EXTRACTION OF COBALT AND LEAD FROM WASTE WATER USING A LIQUID SURFACTANT MEMBRANE EMULSION

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Abstract

The applicability of the Liquid Surfactant Membrane (LSM) process for the removal and the concentration of lead and cobalt was investigated. The aim of this work is to find a process for the purification of wastewater, which contains cobalt and lead. A complete study of the metal extraction by the liquid membrane process using HDEHP as extractant and SPAN 80 as surfactant is performed in terms of extraction and stripping efficiencies, emulsion breaking and swelling. The results show that it is possible to recover 98.83% of cobalt and 94.21% of lead in the inner phase after 2 minutes of contacting time with a concentration factor of 50 for lead and 50 for cobalt.

Introduction

The aim of this work is to find a process for the purification of wastewater, which contains lead and cobalt. The pH of these solutions depends on their origin. A bibliographic survey has led us to select acidic reagents as the extractant,[1-5] and the surfactants enhance emulsions water into oil (HLB ≤ 4) as a stabilizer that gives very good emulsions stability during the transfer even at low concentration. In order to choose the most suitable surfactant, we made a comparison between several commercialised surfactants compounds, which consist of SPAN 80 (monooleate of sorbitan), TWEEN 20 (21.22.etho-Sorbitan monolaurate), the NP4, and the Marlophen (Nonylphenol polyoxyethylene).

In the extraction we used the cationic exchanger, namely, a phosphoric acid (di-2-ethylhexyl phosphoric acid or HDEHP). This latter extracts metallic cations present in aqueous solutions. The cations are exchanged for protons that are released in the aqueous phase leading to its acidification.

The surfactant liquid membrane process introduced by Li[6] was used because of two major advantages: the first one is its possibility of treating diluted solutions and the second one is its high concentration factors. Their principles are described in details in many papers.[7-9]

Experimental and Materials

The selected membrane used in this work, is constituted of an extractant, that is HDEHP (di-2-ethylhexylphosphoric acid). It is the product of the Daihachi Chemical Ind. Co., Ltd., Osaka, Japan, with 95% purity. It was further purified by precipitation as a copper complex from ether and acetone solution, and then dissolved in ether and a sulphuric acid solution of 4 kmol m^{-3}. According to the procedure of Partridge and Jensen[10] the Kerosene (Dodecane) used as a diluent was supplied by Union Chemical Works Ltd., Taiwan.

Several surfactants have been tested such as the SPAN 80 (monolaurate of sorbitan) surfactant non-ionic enhancing water emulsions into oil used in liquid membranes technology, for its accentuated lipophilic character (Kao-Atlas), the TWEEN 20 (21.22.etho-sorbitan monolaureate), the NP4, and the MARLOPHEN (Nonylphenol poly-oxyethylene at 100% active matter over greasy alcohols).

The external aqueous phase is obtained by dissolving the nitrate of cobalt into water $Co(NO_3)_2 6H_2O$ and the nitrate of lead $Pb(NO_3)_2$. The internal aqueous is a sulphuric acid or a hydrochloric acid solution which concentration will be one of the parameters to optimise. The reason for the choice of these ions is that there is an industrial relevance due to the dumping into the regional rivers and lakes of the industrial wastewater by the Giant steel industry of El-Hadjar, Annaba in Algeria.

Procedure

Emulsions are manufactured by means of an ULRA–TURAX disperser T18-10. The two phases (organic and internal aqueous) are placed into a beaker with a well-cut shape obtained by a vigorous agitation. The disperser is introduced and positioned at the interface level; we maintain the stirring at 2000 revolutions per minute (as a maximal speed) during 5 minutes. This was realized by spreading a certain volume of emulsion in a given aqueous phase volume, so that we can treat the metal to be extracted using a helical stirrer, turning at 250 revolutions per minute.

The aqueous phase pH is adjusted by adding ammonia followed by spectrometry with an electrode glass. After extraction, the depleted aqueous phase is separated from the emulsion by simple decantation. The emulsion is then broken by adding octanol, which is heated to 40 °C. The proportion of metal (cobalt to lead) is made by spectrometry (Shumadzu Japan) using the PAR (4-pyridyl-2-azorésorcinol) as complexant.

The lead is proportioned by visible spectrophotometry with the presence of PAR at pH 11 and with a wavelength of 530 nm. The same method is used for the cobalt with the presence of PAR at pH 3 and with a wavelength of 530 nm. The mixture, cobalt-lead is performed by the PAR at pH 3 and a wavelength of 590 nm (visible spectrophotometry); we also performed lead-cobalt mixture by the EDTA (tetra-di-acetic-acid) at pH 11 and a wavelength of 240 nm (ultraviolet spectrophotometry).

Results and discussion

Breaking off the emulsion

This phenomenon was measured by contacting the emulsion with an external phase composed of pure water. The variation of the pH of this phase with time is an indication of the emulsion breaking. The breaking rate "BR" defined by eq. (1) represents the fraction in percent of the expulsed internal phase volume to the external phase by the breaking volume V_r to the initial volume of the internal phase $V_{int.}$. The volume V_r is calculated by the material balance from the external phase pH measure, before and after the contact, so that;

$$BR\,(\%) = \frac{V_r}{V_{\text{int}}} \times 100 \tag{1}$$

with

$$V_r = V_{ext}\frac{10^{-pH_0} - 10^{-pH}}{10^{-pH} - \left[[H^+]_i\right]} \tag{2}$$

Where $V_{ext.}$ is the initial external phase volume, pH_0 is the pH of the initial external phase, pH is the pH of the external phase being in contact with the emulsion

after a certain time of agitation, and $[H^+]_i$ the protons initial concentration in the internal phase.

Choice of surfactant

The surfactant agent is the first factor that enhances the formation of the water emulsion into oil (W/O). For this reason, we have tried some commercial surfactants (SPAN 80, TWEEN 20, NP 4, and the MARLOPHEN). Breaking rates are calculated after 7 minutes of contact between the emulsion and external phase.

Table 1. Choice of surfactant giving the lower breaking rate " BR" in the same experimental conditions.

Surfactant concentration 2%	NP4	TWEEN 20	MARLOPHEN	SPAN 80
BR (%)	20.77	39.27	53.59	5.39

Working conditions

The working condition are summarized as follows: Emulsion volume = 30 mL, external phase volume = 300 mL, membrane volume/internal phase volume = 2, emulsification speed = 2000 rpm, (HDEHP) = 2%, (H$_2$SO$_4$) = 0.5 mol/L, diluent = heptane, Stirrer speed = 350 rpm, emulsification time = 5 minutes, and the SPAN 80 seems to be the best because its breaking rate "BR" is the lowest that offers us the capacity of forming stable emulsions W/O.

Study of water emulsion stability in oil using SPAN 80 as a surfactant

The effect of several parameters was studied. These parameters are the following: SPAN 80 concentration, HDEHP concentration, ratio volume membrane/volume inner phase, sulphuric-acid concentration, rotating speed in the transfer step, emulsification rotating speed, and emulsification time.

Influence of the emulsification rotating speed

Experiments were performed with HDEHP 2%, SPAN 80 2%, sulphuric acid of 0.5 mol/L, heptane 96%, a ratio membrane volume/internal phase of 2, rotating speed of 350 rpm, 7 minutes of contact, emulsion volume 10 mL and the external phase volume of 100 mL, the temperature of 25°C and different emulsification rotating speed. An

efficient emulsification gives a good dispersion of internal phase drops into the membrane. The fact that these drops become smaller will take much more time to coalesce. This procedure has led to a higher stability of the emulsion. The optimal emulsification speed was found to reach the value of 2000 rpm with a breaking rate BR of 3.5%.

Table 2. Variation of the breaking rate with the emulsification speed.

Emulsification rotating speed (rpm)	1000	1400	2000
BR (%)	11.79	4.86	3.35

Emulsification time

The conditions used here are the same conditions used previously, the emulsification speed is 2000 rpm, the emulsification time is insufficient (t = 2 min) so that the breaking rate is great because the internal shearing is high and drops remain small enough for a long emulsion time (more than 5 minutes), so that the breaking rate is high. As shown in Table 3, the lower breaking rate is obtained for emulsion time of 5 minutes.

Table 3. Effect of emulsification time on the breaking rate.

Emulsion time (min)	2	5	7	10
BR (%)	12.36	3.35	7.23	11.26

Effect of rotating speed in the transfer step

As expected the stability depends greatly on the rotating speed when the external interfacial area is increased by an increased rotating speed so that the ejection of the internal phase is facilitated. This can be seen on the following table with a contacting time of 7 minutes. In terms of stability the rotating speed must not exceed 250 rpm.

Table 4. Effect of rotating speed in the transfer step on the breaking rate.

Rotating speed (rpm)	150	200	250	300	350
BR (%)	4.54	4.34	2.73	3.13	3.35

Effect of HDEHP concentration

The concentration of HDEHP has an unfavourable influence on the stability of the emulsion. This may be due to the interfacial properties of HDEHP, which favors O/W emulsions and is therefore opposed to the SPAN 80 action.

Table 5. Variation of breaking rate with the HDEHP concentration.

HDEHP (%)	2	4	6	8
BR (%)	2.73	4.04	6.14	7.39

Effect of sulfuric-acid concentration

When the sulphuric-acid concentration increases, the stability of the emulsion decreases. This may be due to a reaction of the acid with SPAN 80 (2%), resulting in a partial loss of its surfactant properties. This can be seen in the following table.

Table 6. Variation of breaking rate with the sulphuric-acid concentration.

H_2SO_4 (mol/L)	0.25	0.5	0.75	1.0
BR (%)	1.12	2.73	12.77	20.22

From the stability point of view a concentration of sulphuric acid greater than 0.5 mol/L is prohibited.

Effect of the ratio membrane/internal phase

The stability increases slightly with increasing the membrane/inner phase as can be seen on Table 7. This result is expected because the ejection of the internal phase is easier when its proportion in the emulsion is higher. It should be mentioned that in these experiments, the contacting time was 60 minutes with SPAN 80 of 2%.

Table 7. Variation of breaking rate with the ratio membrane volume /internal phase volume.

Membrane/inner phase	1	2	3	4
BR (%)	6.04	3.77	2.09	2.06

Effect of SPAN 80 concentration

Different concentrations of SPAN 80 have been tried, as expected the stability of the emulsion increases with SPAN 80 concentration, but the differences are limited showing that the two concentrations of SPAN 80 are convenient: 5% and 6%.

**Table 8.** Variation of breaking rate with the SPAN 80 concentration.

SPAN 80 (%)	2	3	4	5	6
BR (%)	6.14	2.85	2.01	1.79	1.07

Choice of diluent

The di-2-ethylhexylphosphoric (HDEHP) acid dissolves in several organic solvents such as hexane, heptane, benzene and dodecane. With all parameters previously optimised, and following the same procedure used above, we were able to control the variation of emulsion breaking rate prepared in dodecane and heptane (Figure 1). The dodecane efficiency seems to be better than that of heptane.

Optimal conditions

The optimal conditions can be summarized as follows: SPAN 80 = 5%, HDEHP = 6%, Dodecane = 89%, membrane /inner phase = 4, rotating speed of the transfer step = 250 rpm, sulphuric-acid concentration = 0.5 mol/L, emulsification rotating speed = 200 rpm, emulsification time = 5 min, the diluent is dodecane, and the temperature = 25 °C.
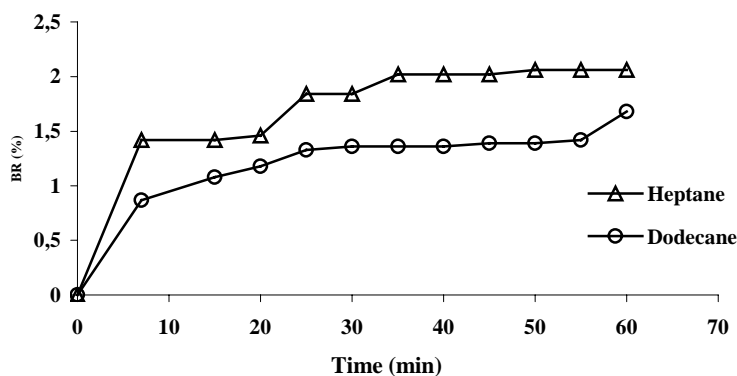
Figure 1. Plot of BR (%) versus time for different diluents with SPAN 80 concentration of 5%.

Extraction of cobalt by membrane liquid emulsion

Cobalt was studied more precisely than the other metals in order to find out the optimal conditions for a good transfer. These conditions were afterwards tested on the other metals such as lead, nickel, mercury. The experiments were generally performed under the following conditions: Initial cobalt concentration = 100 mg/L, concentration of

HDEHP = 6% (in weight), concentration of SPAN 80 = 5%, dodecane = 89%, stripping phase: sulphuric acid = 0.5 mol/L, volume of the aqueous phase to be purified = 100 ml/L, emulsion volume = 10 mL, membrane volume/internal phase volume = 4, and the rotating speed during the transfer step = 250 rpm. During the transfer of cobalt, the pH of the aqueous external phase was kept to the desired value by addition of ammonium acetate. Several chemical and operating parameters were studied as follows:

Effect of external phase pH

The experiments were performed for different values of pH, as shown in Figure 2. In the following figures $(Co)_{ext}$ is the concentration of cobalt in the aqueous external phase at time *t*.

The kinetic of extraction increases with increasing pH. The extraction is indeed slower for pH 2.29, the cationic exchange being more difficult when the acidity increases. In contrast, the extraction is very satisfactory between pH values of 3.09 and 4.6. At a pH 6.11 the emulsion is no more stable. The optimal range of pH is then between 3 to 4.6. Subsequently, all the following experiments were performed at pH 4.6.

Effect of extractant concentration

The cobalt concentration in the external phase decreases with time and an increasing HDEHP concentration (up to 8%). Above this concentration the emulsion is not stable. These results are presented in Figure 3.
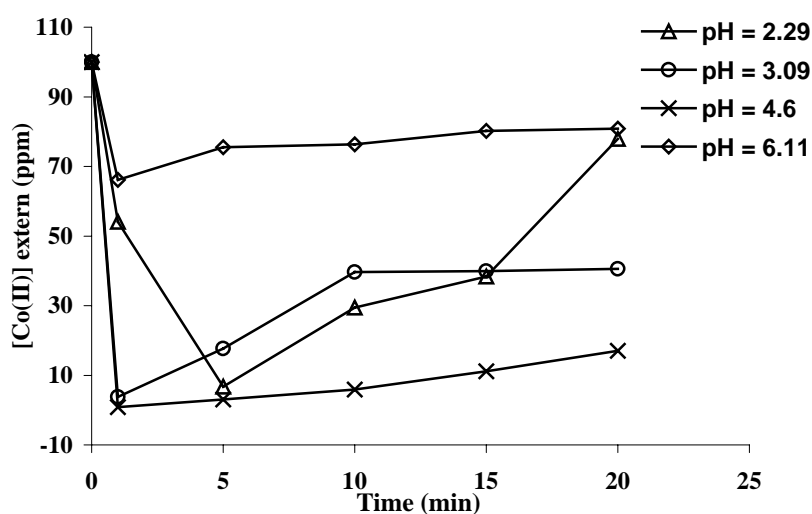

Figure 2. Plot of Cobalt concentration versus time at various pH.

Effect of the rotating speed in the transfer step

In this experiments, concentrations of HDEHP and SPAN 80 are respectively 6% and 5%. As expected the greater the rotating speed is, the better the extraction as shown in Figure 4. Indeed, the greater agitation results with a higher external interfacial area and then a quicker transfer. However, it is not possible to increase the rotating speed over 250 rpm without having a significant breaking of emulsion. Therefore, an intermediate value of the rotating speed must be adopted between the values of 200 to 300 rpm.

Effect of the volume ratio of the aqueous external and emulsion

This ratio (B) was varied from the value of 5 to the value of 15. The contacting time is 5 minutes; this is because it is the interval time where the membrane is very stable.
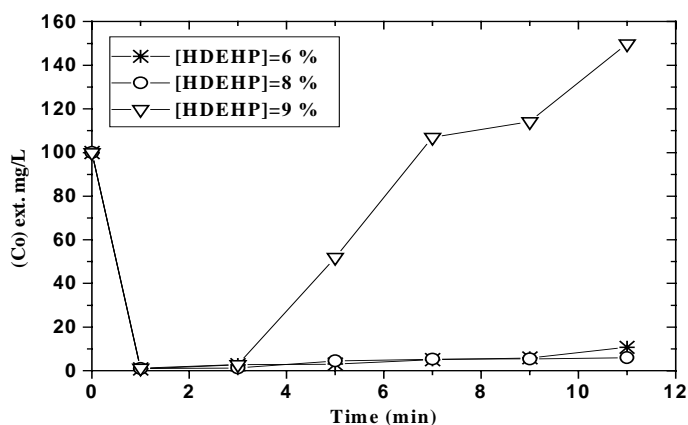

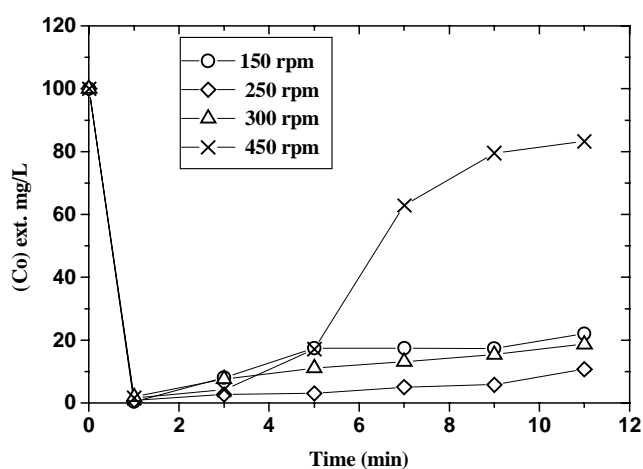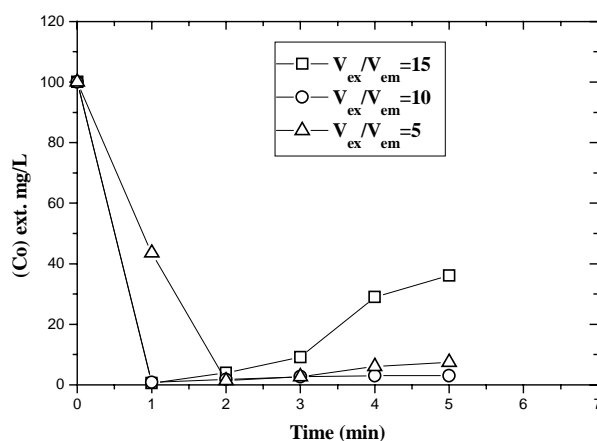**Figure 3.** Plot of cobalt concentration versus time at different HDEHP concentration.

Figure 4. Plot of cobalt concentration versus time at different rotating speed in the transfer step.

Figure 5. Plot of cobalt concentration versus time at different ratio of the aqueous external and emulsion.

As was expected the cobalt extraction slightly increases when the studied ratio decreases, this is mainly due to the greater volume of the emulsion as can be seen on the following in Figure 5, where (Co) is the concentration of metal remaining in the external phase after 2 minutes, but the differences are very limited in this range of values of the ratio (B). The optimal value of the ratio is 10.

Optimal conditions

The optimal conditions were taken to be: SPAN 80 = 5%, HDEHP = 6%, dodecane = 89%, membrane volume/internal phase volume = 4, external phase volume/emulsion volume = 10, contacting time = 1 min, stirrer speed = 250 rpm, and the extracting efficiency ($R_{ext.}$) is calculated from the following equation as $R_{ext.}$ = (quantity of extracted cobalt/quantity of initial cobalt):

$$R_{ext.} = \left(C_{0ext.}.V_{0ext.} - C_{fext.}.V_{fext.} / C_{0ext.} / C_{0ext.}.V_{0ext.} \right) \times 100 \qquad (3)$$

where $C_{0ext.}$ is the initial concentration of cobalt in the external aqueous, $C_{fext.}$ is the final concentration of cobalt in external aqueous phase, $V_{0ext.}$ the initial volume of the external aqueous phase, $V_{fext.}$ is the final volume of the external aqueous phase, the value of $R_{ext.}$ was found to be equal to 99.15% for a contact time of 1 minute.

Cobalt stripping

In this case, the parameter we studied was the concentration of inner phase (sulphuric acid). The other conditions were: HDEHP = 6%, SPAN 80 = 5%, dodecane =

89%, the ratio volume of the emulsion/inner phase = 4, the rotating speed in the transfer step = 250 rpm, the contacting time = 5 minutes, pH of the external phase is 4.6, the external phase volume /emulsion volume = 10, and the initial concentration of cobalt = 100 mg/L.

Effect of the sulphuric-acid concentration

In this case, the value of the ratio membrane/inner phase is taken to be equal to 4. For the acid concentration between the values of 0.5 and 1.5 mol/L, the stripping of cobalt is greater or equal to 60%.

However, for a concentration of sulphuric acid greater than 1.5 mol/L, the emulsion swells up due to the osmosis, which provokes the dilution of the internal phase by the transfer of water from the external phase, resulting in a less effective stripping. In addition, the emulsion stability is poorer. The optimal stripping efficiency $R_{des.}$ is found to be equal to 63.29% for a sulphuric-acid concentration of 1 mol/L.

Case of lead

In the previously determined conditions, a study of the extraction of lead versus the pH of the external phase was performed. At a value of pH 4, the extraction of lead is very satisfactory, and the extraction yield for pH 4 is 99.13%. The de-extraction efficiency (R_{des}) as defined in eq. (5) is calculated from the following material balance:
Initial quantity of lead in the external phase = quantity of extracted lead + quantity of remaining lead:

$$C_{0ext.}V_{0ext.} = XV_{W/O} + C_{fext.}V_{fext.} \tag{4}$$

where $XV_{W/O}$ represents the lead quantity, which has been moved from the external phase to the emulsion W/O. This quantity has a concentration X of lead in a volume $V_{W/O}$ of emulsion, $R_{des.}$ = (Quantity of de-extracted lead by the membrane/quantity of moved lead from the external phase to the emulsion) x100 defined by

$$R_{des.} = \left(C_{f\,int.}V_{f\,int.} / XV_{E/H}\right)\times100 = \left(C_{f\,int.}V_{f\,int.} / C_{0ext.}V_{0ext.} \quad C_{fext.}V_{fext.}\right)\times100 \tag{5}$$

where $C_{fint.}$ is the final lead concentration as internal phase, $V_{fint.}$ is the internal phase final volume, $C_{fext.}$ is the final lead concentration as external, $V_{fext.}$ is the external phase final volume, $C_{0ext.}$ is the initial lead concentration as external phase, and $V_{0ext.}$ is the

external phase initial volume. The stripping efficiency is very satisfactory when R_{des} 70.23% and the internal phase concentration HCl = 0.5 mol/L.

Purification of a solution containing the two metals

The initial external aqueous solutions contained 100 mg/L of Co and Pb at pH 4.6. The organic phase was composed of 6% HDEHP, 5% SPAN 80, and dodecane. The internal solution contained sulphuric acid of 1 mol/L. The volumes of the organic and the external phases were respectively 10 mL and 100 mL, the ratio membrane /internal phase was 4, the stirrer speed was 250 rpm during 5 minutes at a temperature of 25 °C, and the emulsification speed of 2000 rpm during 5 minutes. The results are presented in Figure 6.

For a contacting time of 2 minutes, the extraction efficiencies are 98.83% for cobalt and 94.21% for lead. For de-extraction, we found an efficiency of 78.01% for cobalt and 63.44% for lead.
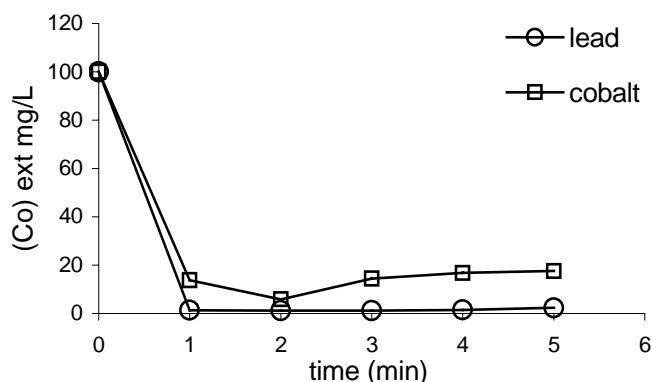

Figure 6. Plot of cobalt and lead concentration versus time.

Conclusion

The surfactant chosen SPAN 80 is an efficient surfactant enhancing the formation of stable emulsion water in oil even at low concentration with a breaking rate equal to 1.07% for a contacting time of 6 minutes. The kinetic of extraction of the two metals is very quick which reduces considerably the swelling up phenomena of the membrane by osmosis. After 1 minute, the extraction efficiency of cobalt at pH 4.6 is 99.15%. For a contacting time of 3 minutes, the extraction efficiency of lead is 98.13% at pH 4. The de-extraction efficiency is 63.29% for cobalt and 70.23% for lead. In the case of the mixture

extraction, the cobalt extraction efficiency is 98.3% and 94.21% for lead for a contacting time of 2 minutes.

Nomenclature

BR.......percentage breaking rate
C..........concentration, mg/L
HLB ....hydrophilic-lipophilic balance
LSM ....liquid surfactant membrane
O ....oil
V ....volume, mL
W.........water

References

1. R. R. Barefoot, A. Wang, J. C. Vanloon, Y. Li, *Talanta* **1992**, *39*, 1337–1341.
2. J. Draxler, W. Furst, R. Marr, *I. S. E. C.* **1988**, 6–1, Moscow.
3. D. Hartmann, « Extraction de l'Uranium contenue dans le lexiviats par membrane émulsionnée », *Thèse de l'école Centrale*, Paris, 1992.
4. T. C. H. Huang, T. H. Tsai, *Acta. Chem. Scand.* **1991**, *45*, 383–391.
5. R. Kopunec, T. H. Ngomanh, *J. Radioanal. Nucl. Chem.* **1994**, *1*, 181–204.
6. N. N. Li, US Pat. 3, 410, 794, **1968.**
7. M. E. H. Samar, D. Pareau, G. Durand, A. Chesne, *International Symposium Hydrometallurgy, ed.* Institution of Mining and Metallurgy, **1994**, 635–654.
8. M. E. H. Samar, D. Pareau, G. Durand, A. Chesne, *Bull. Soc. Chim. Fr.* **1992**, *129*, 259–264.
9. A. Sato, S. Nakamura, K. Akiba, *J. Radioanal. Nucl. Chem.* **1994**, 178, 63–71.
10. J. A. Partridge, R. C. Jensen, *J. Inorg. Nucl. Chem.* **1969**, 31, 2587–2595.

Povzetek

Proučevali smo uporabnost postopka ekstrakcije v emulziji s pomočjo tekoče membrane ob dodatku površinsko aktivne snovi (Liquid Surfactant Membrane - LSM) pri procesih odstranjevanja in koncentriranja svinca in kobalta. Cilj tega dela je bil najti primeren način čiščenja odpadnih vod, ki vsebujejo kobalt in svinec. Izvedli smo obsežno študijo ekstrakcije kovin v HDEHP preko tekoče membrane, pri čemer je bil kot površinsko aktivna snov uporabljen SPAN 80. Določili smo učinkovitost ekstrakcije in stripinga ter stabilnost in nabrekanje emulzije. Rezultati so pokazali, da je možno odstraniti do 98.83% kobalta in 94.21% svinca pri kontaktnem času 2 minuti. Koncentracijska faktorja za svinec in kobalt sta bila 50.