Removal of Copper ions from wastewater using Emulsion Liquid Membrane: Optimization and Performance Analysis

Sara Mobasser[1], Malihe Raji[1*]
Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

ABSTRACT

Extraction using emulsion liquid membranes has recently become an area of rapid research interest due to its efficiency in the removal of heavy metal ions and toxic substances from industrial wastewater. This study is a comprehensive investigation for copper ion removal from wastewater using emulsion liquid membranes (ELM). Hydrochloric acid (HCl) was used as the internal phase, while di(2-ethylhexyl) phosphoric acid (D2EHPA) was used as the carrier and Span 80 as surfactant. In addition, sunflower oil was used as the organic phase. A number of significant parameters such as pH, mixing speed, and surfactant concentration, were evaluated to optimize copper extraction efficiency. The results show that the maximum amount of extraction was %96.31 which obtained under optimal conditions with a pH of 3.0, surfactant concentration of 2 V/V%, and a stirring speed of 180 rpm.

Keywords: Emulsion Liquid Membrane, Copper Ion removal, Industrial Wastewater Treatment, Heavy Metal Extraction

1. INTRODUCTION

Heavy metal ions are generally defined as elements with atomic weights between 63.5 and 200.6 with a specific gravity greater than 5.0[1]. Many heavy metal ions are toxic, or the accumulation of heavy metal ions can be harmful to living organisms. Among them, copper is particularly concerning due to its widespread industrial use and significant toxicity even at low concentrations. Excessive exposure to heavy metals, particularly copper, can damage human cells and tissues leading to various health issues and diseases[2]. For instance, high levels of copper can result in symptoms such as vomiting, convulsions, and cramps[1]. Considering the direct effect of wastewater pollution on human health, it is necessary to implement efficient methods for wastewater treatment. The release of copper-containing wastewater from industrial activities poses a serious environmental challenge. Recognizing the risks, governments worldwide have established strict regulations for permissible copper levels in wastewater, typically limited to 0.1 milligrams per liter[1]. However, achieving such low concentrations requires highly efficient treatment methods.

Various technologies such as adsorption, precipitation, biosorption, reverse osmosis, ion exchange and electrochemical methods are being used to eliminate metal ions from many sources of wastewater. However, overcoming the inherent disadvantages of these techniques is still a challenge that have fueled competition among industries to develop better alternatives. Common drawbacks of these techniques include operation complexity for ion exchange and reverse osmosis, high operating costs for liquid-liquid extraction and high consumption time and low efficiency for adsorption and precipitation[2].

To overcome the problems of previous techniques, membrane-based separation processes (MSPs) have emerged as a superior alternative to traditional methods. These MSPs offer numerous advantage, such as low chemical and energy consumption, low maintenance cost, clean, and easily scale up by simply joining to the additional membrane modules. Among the various MSPs, liquid membranes (LMs) are the recently introduced separation techniques for the removal of low-concentrated solutes. Currently, LM technology has rapidly gained acceptance as a versatile unit operation, with applications spanning biotechnology, textiles, pulp and paper, food and beverage processing, wastewater treatment, pharmaceuticals, and environmental engineering[3].

Emulsion liquid membrane (ELM) is an innovative liquid-liquid separation technique that combines extraction and stripping steps. It was first introduced in 1968 by Li for metallurgical applications[2]. Emulsion liquid membrane (ELM) is a highly effective separation technique, offering a 40% cost reduction compared to solvent extraction, lower energy consumption, a large interfacial area, and high mass transfer rates[3]. ELM technology is particularly advantageous for wastewater treatment due to its cost-effectiveness and environmental sustainability. It can utilize non-toxic, biodegradable materials derived from renewable plant sources, reducing both environmental impact and costs associated with hazardous chemicals. furthermore, its efficiency in combining extraction and stripping within a single process step results in substantially lower energy consumption compared to energy-intensive methods like ion exchange or reverse osmosis[2]. The simplicity of ELM system design also contributes to its cost advantages. Unlike more complex methods such as membrane separation or electrodialysis, ELM systems require minimal equipment, leading to reduced capital and maintenance expenses. Additionally, the capacity for resource reuse and recycling within the ELM process further reduces operational costs, offering significant savings in long-term industrial applications[2]. Despite its advantages, ELM faces challenges related to stability. Issues such as internal reagent leakage, emulsion droplet coalescence, membrane dissolution, and solute transport into the emulsion phase have been reported. To address these problems, various approaches have been explored, including increasing membrane phase viscosity by adding surfactants or using Newtonian additives to enhance stability[3].

With the increasing demand for sustainable and efficient ways to treat wastewater, this study focuses on using ELM technology to remove copper from wastewater.

2. MATERIALS AND METHODS

The emulsion liquid membrane (ELM) was prepared by mixing sunflower oil, Span 80, and D2EHPA with further addition of HCl solution by constant stirring at the rate of 12000 rpm for 10 minutes. The emulsion was added slowly dropwise to a feed solution of 100 mg/L copper sulfate under edified stirring speed. Copper was analyzed using atomic absorption spectroscopy. The optimization of key parameters, including pH, surfactant concentration, and mixing speed, was conducted using the One Variable at a Time (OVAT) approach.

In order to use this approach, internal phase concentration was set to 1M, the volume ratio of the internal to organic phase was 1:1, the volume ratio of the primary emulsion to the external phase was maintained at 1:10. These parameters were selected based on their importance in maintaining emulsion stability and optimizing extraction efficiency.

3. RESULTS AND DISSCUSSION

The extraction of copper using emulsion liquid membrane (ELM) is influenced by three key variables such as pH, surfactant concentration, and mixing speed. The impact of each parameter on the extraction percentage is discussed in detail to provide a better understanding of the process.

3.1 Effect of pH

This chart illustrates the relationship between initial feed phase pH and the copper extraction efficiency.

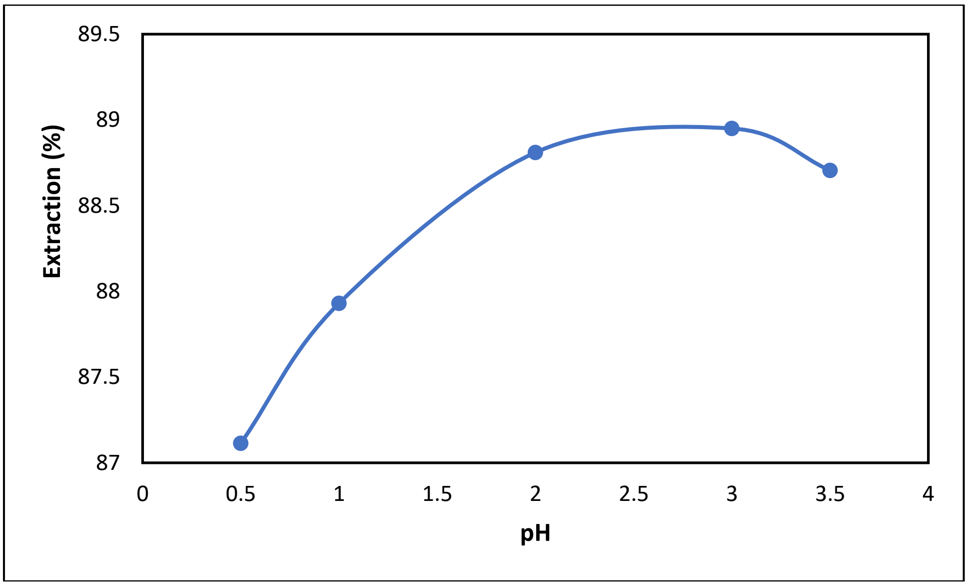

Fig. 1. *Effect of pH on Cu(II) extraction (Surfactant Concentration= 1 V/V%, Mixing Speed= o rpm)*

The pH gradient between the external phase and the receiving feed phase forms the main driving force behind solute transport in separation processes using emulsion liquid membranes (ELM). The external feed phase's acidity helps to bring about the transfer of the solute molecules from the outer phase to the internal phase [3].

At low pH values (below 1.0), the extraction efficiency is relatively low. This can be explained by the competition between hydrogen ions (H^+) and solute molecules at the feed phase interface, which hinders the formation of the metal-chelating complex. Furthermore, inefficient deprotonation of the extracting agent reduces its ability to form stable complexes with the target ions[1, 4].

As the pH increases toward the optimal range (2.0–3.0), extraction efficiency is considerably enhanced. In this range, the deprotonation of the extracting agent becomes more effective, leading to better formation of metal-chelating complexes. Additionally, osmotic pressure-induced swelling of the membrane stabilizes, reducing emulsion instability[5, 6].

Beyond the optimal pH of approximately 3.0, the extraction efficiency begins to decrease. This is likely due to increased osmotic pressure differences that result in excessive water transport into the internal phase, causing membrane swelling and emulsion instability. Furthermore, the decline may also be influenced by the nature of the extracting agent, as its ability to form complexes diminishes at higher basic pH levels[1, 4].

This indicates that maintaining an appropriate pH level is essential for maximizing the effectiveness of the ELM process.

3.2 Effect of surfactant

The graph above illustrates the effect of surfactant concentration on the effectiveness of Cu(II) extraction processes. The results highlight that the surfactant concentration is crucial for maintaining emulsion stability and achieving efficient extraction.

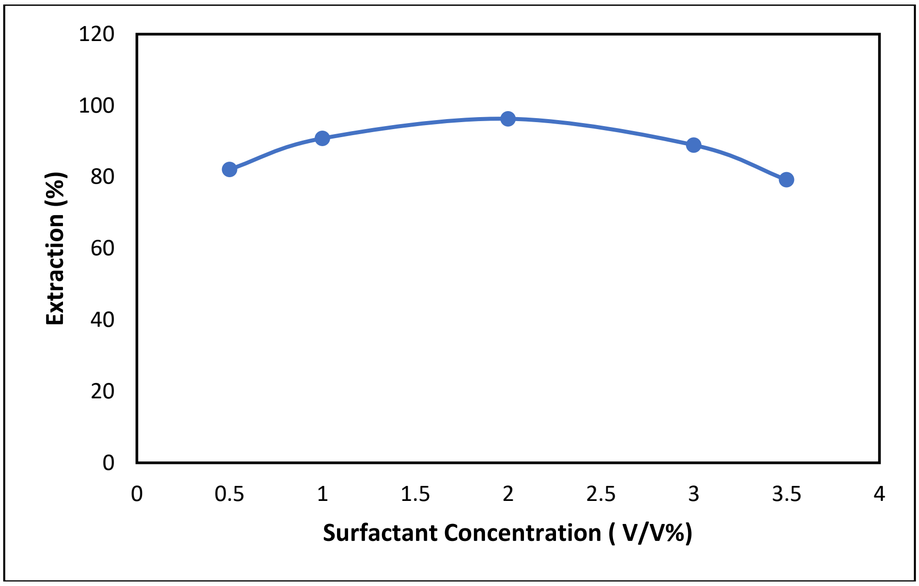

Fig. 2. *Effect of surfactant on Cu(II) extraction (pH=1, mixing speed= 0 rpm).*

The results indicate that the efficiency of extraction increases initially with the surfactant concentration to a maximum of %96.31 at a concentration of 2 V/V%. But then the efficiency decreases with the increase in concentration as the rate of extraction is falling down to around %79 for a concentration of 3.5% of surfactant. The observation suggests a requirement of optimum concentration of the surfactant to achieve better extraction performance.

There are several reasons for the observed behavior. When the surfactant concentration is low, the amount of surfactant is insufficient to effectively stabilize the emulsion. Therefore, the internal phase is not completely enveloped and the emulsion destabilizes rapidly with reduced extraction efficiency. At higher surfactant concentration, more droplets are formed as a result of the reduction in surface tension, thus a more stable emulsion is formed. But as the surfactant concentration is greater than the optimum, the emulsion viscosity rises considerably, and the mass transfer resistance is increased. This increased resistance restricts the transfer of Cu(II) ions to the internal phase, ultimately reducing extraction efficiency. Furthermore, excessive surfactant concentrations decrease the emulsion globules' mobility, and the emulsion swells, resulting in reducing extraction efficiency[5-7].

3.3 Effect of mixing speed

Mixing speed is also a key emulsion stability parameter. The following chart shows the relationship between stirring speed and copper extraction efficiency.

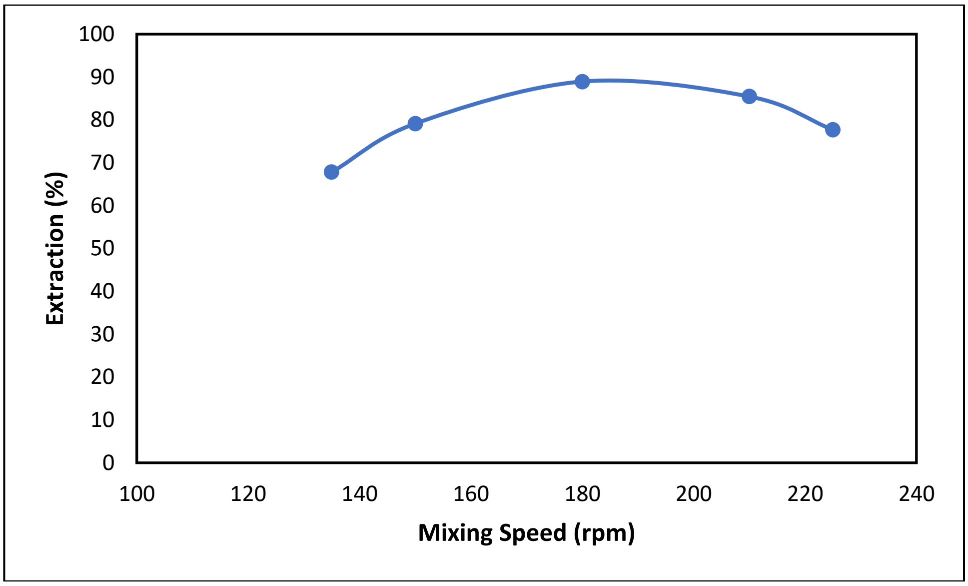

Fig. 3. *Effect of mixing speed on Cu(II) extraction (Surfactant Concentration==1 V/V%, pH=1)*

At low speeds of stirring (below 100 rpm), the efficiency of extraction is very low. This is likely because the emulsion globules are larger at these speeds, which reduces the interfacial area available for mass transfer[3, 6].

As the stirring speed increases, the extraction efficiency improves, peaking at 180 rpm. At this range, the increased shear force of the impeller leads to small and consistent droplets, which significantly increases the interfacial area of phases. This improvement allows for better mass transfer and solute recovery. These conditions are ideal for maintaining emulsion stability while achieving high extraction efficiency[3].

However, at stirring speeds above 180 rpm, extraction efficiency begins to decline. At these higher speeds, the intense agitation leads to problems like droplet coalescence, internal phase swelling, and even rupture of the emulsion globules. These issues reduce the stability of the emulsion and cause the receptor phase to leak into the feed phase[1, 3].

The results highlight the necessity to maintain the mixing speed optimum to strike a balance between stability of emulsion and extraction efficiency.

4. CONCLUSION

The present work was carried out with the aim of removing copper ions from the wastewater by the emulsion liquid membrane (ELM) technique. The key parameters of the process such as pH, surfactant concentration, and mixing speed were determined to achieve the optimal performance of the system. Results showed that the optimal pH of 3 facilitated effective metal-chelate formation while ensuring emulsion stability. Furthermore, the best surfactant concentration condition, achieving an extraction efficiency of %96.31, was found to be 2 V/V%, which maintained emulsion stability and enabled mass transfer. moreover, the 180 rpm stirring rate was considered ideal in gaining high interfacial area with small droplet size without rupture of the emulsion. These findings highlight the importance of precisely controlling process conditions to maximize the efficiency of ELM technology, offering valuable insights for its application in industrial wastewater treatment.

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