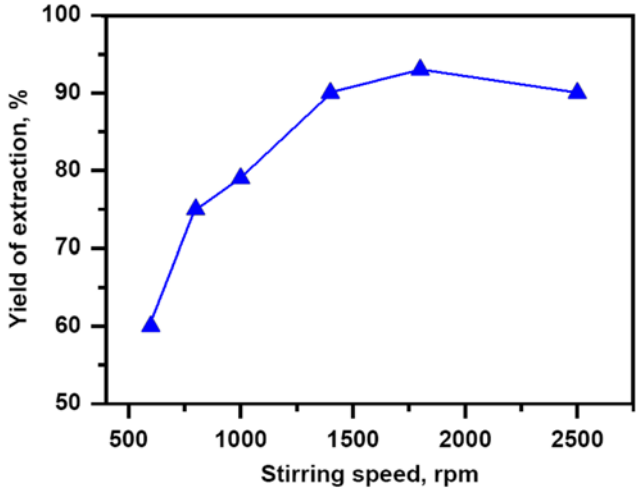

Fig. 5. Effect of stirring speed on the emulsion formation. Stripping solution: 4.5 mL of H_2SO_4 (0.5 M); reaction stirring: 210 rpm; [Bi^{3+}]=500 ppm (pH=1); D2EHPA/TritonX-100=2.

due to the instability of the emulsion. As presented in Fig. 3(a) and Fig. 3(b), the effect of D2EHPA/TritonX-100 ratio on the extraction of Bi(III) at constant concentration of D2EHPA=1% w/w (Fig. 3(a)), and at constant concentration of TritonX-100=0.5% w/w (Fig. 3(b)) is illustrated. Indeed, the previous study showed that a higher concentration of surfactant increased the viscosity of the membrane solution, which led to a decrease in the performance of chromium (VI) extraction [36,43]; other work [44] showed that amounts of surfactant in the membrane must be optimal to stabilize the emulsion.

3. Influence of the Nature of Diluents on Bi(III) Extraction

Polar and non-polar diluents were tested in the preparation of the emulsion liquid membrane ELM, namely dichloromethane (polarity=3.1), n-heptane (polarity=0.0), chloroform (polarity=4.1), kerosene (polarity=0.0), and n-pentanol (polarity=4.1). Fig. 4 shows the evolution of extraction yield of Bi(III) by ELM in function of the nature of diluents. From where, the higher extraction yields of Bi(III) from nitrate medium occurred using non-polar just one of the polar diluents in the exception of chloroform diluents, where the maximum extraction of Bi(III) was 93% using n-pentanol as diluent. The results revealed that the solvent polarity and viscosity do not have any effect in the extraction performance of this experiment. Thus, the D2EHPA extractant exists as monomer form with strong diffusivity from which the complexation of metal is higher and the extraction will be more effective. However, n-pentanol was chosen as diluent for the continuation of our further experiments. On the other hand, there are researches that show the polarity of the diluents is the main factor influencing the extraction performance and stability of a liquid membrane. The decreasing of diluent polarity prolongs the membrane stability, but the percentage of stripping and extraction decreases [45].

4. Effect of Stirring Speed on the Emulsion Formation

The preparation of the emulsion played an important role in the extraction of Bi(III) by emulsion liquid membrane technique. The effect of stirring speed on the emulsion formation was followed in function of the ELM extraction of with respect to Bi(III) extraction. Experiments were conducted at different emulsification speeds from 600 to 2,500 rpm (see Fig. 5). The results showed that increasing the stirring speed of the bulk membrane phase led to increase the efficiency of ELM extraction of Bi(III) extraction from nitrate medium. In fact, the extraction yield of ELM extraction of Bi(III) was 93% at 1,800 rpm. An efficient emulsification gives a good dispersion of the internal phase to membrane phase. The droplets of stripping phase formed become smaller and will take much more time to coalesce. This is conducive to good stability of the emulsion. In addition, the size of the internal phase droplets was smaller at greater agitation intensity, creating a larger surface area for extraction and, hence, obtaining higher recovery of ion [13,46].

5. Effect of Stirring Time on the Emulsion Formation

If the stirring speed affects the formation of droplets of stripping phase in the preparation of the emulsion, the stirring time governs their overall maturation [21,22]. Fig. 6 shows the effect of emulsification time on ELM extraction of Bi(III) when the time was varied from 10 to 40 min. The yield of Bi(III) extraction of Bi(III) increased with emulsification time to achieve 93% at 20 minutes min of stirring time. After this, the yield of extraction decreased. This was due

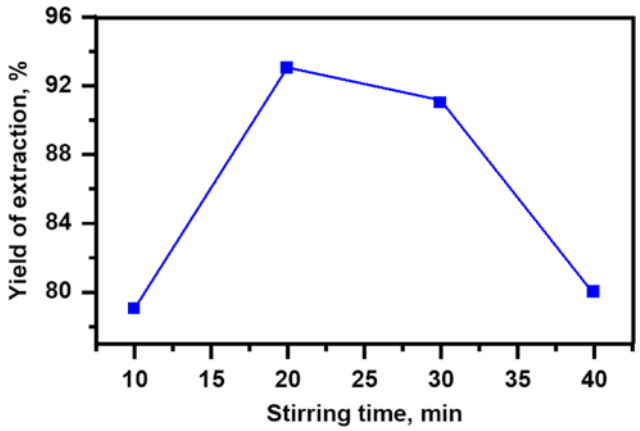

Fig. 6. Evolution of the Bi(III) extraction versus the stirring time of emulsion. Stripping solution: 4.5 mL H_2SO_4 (0.5 M); reaction stirring: 210 rpm; [Bi^{3+}]=500 ppm (pH=1); D2EHPA/TritonX-100=2.

to the instability of emulsion. Then, owing to the instability of emulsion, the yield of extraction decreased.

6. Effect of Type and Concentration of Stripping Solution on the Extraction

From the literature, the stability of the emulsion is a key factor in the extraction by ELM [12,36]. The choice of treatment options was paramount. In fact, the nature of the stripping solution depends on the physical-chemical properties of the D2EHPA and their mode of extraction. The influence of the nature of the stripping phase on the ELM extraction of Bi(III) extraction was determined by examining the various acid solutions such as nitric acid, sulfuric acid and hydrochloric acid (see Fig. 7). From this last, the results obtained showed that the bismuth ions were more pre-concentration with pre-concentrated using sulfuric acid solution. Then in this case, the extraction yield of ELM extraction of Bi(III) was 93%. In 0.5 M acid concentration, sulfuric acid shows higher acidity than nitric acid and hydrochloric acid since its acidic equivalent is duplicated. Concerning the lower extraction efficiency of nitric acid compared to hydrochloric acid, the interfering effect of nitrate anions is responsible.

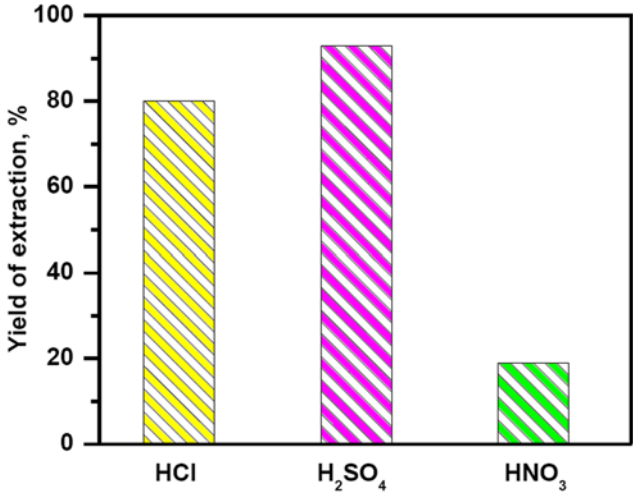

Fig. 7. Effect of type of stripping solution on the Bi(III) extraction. Stripping solution: 4.5 mL (0.5 M); reaction stirring: 210 rpm; [Bi^{3+}]=500 ppm (pH=1), D2EHPA/TritonX-100=2.

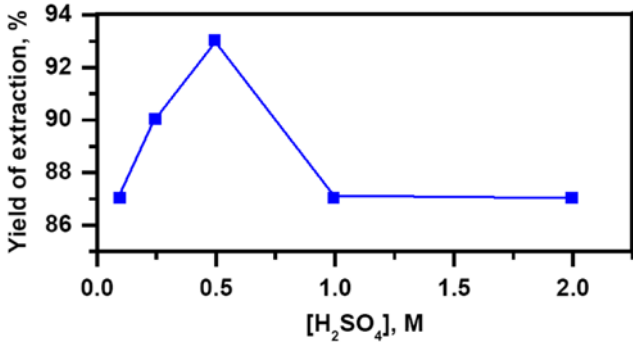

Fig. 8. Effect of the stripping solution concentration on Bi(III) extraction. Stripping solution: 4.5 mL H_2SO_4; reaction stirring: 210 rpm; [Bi^{3+}]=500 ppm (pH=1); D2EHPA/TritonX-100=2.

7. Effect of the Stripping Solution Concentration on Bi(III) Extraction

The capacity to trap and to concentrate the solute in the stripping solution was determined by the concentration of the aqueous solution acid in the internal phase. The influence of the concentration of internal phase on Bi(III) extraction by ELM is shown in Fig. 8. This last indicated clearly that by increasing of the sulfuric acid concentration, the extraction yield of Bi(III) extraction increased. It reached 93% at 0.5 M. Beyond the latter, the extraction yield dropped and then became constant at high concentrations of acid. This is due to the increase in the driving force of the diffusion through the ELM, owing to an increase of the metal complexes concentration at the interface of membrane-stripping solution [43].

8. Effect of Contact Time and Stirring Speed on Extraction

The stirring speed influences the mass transfer during the extraction. The study of the effect of stirring speed on Bi(III) extraction by ELM is shown in Fig. 9. From this last, we note that for a given stirring speed, the extraction yield of Bi(III) by ELM increased according to the time. In general, it became constant for the times higher than 30 min. When the agitation speed reached 210 rpm the concentration profile did not change any more. This was observed in the case of 230 rpm of stirring. This phenomenon indicates that the effect of the fluid to Bi(III) mass transfer resistance became negligible. Thus, we obtained a maximum value of 93% of extraction yield at 210 rpm after 30 min of stirring. Further experiments were conducted at a stirring speed of 210 rpm in order to save the energy and a contact time of 30 min to avoid concentration effects.

9. Effect of Feed Concentration on Extraction

The influence of the initial concentration of Bi(III) on ELM extraction was investigated at different concentrations with their initial pH=1 (see Fig. 10). It was observed that for the given initial concentration of Bi(III), the extraction yield of Bi(III) increased until 30 min of extraction time after it became constant. In fact, when increasing the feed concentration of Bi(III) from 350 to 650 ppm, the yield of Bi(III) extraction decreased. It reached 97% at 350 ppm of initial concentration of Bi(III). Thus, when the initial Bi(III) concentration was low, most of the solutes which were situated in the

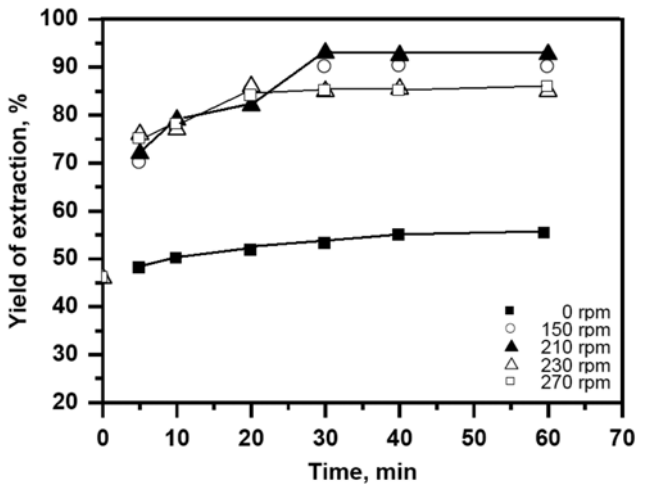

Fig. 9. Effect of stirring speed on the extraction of Bi(III). Stripping solution: 4.5 mL of H_2SO_4 (0.5 M); [Bi^{3+}]=500 ppm (pH =1); D2EHPA/TritonX-100=2.

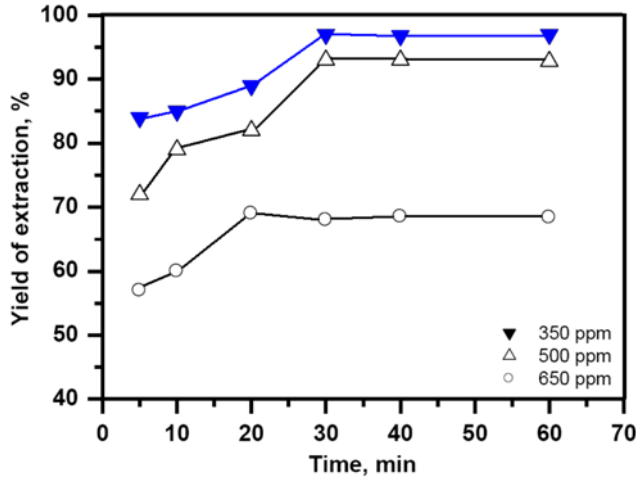

Fig. 10. Effect of the feed concentration on the Bi(III) extraction. Stripping solution: 4.5 mL of H_2SO_4 (0.5 M); reaction stirring: 210 rpm; D2EHPA/TritonX-100=2.

peripheral regions of the emulsion globule, diffusing within the emulsion globule, were stripped by the internal aqueous phase droplets [13]. In fact, when increasing the initial concentration of Bi(III) at 650 ppm, extraction yield of Bi(III) reached of the 69%. This result was due to the saturation of the internal droplets of the stripping emulsion. On other hand, the mass transfer resistance in the emulsion globule became important when the concentration of Bi(III) complex was higher, which made decreasing the rate of stripping leading to decrease the extraction yield of Bi(III) [43].

10. Effect of the V_S/V_M Ratio

In the separation and pre-concentration process of metal ions by emulsion liquid membrane technique, the volume ratio of the stripping solution (V_S) and membrane solution (V_M) played a very important role [20,43]. Fig. 11 shows the influence of the V_S/V_M ratio on the extraction yield of Bi(III) by ELM while maintaining the membrane volume (V_M) constant. The result shows that the extraction of Bi(III) was total with increasing the V_S/V_M ratio until 14, from

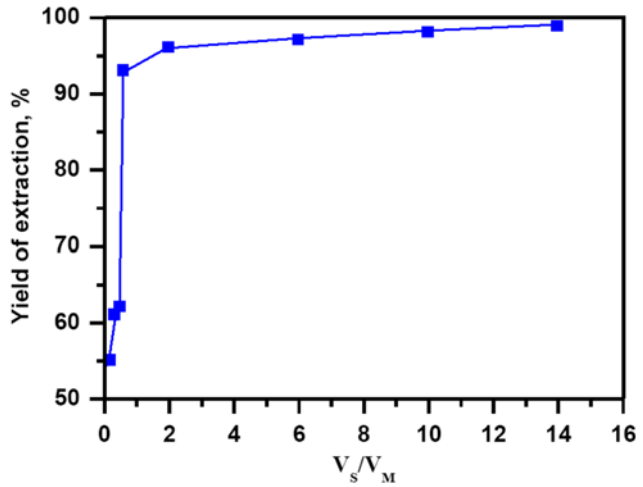

Fig. 11. Effect of V_S/V_M ratio on the Bi(III) extraction. Stripping solution: 4.5 mL of H_2SO_4 (0.5 M); reaction stirring: 210 rpm; [Bi^{3+}]=350 ppm (pH=1); D2EHPA/TritonX-100=2.

where the yield of Bi(III) extraction reached 100%. The increase in the volume of the stripping phase involved an increase in the medium receiver where the increase in the incarceration of Bi(III) ions in the internal phase.

11. Comparison with other Techniques Used in Separation of Bi(III)

Otu [47] used the synergistic extraction of bismuth by 2-ethylhexyl phenylphosphonic acid (HEHΦP) and dinonyl naphthalene sulfonic acid (HDNNS). He determined the thermodynamic parameters for the extraction of bismuth from $HClO_4$ (1 M). The mixed ligand system for HEHΦP and HDNNS was enthalpy controlled and entropy controlled, respectively. That manuscript didn't focus on the extraction parameters and no data are reported. On the other hand, the present work discusses the extraction parameters, especially those related to the membrane technology.

Alonso et al. [48] converted the bismuth into tetraiodobismuthate(III) anion (TIB) in aqueous solution. Then a solution of tetraphenylar-sonium (TPA) chloride in chloroform was added to the previous solution. The ion-pair TPA-TIB was formed and extracted into the organic phase where its concentration was measured spectrophotometrically. The whole process was carried out in a flow injection system with continuous liquid-liquid extraction. They studied the maximum extraction efficiency of Bi(III) at pH<2.2 and at TPA concentration of 1.0×10^{-2} M. That manuscript didn't focus on all of the extraction parameters such as feed concentration, contact time and stirring speed, type and concentration of stripping solution, stirring time and stirring speed on the emulsion formation, nature of diluents and extractant/surfactant ratio. On the other hand, the present work discusses all of those extraction parameters.

Reyes-Aguilera et al. [49] reported a supported liquid membranes technique for recovery of bismuth from aqueous solutions. In this research, tri-noctylphosphine oxide (Cyanex 921) was used as extractant. They revealed that Bi(III) reacts with two molecules of Cyanex 921 to form the solvate $BiCl_3$·2Cyanex 921. Addition of HCl (0.5 M) to the feed solution increased Bi(III) extraction and further increase in HCl concentration caused a decrease in Bi(III) transfer. The optimum concentration of Cyanex 921 in the organic phase was found to be 0.3 M. The performance of H_2O and H_2SO_4 (0.2 M) as stripping solutions was evaluated, and it was found that only H_2SO_4 enabled Bi(III) transfer. The initial Bi(III) concentration was optimized at 18 ppm.

Yang et al. [50] optimized the Bi(III) recovery at pH 0.2, time 3 min, diluent kerosene, carrier type and concentration N235 (trialkyl amine, a widely-used amic extractant for extracting the cations) at 8.0×10^{-2} M, type and concentration of stripping agent EDTA at 0.5 M. On the other hand, the present work studied different parameters.

Song et al. [51] investigated the solvent extraction of bismuth in nitric acid medium using different mixtures of acidic phosphorus extractants including D2EHPA, 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEHEHP), sec-octylphenoxyacetic acid (CA12), sec-nonylphenoxy acetic acid (CA100), 8-hydroxyquinoline (HQ), and 2,20-bipyridyl (bipy). The synergistic coefficients were determined to be greater than 1.0 at any mole fractional ratio of HEHEHP and bipy. The synergistic extraction proved to be an exothermic and spontaneous process. They didn't focus on all of the extraction parameters such as feed concentration, contact time and stirring speed,

Table 2. Comparison data for the extraction of Bi(III)

Diluent	Carrier/extractant	Time, min	Feed solution	Other parameters	Reference
Kerosene	Tri-noctylphosphine oxide (Cyanex 921), 0.28 M)	160	HCl, 0.5 M	Bi(III) initial concentration: 17.92 mg L^{-1}	[49]
Kerosene	N235 (trialkyl amine), 8.0×10^{-2} M	3	HCl, pH=0.2	Stripping agents: EDTA, 0.5 M	[50]
n-Pentanol	D2EHPA=1% w/w and TritonX-100=0.5% w/w	30	H_2SO_4, 0.5 M	a) Bi(III) initial concentration: 350 mg L^{-1} b) Stirring speed: 210 rpm c) V_S/V_M ratio: 14	Present work

type and concentration of stripping solution, stirring time and stirring speed on the emulsion formation, nature of diluents and extractant/surfactant ratio. On the other hand, the present work discusses all of those extraction parameters. Table 2 shows the comparison data for extraction of Bi(III) by the present approach and the aforementioned works [49,50].

CONCLUSION

Bi(III) ions were extracted and recovered from nitrate medium by emulsion liquid membrane technique, using di-(2-ethylhexyl)phosphoric acid (as extractant) and TritonX-100 (as biodegradable commercial surfactant). The study of the influence of the experimental parameters on the kinetic extraction showed that the Bi(III) ions can be extracted at 100% 97%. The liquid membrane was constituted from 1% w/w of D2EHPA (1% w/w) with 0.5% w/w of TritonX-100 (0.5% w/w), in n-pentanol bulk membrane. The emulsion was performed with 0.5 M of sulfuric acid solution (0.5 M) under 1,800 rpm of stirring, during 20 min. The extraction reaction of Bi(III) ions from nitrate medium was reached with 350 ppm of feed concentration during 30 min of equilibrium time, under 210 rpm of stirring. In this case, the V_S/V_M ratio was equal to 14.

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