We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Removal of Copper Ions from Aqueous Solution Using Liquid Surfactant Membrane Technique

Huda M. Salman and Ahmed Abed Mohammed

Abstract

Liquid Surfactant Membrane (LSM) as an alternative extraction technique shows many advantages without altering the chemistry of the oil process in terms of efficiency, cost effectiveness and fast demulsification post extraction. Copper (Cu) extraction from aqueous solution using Liquid Membrane (LM) technology is more efficient than the sludge-forming precipitation process and has to be disposed of in landfills. In this chapter, a liquid surfactant membrane (LSM) was developed that uses kerosene oil as LSM 's key diluent to extract copper ions as a carrier from the aqueous waste solution through di-(2-ethylhexyl) phosphoric acid (D2EHPA). This technique has several benefits, including extracting one-stage extracts. The LSM process was used to transport Cu (II) ions from the feed phase to the stripping phase, which was prepared, using H_2SO_4 . For LSM process, various parameters have been studied such as carrier concentration, treat ratio (TR), agitating speed and initial feed concentration. After finding the optimum parameters, it was possible to extract Cu up to 95% from the aqueous feed phase in a single stage extraction.

Keywords: copper, D2EHPA, extraction, surfactant, liquid membrane

1. Introduction

Increased use of metals and chemicals in process industries has led to the production of large volumes of effluent containing high levels of toxic heavy metals and their presence, due to their non-degradable and persistent existence, poses problems with disposal. World Health Organization (WHO)-based aluminum, cobalt, chromium, iron, cadmium, nickel, zinc, copper, lead and mercury are the most toxic metals [1–3].

Leather tanning, mining, electroplating, textile dyeing, coating operations, aluminum conversion, and pigments are the main industries that introduce water contamination by chromium. Owing to the decreasing availability of natural resources and the rising contamination in the atmosphere, the removal of ions from their effluents has taken on greater significance in the recent past [4–6]. For environmental purposes, the removal of copper (Cu) from aqueous solutions requires an effective method (toxic ions if they are beyond the WHO limits). The minimization of liquid effluents containing hazardous metals is a general concern.

The solvent extraction process is a conventional method to eliminate Cu from solutions. A well-established Cu extract, such as diketones or hydroxytoxic agents [7], should be used in this technique. Both are LIX acid (Cognis) and phosphoric acid (D2EHPA) di- (2-ethylhexyl) [8–11].

Liquid surfactant membrane (LSM) for the isolation of solvents, such as phenols, biochemical products and metal pollutants [2, 12–19], has been considered as an alternative to solvent extraction. LSM is a form of triple dispersion, where a primary emulsion (water/oil or oil/water) is dispersed to be processed in the feed process (E). The liquid membrane consists of three phases: I internal, ii) external and iii) organic. The organic phase includes a diluent, an emulsifier to stabilize the emulsion and, in the case of metal ion separation [10], an extractant. The solution is transferred through the membrane through the stripping phase droplets during the mixing between the feed phase (E) and the emulsion (organic + internal) and is concentrated [20]. After extraction, the emulsion is isolated from the raffinate process and the emulsion is typically demulsified by high voltage or heat application. There are several advantages to LSM, such as single-stage re-extraction, large specific surface area for extraction, concurrent extraction and the need for an expensive extractant in small quantities [10, 21, 22].

The aim of this research was to investigate the potential of a liquid surfactant membrane (LSM) to extract copper ions from the feed solution. Despite studies in this area, the study examined different experimental parameters, such as extractant concentration, ratio of treatment, rate of agitation, and initial feed concentration, to determine the best conditions that would give the LSM the greatest efficiency.

2. Experimental protocols

2.1 Reagents

The phosphoric acid di-(2-ethylhexyl) (D2EHPA) worked as a shuttle and the nonionic emulsifier was Sorbitan monooleate (Span 80 C₂₄H₄₄O₆), both of which were supplied by Sigma-Aldrich (Merck, Darmstadt, Germany). The Southern Oil Company (SOC) (Al Basra-Iraq) supplied kerosene used as a diluent, while the removing agent was sulfuric acid (H₂SO₄) and was purchased from the acid and base factory (Babylon, Iraq). Copper solutions were prepared from nitrate of copper (Chemical, Company, Co., Ltd. Korea).

2.2 Procedure

The experimental work consists of four parts: emulsion preparation as a first step, stock solution preparation, extraction process execution, and emulsion demulsification. In this article, **Figure 1** shows the LSM process.

2.2.1 Emulsion preparation

Mixing those volumes of kerosene, Span80, and D2EHPA using SR30 digital Homogenizer, (model: 670/340 W, 10-2000 ml, 3000–27,000 rpm) at a speed of 17,500 rpm to reach the oil process. The sulfuric acid (H₂SO₄) solution was applied dropwise to the oil process as a stripping agent until the necessary volume ratio was obtained from the oil solution to the stripping solution. To achieve a stable Water/Oil LSM, the solution was continuously stirred for 10 minutes.

Figure 1.
 LSM technique: (1) droplets, (2) organic phase, (3) globules, (4) emulsifier, (5) internal phase and Cu.

2.2.2 Feed phase preparation

This stage was prepared to obtain the necessary concentrations (200 ppm) of copper by adding distilled water (conductivity, $1 \mu\text{S/m}$) to $\text{Cu}(\text{NO}_3)_2$ (solid form) and then adding some drops of sulfuric acid to pH 4.

2.2.3 Extraction

At a temperature of $25 \pm 1^\circ\text{C}$, all experiments were performed. The prepared emulsion (2.2.1) has been added to a specific feed solution volume. The production of double emulsions of water / oil/water was obtained by stirring the contents with a digital stirrer (12,700 rpm) for 12 minutes. The external solution (E) was drawn from the syringe and filter syringe and then analyzed by AAS (atomic absorption spectrophotometry). The resulting solution was allowed to be separated by gravity into an emulsion (water/oil) and an external solution (E) in a 24-hour separation funnel. The external phase was drawn after two-phase separation and the concentration of Cu was analyzed using AAS (Atomic Absorption Spectrophotometer) in the internal phase. The Cu(II) ions remain in membrane process can be determined by mass balance. The extractant concentration, initial Cu concentration, treatment

ratio (TR) and stirring speed were varied to observe their effects on Cu extraction in order to understand the important variables relating to the extraction of Cu.

2.2.4 Demulsification of the emulsion

After the extraction experiment, the loaded emulsion was broken into the internal Cu concentrated phase and the organic phase by means of a hot plate magnetic stirrer (70° C for 43 minute). The internal phase (I) was analyzed and the Cu concentration determined after that.

2.3 Extraction mechanism in the ELM system

The prepared emulsion (Section 2.2.1) containing a certain concentration of copper ions at pH 4 (adding some drops of 0.2 M H₂SO₄) was transferred to the external process. For 0–12 minutes, a robotic mixer was used to stir the solution. Eqs. 1 and 2 elucidate the extraction and stripping reactions of the copper ions.

Here, RH refers to an extractant's protonated form (D2EHPA in this paper) [23]. **Figure 2** [24, 25] reveals the D2EHPA structure.

Extraction reaction of the copper ions:

Stripping reaction of the copper ions:

At the membrane (O)-external (E) interface, Eq. (1) denotes the reaction, whereas Eq. (2) shows the reaction where the copper ions are stripped at the oil (O)-internal (W) interface. **Figure 3** describes the movement of Cu (II) ions by an extractant from the external phase to the internal phase. Based on the Eq. (3), the extraction percentage (E percent) is found:

$$E\% = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (3)$$

In the external phase, where C_{in} is the initial copper concentration, and C_{out} is the concentration of copper ions after the extraction phase.

Figure 2.
Depicts the structure of D2EHPA.

Figure 3.
Depicts the transfer mechanism of LSM.

3. Results and discussion

3.1 Effect of changes in carrier concentration on copper removal efficiency

As expected, this paragraph presented in **Figure 4**, as soon as the mixing began, the extraction efficiency increased in the first 0.5 minutes due to the efficacy of the carrier in carrying the copper ions and the increase of the shuttle D2EHPA concentration from 6–8% (v / v) provides only a 2% increase in the quantity extracted using LSM. At 10% D2EHPA, the E percentage decreased significantly. It should be noted that the D2EHPA concentration in the membrane process was observed to decrease the rate of copper extraction in the range of 2% (v / v) to 4% (v/v) under optimum conditions for copper extraction from nitrate solution, as observed by [2, 23]. An improvement of 2 percent from an economic point of view is very low, so 6 percent of D2EHPA is used in the experiments.

Figure 4.
Effect of D2EHPA concentration on the Cu extraction at optimal conditions using LSM. (O/I = 1/1, span 80 = 4 v/v%, H_2SO_4 = 0.5 M, feed concentration $\approx$ 200 mg/L, pH = 4, TR = 1:10, mixing speed = 250 rpm).

3.2 Effect of changes of stirring speed on the copper removal efficiency

Stirring speed was found to be another parameter affecting extraction to a large extent, and it was studied using LSM1 in the 150 to 550 rpm range and shown in **Figure 5**. Using LSM, as the stirring speed increased from 150 to 250 rpm, copper removal increased from 82% to 94.7% in 11 minutes. This was due to the small size of the globules (SSG) formed by the shear force of the stirrer impellers, which provided more interfacial surface area for efficient mass transfer. In the external phase, no copper was detected for more than 11 minutes due to membrane breakage. However, as the stirring rate was increased to 300 rpm, the emulsion and external phase were introduced with more shear, which promotes emulsion breakage. The interfacial contact area and mass transfer between the external phase and the emulsion decreased due to the larger size of the emulsion for lower agitating velocity. For a satisfactory extraction percentage, 250 rpm was appropriate.

The proportion starts to decrease after 250-rpm extraction. A further increase in the mixing speed resulted in a breakdown of the liquid surfactant membranes, resulting in the outflow of extracted lead into the external phase. This is due to a higher mixer speed, which usually results in greater transport of water into the inner strip process beyond limits, causing the membrane to swell [26, 27]. 250 rpm was therefore chosen as the optimum speed of mixing for Cu (II) extraction.

3.3 Effect of changes of treat ratio (TR) on the copper removal efficiency

The ratio of the emulsion phase to the feeding phase in an LSM extraction is the treatment ratio. Generally, rising TR contributes to an improvement in the loading ability and extraction rate. This case occurred due to an increase in emulsion volume and an increase in D2EHPA and H_2SO_4 [28, 29]. **Figure 6** illustrates the effect of TR on the copper extraction from copper nitrate solutions using LSM. As TR improved, there was an improvement in the efficiency of this ratio as it improved from 1:15 to 1:10. Because of the increased hold-up of the emulsion, this trend may be known from a potential rise in distribution of globule size. Due to increased globule-size distribution at larger emulsion hold-ups, Sengupta et al. (2006) observed a strong decrease in the extraction percentage of silver ions when TR was raised from 1:6 to 1:4.

The formation of LG (larger-globules) decreases the outer surface areas and increases the effective duration of the pathways of diffusion between the globules, resulting in a low removal rate of Cu. Treatment ratios of 1:15, 1:10 and 1:5 indicate a substantial increase in extraction capacity at which time TR increased from

Figure 5.
The effect, of stirring speed on a rate of copper extraction using LSM.

Figure 6.
Effect of (TR) on the Cu-extraction by LSM

1:15 to 1:10, owing to an increase in emulsion retention, the size distribution of the globules tended to shift to LG with a consequent decrease in the pace.

3.4 Effect of changes of initial copper concentration on copper removal efficiency

Using emulsions with O/I = 1/1, span80 = 4 v / v percent of the organic phase and H₂SO₄ = 0.5 M, D2EHPA = 6 percent (v/v), the effect of initial Cu (II) ion concentrations in the feed on the rate of copper extraction was investigated. At 4 and 1:10 respectively, the original (pH) and (TR) were retained. The extraction results are shown in **Figure 7**, which is a plot of the change in copper concentration over time in the feed stage.

Figure 8 demonstrates the pattern of copper loading in LSM along with a quantitative assessment of the quantity of copper stripped in the internal stripping step of the emulsion after a 12-minute contact between the feed and LSM for differences in the initial feed concentration.

Figure 7.
Effect of initial-feed concentration on rate of copper extraction using LSM (O/I = 1/1, span 80 =,4 v/v%, H₂SO₄=,0.5 M, D2EHPA = 6%, feed concentration≈ 200 mg/L, pH = 4, TR = 1:10, mixing speed = 250 rpm). (Cu IE, initial-concentration of copper, in the external phase).

Figure 8.

Copper extraction, stripping patterns in LSM. (Int., internal phase; roil, retained in the oil phase; FExt, final concentration in the external phase).

The extent of copper-extraction-into LSM was also increased as the initial-feed concentration increased. When Cu loading was low, most of the Cu extracted in the membranes was stripped during the inner process of the membranes. However, the amount of copper stripped during the internal process of the LSMs did not increase significantly at high copper loadings, so most of the copper removed by the LSMs was retained during the membrane phase [4, 21, 22].

From the slow stripping kinetics, as well as the diffusional effects that play an important role in further slowing down the stripping rates, the low percentage of Cu stripping could be recognized. Strong CuIE (Initial copper concentration) values lead to higher copper loads in the LSMs, resulting in rapid saturation of the peripheral internal phase droplets in the emulsion, requiring deeper penetration of the Cu-D2EHPA complex inside the emulsion globules to be stripped.

4. Conclusions

Using a liquid surfactant membrane (LSM), copper Cu (II) extraction from an aqueous process was studied. The membrane consisted of D2EHPA dissolved as a solvent as an emulsifier in kerosene and span80, respectively. The stripping-solution was used for sulfuric acid (H_2SO_4). The optimum conditions for Cu extraction are: (a) 6–8 percent (v / v) concentration of D2EHPA, (b) 4 percent (v/v) concentration of span80, (c) concentration of 0.5 M concentration of H_2SO_4 in the internal phase, (d) 1:1 the internal phase-to-membrane phase ratio; (e) the external phase acidity is 4; (f) the external phase volume is 1/10 of the membrane volume; (g) the extraction time is 11 minutes; and (h) the agitation speed is 250 rpm. The results also showed that many parameters are very important in Cu extraction, stirring speed, D2EHPA concentration, feed concentration and treatment ratio, (2) Cu extraction efficiency (E) is 95 percent at 11 minutes. (3) Small emulsion droplets are produced at the higher agitating velocity of the water /oil/water emulsion, thus increasing the carrier/Cu reaction interface area. However, in order to increase the extraction efficiency, this paper considered a maximum limit (250 rpm); (4) the results showed that the LSM method is a beneficial method for removing Cu from aqueous solution.

IntechOpen

IntechOpen

Author details

Huda M. Salman* and Ahmed Abed Mohammed
Environmental Engineering Department, College of Engineering,
University of Baghdad, Baghdad, Iraq

*Address all correspondence to: hudamohammad20@gmail.com

IntechOpen

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

- [1] Hegazi HA. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC Journal*. 2013;**9**:276-282
- [2] Mohammed AA, Selman HM. Liquid surfactant membrane for lead separation from aqueous solution: Studies on emulsion stability and extraction efficiency. *Journal of Environmental Chemical Engineering*. 2018;**6**:6923-6930
- [3] Algureiri AH, Abdulmajeed YR. Removal of heavy metals from industrial wastewater by using RO membrane. *Iraqi Journal of Chemical and Petroleum Engineering*. 2016;**17**:125-136
- [4] Lu D, Chang Y, Wang W, Xie F, Asselin E, Dreisinger D. Copper and cyanide extraction with emulsion liquid membrane with LIX 7950 as the mobile carrier: Part 1, emulsion stability. *Metals*. 2015;**5**:2034-2047
- [5] Hasan M, Selim Y, Mohamed K. Removal of chromium from aqueous waste solution using liquid emulsion membrane. *Journal of Hazardous Materials*. 2009;**168**:1537-1541
- [6] Hochhauser AM, Cussler E. Concentrating Chromium with Liquid Surfactant Membranes. *American Institute of Chemical Engineers: AIChE Symposium Series*; 1975. pp. 136-142
- [7] Rydberg J, Musikas C, Choppin GR. Principles and practices of solvent extraction. M. Dekker New York. 1992
- [8] Kongolo K, Mwema M, Banza A, Gock E. Cobalt and zinc recovery from copper sulphate solution by solvent extraction. *Minerals Engineering*. 2003;**16**:1371-1374
- [9] Hu S-YB, Wiencek JM. Copper—LIX 84 extraction equilibrium. *Separation Science and Technology*. 2000;**35**:469-481
- [10] Abdel-Halim S, Shehata A, El-Shahat M. Removal of lead ions from industrial waste water by different types of natural materials. *Water Research*. 2003;**37**:1678-1683
- [11] E.A. Fouad, Zinc and copper separation through an emulsion liquid membrane containing Di-(2-Ethylhexyl) phosphoric acid as a carrier, *Chemical Engineering & Technology: Industrial chemistry-plant equipment-process engineering-Biotechnology* 31 (2008) 370-376.
- [12] P.F. Correia, J.M. de Carvalho, Recovery of 2-chlorophenol from aqueous solutions by emulsion liquid membranes: Batch experimental studies and modelling, *Journal of Membrane Science* 179 (2000) 175-183.
- [13] Mohammed AA, Selman HM. Extraction of Lead ions from aqueous solution by CO-stabilization mechanisms of magnetic Fe₂O₃ particles and nonionic surfactants in emulsion liquid membrane. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2019
- [14] Fouad E, Ahmad F, Abdelrahman K. Optimization of emulsion liquid membrane for Lead separation from aqueous solutions. *Engineering, Technology & Applied Science Research*. 2017;**7**:2068-2072
- [15] Zeng L, Wang W, Chen W, Bukirwa C, Yang Y. Experimental and modeling of nickel removal from sulfate solutions by emulsion liquid membrane using PC 88A. *Desalination and Water Treatment*. 2016;**57**:11184-11194
- [16] Ng YS, Jayakumar NS, Hashim MA. Performance evaluation of organic emulsion liquid membrane on phenol

removal. *Journal of Hazardous Materials*. 2010;**184**:255-260

[17] Correia PF, de Carvalho JM. A comparison of models for 2-chlorophenol recovery from aqueous solutions by emulsion liquid membranes. *Chemical Engineering Science*. 2001;**56**:5317-5325

[18] Diaconu I, Gîrdea R, Cristea C, Nechifor G, Ruse E, Totu EE. Removal and recovery of some phenolic pollutants using liquid membranes. *Romanian Biotechnological Letters*. 2010;**15**:5702-5708

[19] Mahmoud HE, Al-Hemiri AA. Minimization of toxic ions in waste water using emulsion liquid membrane technique. *Iraqi Journal of Chemical and Petroleum Engineering*. 2010;**11**:11-19

[20] Zing-Yi O. N. Oth+mn, M. Mohamad, R. Rashid, Removal performance of lignin compound from simulated pulping wastewater using emulsion liquid membrane process, *International Journal of Global Warming*. 2014;**6**:270-283

[21] Sengupta B, Bhakhar MS, Sengupta R. Extraction of copper from ammoniacal solutions into emulsion liquid membranes using LIX 84 I®. *Hydrometallurgy*. 2007;**89**:311-318

[22] Rouhollahi A, Zolfonoun E, Salavati-Niasari M. Effect of anionic surfactant on transport of copper (II) through liquid membrane containing a new synthesis Schiff base. *Separation and Purification Technology*. 2007;**54**:28-33

[23] Ren Z, Zhang W, Meng H, Liu Y, Dai Y. Extraction equilibria of copper (II) with D2EHPA in kerosene from aqueous solutions in acetate buffer media. *Journal of Chemical & Engineering Data*. 2007;**52**:438-441

[24] He J, Li Y, Xue X, Ru H, Huang X, Yang H. Extraction of Ce (IV)

from sulphuric acid solution by emulsion liquid membrane using D2EHPA as carrier. *RSC Advances*. 2015;**5**:74961-74972

[25] Irannajad M, Afzali Z, Haghghi HK. Solvent extraction of copper using TBP, D2EHPA and MIBK. *Russian Journal of Non-Ferrous Metals*. 2018;**59**:605-611

[26] Kumbasar RA. Extraction and concentration of cobalt from acidic leach solutions containing Co–Ni by emulsion liquid membrane using TOA as extractant. *Journal of Industrial and Engineering Chemistry*. 2010;**16**:448-454

[27] Abdulmajeed YR, Haweel CK, Slaiman QJ. Removal of heavy metals ions from aqueous solutions using biosorption onto amboo. *Iraqi Journal Of Chemical And Petroleum Engineering*. 2010;**11**:23-32

[28] Kusumastuti A, Syamwil R, Anis S. Emulsion Liquid Membrane for Textile Dye Removal: Stability Study. *AIP Conference Proceedings: AIP Publishing*; 2017. p. 020026

[29] Perumal M, Soundarajan B, Thazhathuveettil Vengara N. Extraction of Cr (VI) by Pickering emulsion liquid membrane using amphiphilic silica nanowires (ASNWs) as a surfactant. *Journal of Dispersion Science and Technology*. 2018:1-10