

Article

Optimization of Copper Removal from Aqueous Solutions Using Emulsion Liquid Membranes with Benzoylacetone as a Carrier

Loreto León ¹, Gerardo León ^{2,*}, Javier Senent ¹ and Carmen Pérez-Sirvent ³

¹ Departamento de Ciencias Politécnicas, UCAM, Campus de los Jerónimos, Guadalupe, 30107 Murcia, Spain; lleon@ucam.edu (L.L.); jsenent@ucam.edu (J.S.)

² Departamento de Ingeniería Química y Ambiental, Universidad Politécnica de Cartagena, 30203 Cartagena, Spain

³ Departamento de Química Agrícola, Geología y Edafología, Facultad de Química, Universidad de Murcia, 30169 Murcia, Spain; melita@um.es

* Correspondence: gerardo.leon@upct.es; Tel.: +34-868-071-002

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Abstract: The presence of heavy metals in aqueous solutions above certain limits represents a serious threat to the environment due to their toxicity and non-degradability. Thus, the removal of these metals from contaminated waters has received increasing attention during recent decades. This paper describes the removal of Cu(II) from aqueous solutions by emulsion liquid membranes, through a carrier-facilitated counter-transport mechanism, using benzoylacetone as the carrier and HCl as the stripping agent (protons as counter-ions). To optimize the Cu(II) removal process, the effect of the following operating parameters on the on the stability of the emulsion liquid membrane and on the Cu(II) removal efficiency was studied: feed pH, HCl concentration in the permeate phase, carrier and emulsifier concentration in the membrane phase, feed phase/emulsion phase and permeate phase/membrane phase volume ratios, emulsification time and speed in the primary emulsion preparation and stirring speed in the whole feed phase/emulsion phase system. Typical membrane transport parameters, such as flux and permeability, were also determined. Optimal Cu(II) removal conditions were: 5.5 feed pH, 10 kg/m³ benzoylacetone concentration in the membrane phase, 18.250 kg/m³ HCl concentration in the permeate phase, 50 kg/m³ Span 80 concentration in the membrane phase, 200 rpm stirring rate, 5 min emulsification time, 2700 rpm emulsification rate, 2:1 feed:emulsion volume ratio and 1:1 permeate:membrane volume ratio. In these optimal conditions, 80.3% of Cu(II) was removed in 15 min with an apparent initial flux and permeability of 0.3384 kg·m⁻³·min⁻¹ and 0.3208 min⁻¹, respectively.

Keywords: emulsion liquid membrane; copper(II); benzoylacetone; carrier mediated countertransport

1. Introduction

Illnesses related to water pollution are considered among the major causes of death in the world, and it is estimated that over two million people die each year for this reason [1]. The contamination of industrial and natural waters by organic and heavy metal pollutants is recognized as one of the greatest environmental problems nowadays. Heavy metals are not biodegradable in natural conditions, so they tend to accumulate in living organisms, causing various diseases and disorders [2]; furthermore, their presence in wastewater inhibits the biodegradation of organic pollutants, which might be present in the wastewater [3]. According to the World Health Organization, the metals of most immediate concern are chromium, copper, zinc, iron, mercury and lead [4].

Copper(II) is introduced in large quantities into the aqueous environment in the wastewater of many industries, including mining, metallurgy, plating, steelworks, paper and pulp, fertilizer, petroleum refining, wood preservatives, and circuits printing [5,6].

Although copper(II) is a micronutrient element, it is considered a hazardous pollutant when it cannot be maintained at an appropriate physiological concentration, and several disorders have been described as a consequence of copper accumulation in animals and humans. Acute copper poisoning causes gastroenteritis, diarrhea, anorexia, dehydration, and shock, while chronic copper poisoning contributes to Alzheimer's, Memkes and Wilson's diseases [7]. For these reasons, copper(II) has been classified as one of the priority pollutants by the US Environmental Protection Agency [8].

Several approaches have been studied and developed for the effective removal/recovery of copper ions including chemical precipitation [9], cementation [10], adsorption [6,11–13], biosorption [14–16], ion exchange [17], chelation [18], electro-driven processes [19–21] and pressure-driven membrane processes [22,23]. Liquid membranes have also been used for the removal of copper from aqueous solution [24–26].

Liquid membranes have demonstrated considerable potential as effective tools for the removal of a wide variety of compounds from aqueous solutions [27]. Liquid membrane systems involve two miscible liquids (feed and product phases) separated by a third immiscible liquid (membrane phase). Three kinds of liquid membranes are usually considered: bulk, supported and emulsion liquid membranes [27]. Emulsion liquid membranes are obtained by forming an emulsion between the membrane and the product phases and dispersing this emulsion in the feed phase. The membrane phase separates the encapsulated internal droplets of the product phase from the external feed phase (Figure 1). The possibility of regenerating the membrane to permit its reuse [28,29] makes this technique as interesting as the adsorption processes which use recently developed easily recyclable adsorbents [30,31]

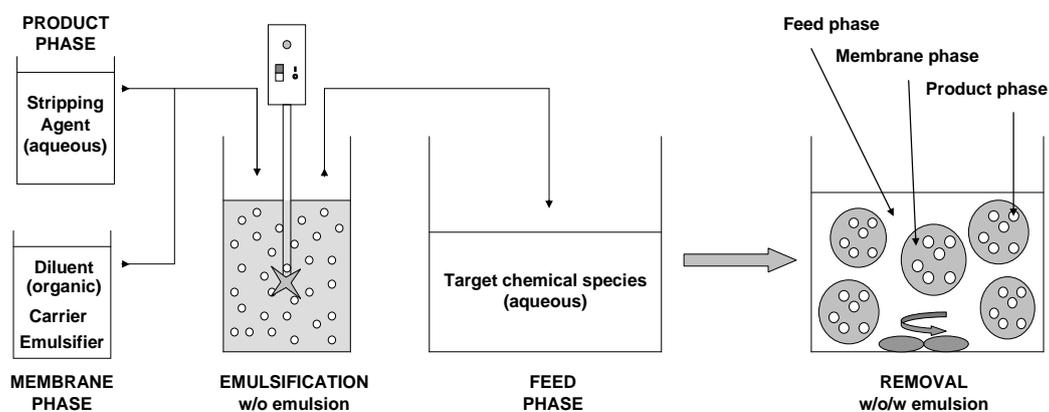


Figure 1. Schematic representation of an emulsion liquid membrane process.

In order to maximize the removal process, facilitated transport mechanisms have been described [32]. Carrier-mediated transport combines chemical reactions with diffusion processes: the carrier reacts with the target chemical species to form a complex, which diffuses through the membrane to finally release the target species in the product phase. The process is usually accompanied by the transport of other chemical species from the product to the feed phase. This coupled carrier-facilitated counter-transport mechanism is interesting because it offers the possibility of transporting a component against its own concentration gradient [33].

This paper studies the removal of Cu(II) from aqueous solutions by emulsion liquid membranes through a carrier-facilitated counter-transport mechanism using benzoylacetone (HBA) as the carrier and protons (HCl) as counter-ions. In order to optimize the Cu(II) removal process, the effect of the different operating parameters (feed pH, HCl concentration in the permeate phase, carrier and

emulsifier concentration in the membrane phase, feed phase/emulsion phase (V_f/V_{emul}) and permeate phase/membrane phase (V_p/V_m) volume ratios, emulsification time (t_{emul}) and rate (r_{emul}) in the primary emulsion preparation and stirring rate (r_{stir}) in the whole feed phase/emulsion phase system) on the stability of the emulsion liquid membrane, the Cu(II) removal efficiency and the value of typical membrane transport parameters, such as flux and permeability, is analyzed.

2. Materials and Methods

2.1. Materials

Analytical grade chemicals and distilled water were used throughout this study. Benzoylacetone (99%), kerosene and Span 80 were obtained from Sigma Aldrich (Madrid, Spain); copper(II) chloride (98.5%) and HCl (37%) were supplied by Panreac (Barcelona, Spain).

2.2. Procedure

The aqueous external feed phase comprised a solution of Cu(II) 0.025 M in acetate buffer, while the organic membrane phase was prepared by dissolving the carrier (benzoylacetone) and the surfactant (Span 80) in the solvent kerosene. The internal phase consisted of aqueous solutions of hydrochloric acid.

To prepare stable water in oil emulsions (w/o), the internal aqueous phase was added drop wise to the organic phase under stirring and the mixture was emulsified at a high stirring rate, using an OMNI MIXER homogeniser (Omni International, Kennesaw, GA, USA), to obtain a stable milky white emulsion. This emulsion was slowly poured on the external Cu(II) aqueous phase in a glass cell, equipped with a variable-rate propeller, and stirred to disperse the w/o emulsion in the external aqueous phase.

To study the breakdown of the emulsion, pure water was used as external phase and the pH was measured at intervals using a Crison micro pH 2000 pH-meter (Crison, Barcelona, Spain).

In the studies of Cu(II) removal, the external feed phase was periodically sampled and the samples were allowed to settle for 3 min to separate the (w/o) emulsion phase from the external aqueous phase. The Cu(II) content in the aqueous feed phase was analyzed by atomic absorption spectrometry, using a ContrAA 700 (Analytik Jena) instrument (Edinburgh Instruments, Livingston, UK) at a wavelength of 324.8 nm. All the experiments were performed at room temperature and in duplicate. The results obtained showed a maximum deviation of 3%. No Cu(II) removal from the feed phase was observed in the transport experiments without carrier present in the membrane phase.

Different experimental conditions analyzed to study emulsion breakage and Cu(II) removal are shown in Table 1.

Table 1. Values of the different parameters studied.

Parameter	Values	Parameter	Values
Feed pH	4.0; 4.5; 5.0; 5.5 *	[HCl] (kg/m ³)	1.825; 3.650; 18.250 *; 36.500
[HBA] (kg/m ³)	1; 5; 10 *; 20	[Span 80] (kg/m ³)	5; 10; 50 *; 100
r_{stir} (rpm)	50; 100; 200 *; 300	V_f/V_{emul}	1; 2 *; 4; 8
V_p/V_m	0.75; 1.00 *; 1.25; 1.50	t_{emul} (min)	2.5; 5.0 *; 10.0
		r_{emul} (rpm)	1800; 2700 *; 3600

* typical values used in the experiments.

2.3. Methods

Emulsion breakage is determined from the ratio between the volume of internal product phase leaked into the external feed phase by splitting (V_{leak}) and the initial volume of the internal phase (V_p) [34].

$$\text{BR}(\%) = \frac{V_{\text{leak}}}{V_p} \times 100 \quad (1)$$

The volume V_{leak} is calculated by the material balance obtained from the feed phase pH at any time before or after contact [35], according to:

$$V_{\text{leak}} = V_f \frac{10^{-\text{pH}_{f,0}} - 10^{-\text{pH}_{f,t}}}{10^{-\text{pH}_{f,t}} - 10^{-\text{pH}_{p,0}}} \quad (2)$$

where V_f is the initial feed phase volume, $\text{pH}_{f,0}$ and $\text{pH}_{f,t}$ are the pH in the feed phase at time 0 and at time t , respectively, and $\text{pH}_{p,0}$ is the initial pH of in the product phase.

The extent of Cu(II) removal from the feed phase (RE), was calculated, as a percentage, by using the following equation:

$$R(\%) = \frac{[\text{Cu}^{2+}]_{f,0} - [\text{Cu}^{2+}]_{f,t}}{[\text{Cu}^{2+}]_{f,0}} \times 100 \quad (3)$$

where $[\text{Cu}^{2+}]_{f,0}$ and $[\text{Cu}^{2+}]_{f,t}$ are the concentrations of Cu(II) in the feed phase initially and at time t , respectively. Higher removal efficiencies were obtained at 15 min.

Initial copper(II) apparent fluxes (J) and permeabilities (P) through the membrane phase were calculated from the slopes of the straight lines obtained when plotting the Cu(II) concentration in the feed phase and $\ln[C_{f,t}/C_{f,0}]$, respectively, against time during the first 5 min of the experiments, according to Equations (4) and (5) [32]. The use of these equations assumes that A is proportional to the volume of the emulsion ($A = k \cdot V_{\text{emul}}$), that the stripping reaction at the membrane phase/internal phase interface is very fast, with no accumulation of solute in the membrane phase, and that the emulsion globules obtained are of uniform size when the emulsion preparation conditions are the same [36].

$$J = - \frac{V_f \cdot dC_f}{V_{\text{emul}} \cdot dt} \quad (4)$$

$$\ln \frac{C_{f,t}}{C_{f,0}} = - \frac{V_{\text{emul}} \cdot P \cdot t}{V_f} \quad (5)$$

3. Results

3.1. Emulsion Stability

Breaking percentages, at 30 min, of the emulsion liquid membranes prepared at different values of the different parameters are shown in Table 2. The results show that breaking percentages lower than 3% were obtained in most of the experimental conditions. Only a high hydrochloric acid concentration in the internal product phase, low Span concentrations in the membrane phase and high stirring rates led to higher breakage values. The respective reasons for this were the hydrolytic rupture of some of the ester bonds of Span 80 at high HCl concentrations in the product phase [37], which leads to some destabilization of the emulsion, the increase in surface tension between the inner phase and kerosene at low Span concentrations in the membrane phase [38], and the rupture of the emulsion globules through impact with the impeller with the wall of the cell and with other emulsion globules at high stirring rates [39].

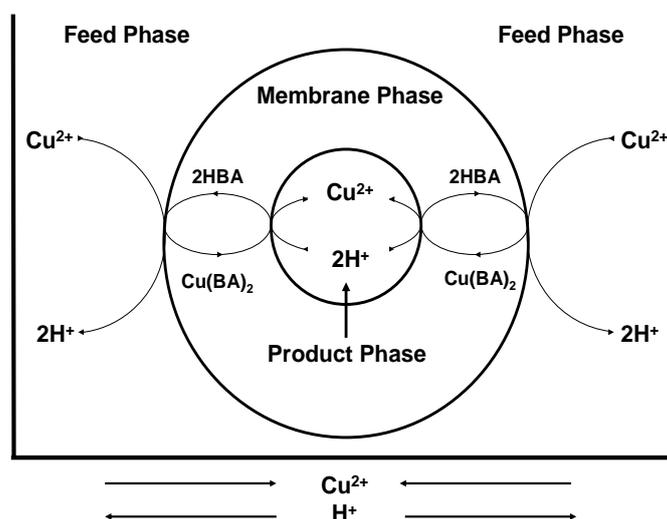
Table 2. Breaking percentages (*B*), at 30 min, of emulsion liquid membranes in different experimental conditions.

Parameter	Value	<i>B</i> (%)	Parameter	Value	<i>B</i> (%)
Feed pH	4.0	0.8	[HCl] (kg/m ³)	1.825	0.5
	4.5	0.9		3.650	0.8
	5.0	0.9		18.250	0.9
	5.5	0.8		36.500	4.2
[HBA] (kg/m ³)	1	0.8	[Span 80] (kg/m ³)	5	4.1
	5	0.8		10	2.8
	10	0.9		50	0.9
	20	1.3		100	0.3
<i>r</i> _{stir} (rpm)	50	0.6	<i>V_f</i> / <i>V_{emul}</i>	1	2.5
	100	0.8		2	0.9
	200	0.9		4	0.6
	300	3.7		8	0.4
<i>V_p</i> / <i>V_m</i>	0.75	0.4	<i>t_{emul}</i> (min)	2.5	0.6
	1.00	0.9		5.0	0.9
	1.25	1.8		10.0	2.2
	1.50	2.3		900	0.7
			<i>r_{emul}</i> (rpm)	1800	0.8
				2700	0.9

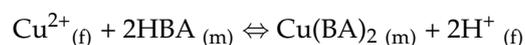
3.2. Copper(II) Removal

3.2.1. Transport Mechanism

The carrier-facilitated counter-transport of Cu(II) using benzoylacetone (HBA) as a carrier in the membrane phase and protons (HCl) as counter-ions in the product phase is represented in Figure 2.

**Figure 2.** Schematic representation of the carrier-mediated transport of Cu²⁺ using benzoylacetone as a carrier and protons as counter-ions.

The Cu(II) present in the feed phase reacted, at the feed/membrane interface, with the carrier (HBA), which diffused from the bulk membrane phase to the interface, according to the chemical equation:



The formed $\text{Cu}(\text{BA})_2$ complex diffused through the membrane (down its concentration gradient) to the membrane/product interface, where the high proton concentration of the product phase led to the break of the complex, by exchanging protons for $\text{Cu}(\text{II})$ and reversing the above reaction, which resulted in the release of $\text{Cu}(\text{II})$ into the product phase and in the regeneration of the HBA, thus initiating a new separation cycle. The described mechanism is therefore a coupled counter-transport mechanism, with $\text{Cu}(\text{II})$ and H^+ traveling in opposite directions.

3.2.2. Influence of Different Experimental Parameters on Flux, Permeability and Removal Efficiency

The effect of feed pH on $\text{Cu}(\text{II})$ removal was studied between pH 4.0 and pH 5.5 (Figure 3). A higher pH was not considered because cupric hydroxide begins to precipitate above pH 6. In the studied range, $\text{Cu}(\text{II})$ flux, permeability and removal efficiency increased as the feed pH increased. This result was expected because the driving force of the transport process is the gradient of the proton chemical potential (concentration) between the product and the feed phases [40], so the higher the feed pH, the higher the proton gradient and the driving force. The presence of acetate buffer to maintain the feed pH constant is therefore an important factor of the transport process.

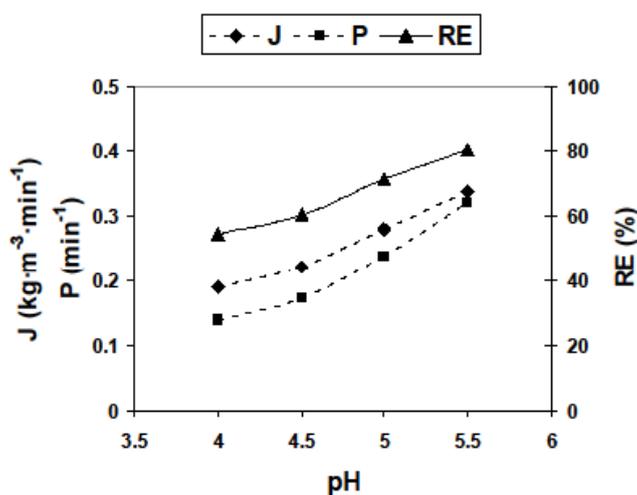


Figure 3. Effect of initial feed phase pH on $\text{Cu}(\text{II})$ flux (J), permeability (P) and removal efficiency (RE). Value of other parameters: typical experimental conditions.

Figure 4 shows the influence of the concentration of hydrochloric acid in the internal aqueous phase on the extent of $\text{Cu}(\text{II})$ removal. It can be observed that $\text{Cu}(\text{II})$ flux, permeability and removal efficiency increased with the increasing HCl concentration from 1.825 to 18.250 kg/m^3 , due to the greater difference in hydrogen ion concentrations between the internal and the external phases, which increases the stripping driving force, delaying the accumulation of the $\text{Cu}(\text{II})$ -BA complex in the membrane phase [40]. A further increase in the HCl concentration to 36.500 kg/m^3 led to a decrease in the $\text{Cu}(\text{II})$ flux, permeability and removal efficiency due to both an increase in the emulsion viscosity, which leads to the increase in the size of the emulsion droplets (decreasing the mass transfer surface area), and a decrease in the emulsion stability, due to the hydrolysis of Span 80, which produces a partial loss of its surfactant properties and, consequently, a partial destabilization of the emulsion, which leads to a diminution in the removal performance [37].

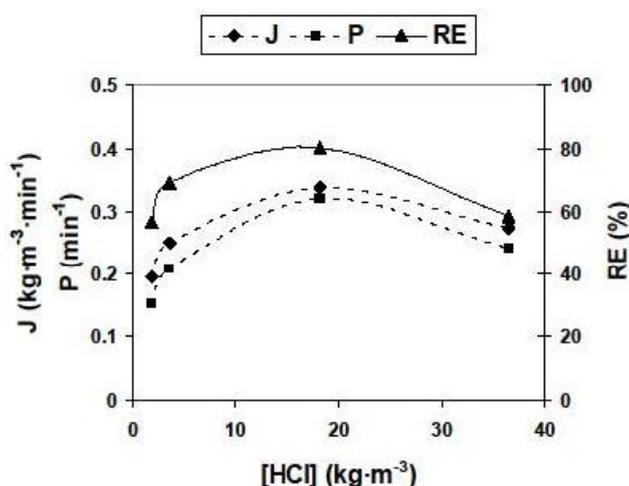


Figure 4. Effect of stripping agent concentration on Cu(II) flux (J), permeability (P) and removal efficiency (RE). Value of other parameters: typical experimental conditions.

The effect of the benzoylacetone concentration in the membrane phase on Cu(II) removal is shown in Figure 5. The Cu(II) flux, permeability and removal efficiency increased as the carrier concentration in the membrane phase increased from 1 to 10 kg/m³, but a further increase of the carrier concentration had little effect on the transport efficiency. This is the result of two contrary effects: (i) the increase in the HBA concentration enhances the extraction of Cu(II) as a higher number of HBA molecules are associated to the Cu(II) ions to form the Cu(BA)₂ complex, increasing its concentration gradient through the membrane phase and favoring its diffusion to the membrane/product interface; and (ii) the increase in the carrier concentration leads to a slight increase in the emulsion viscosity, which leads to an increase of the droplet size, with a corresponding decrease in the mass transfer surface area, which leads to a decrease in the transport efficiency.

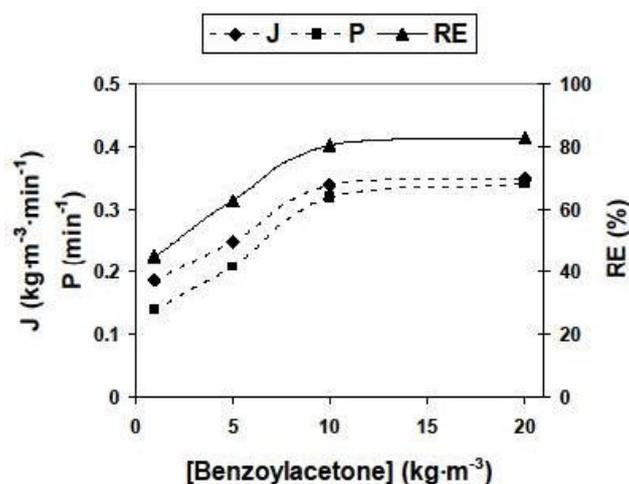


Figure 5. Effect of carrier concentration on Cu(II) flux (J), permeability (P) and removal efficiency (RE). Value of other parameters: typical experimental conditions.

The effect of the surfactant concentration on Cu(II) removal is shown in Figure 6. As can be seen, the Cu(II) flux, permeability and removal efficiency increased as the surfactant concentration in the membrane phase increased from 5 to 50 kg/m³. The increase of the surfactant concentrations tends to reduce the interfacial tension between the phases [38], which favors the formation of smaller emulsion droplets, leading to a much larger mass transfer surface area. A further increase in the

surfactant concentration leads to a slight decrease in Cu(II) transport through the membrane due to the increase in the viscosity of the emulsion, which produces an increase in the emulsion droplet size and, consequently, a decrease in the mass transfer surface area, and to the increase in the thickness of the liquid membrane in the emulsion droplets [41], which leads to an increase in the Cu(II) mass transfer resistance.

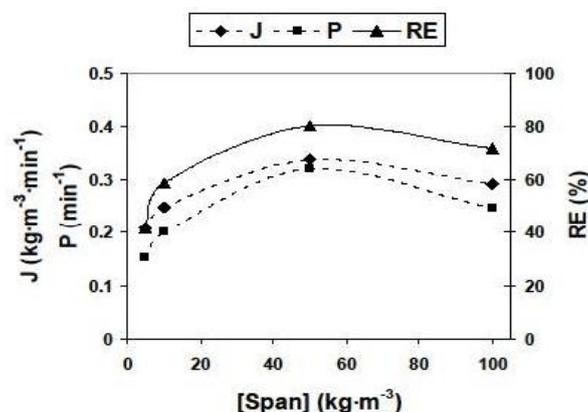


Figure 6. Effect of surfactant concentration on Cu(II) flux (J), permeability (P) and removal efficiency (RE). Value of other parameters: typical experimental conditions.

The effect of the stirring speed, used to mix the emulsion and the feed solution, on the removal of Cu(II) is shown in Figure 7. The Cu(II) flux, permeability and removal efficiency increased as the stirring speed increased from 50 to 200 rpm, due to the increase in the number of smaller emulsion droplets, which increased the interfacial area between the feed phase and the membrane phase, leading to an increase in the mass transfer surface area. Any further increase in the stirring speed drastically affects the emulsion stability, leading to a decrease in Cu(II) transport through the membrane, resulting in the rupture of the emulsion globules, as already mentioned, through impact with the impeller with the wall of the cell and with other emulsion globules [39].

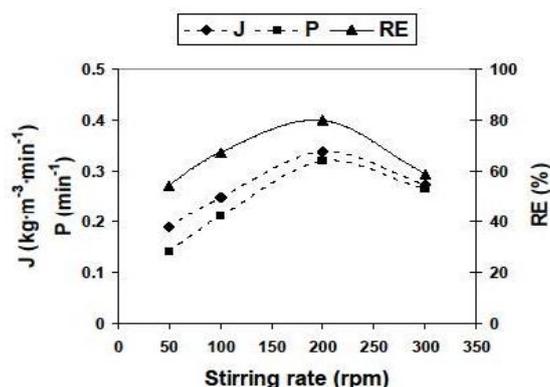


Figure 7. Effect of stirring rate on Cu(II) flux (J), permeability (P) and removal efficiency (RE). Value of other parameters: typical experimental conditions.

The effect of the feed phase/emulsion phase volume ratio on the permeation of Cu(II) was studied at a constant permeate phase/membrane phase volume ratio by changing the volume of the feed aqueous phase while keeping the volume of the emulsion (membrane phase volume plus permeate phase volume) constant. As can be seen from Figure 8, the Cu(II) flux and permeability through the membrane significantly increased when that volume ratio increased from one to four, but increased only slightly when the ratio increased from four to eight. As the volume ratio increased, the number of

Cu(II) ions to be transported increased, but with no change in the number of molecules of carrier (in the membrane phase) or in the number of counter-ion molecules (in the product phase). The result was an increase in both flux and permeability through the membrane as the ratio increased from one to four, but with no further increase at a higher ratio. This was accompanied by a decrease in the removal efficiency (the percentage of Cu(II) ions removed from the total Cu(II) ions present in the feed phase), as a consequence of the substantial increase in the number of Cu(II) ions to be removed in the feed phase (due to the increase in the feed phase volume) compared with the number of Cu(II) ions that can be effectively transported by a constant number of carrier and counter-ion molecules.

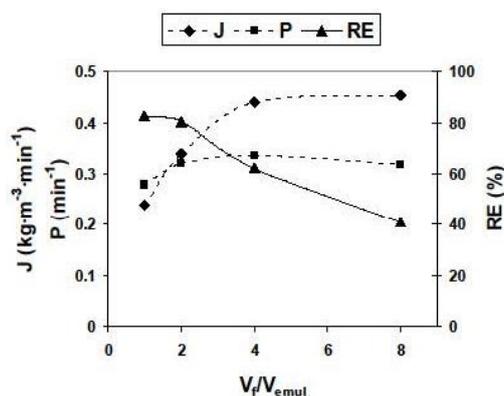


Figure 8. Effect of feed phase/emulsion phase volume ratio on Cu(II) flux (J), permeability (P) and removal efficiency (RE). Value of other parameters: typical experimental conditions.

The effect of the permeate phase/membrane phase volume ratio on the removal of Cu(II) was studied at a constant feed phase/emulsion phase volume ratio. The results showed that the removal of Cu(II) increased as the volume ratio increased to one, while higher ratios led to a decrease in Cu(II) removal (Figure 9). This may be explained by the fact that the increase of the internal aqueous phase volume produces two contrary effects: (i) an increase in both the viscosity of the emulsion phase (producing an increase in the size of the emulsion droplets and, consequently, a decrease of the mass transfer surface area) and the emulsion breakage, which leads to a decrease of the removal efficiency; and (ii) an increase in the amount of stripping agent in the product phase at a constant amount of Cu(II) in the feed phase, which increases the stripping driving force, delaying the accumulation of the Cu(II)-BA complex in the membrane phase [40] and leading to an increase in the removal efficiency. The overall result of these two effects was an increase in the Cu(II) removal as the volume ratio increased to one, but a decrease at higher volume ratios.

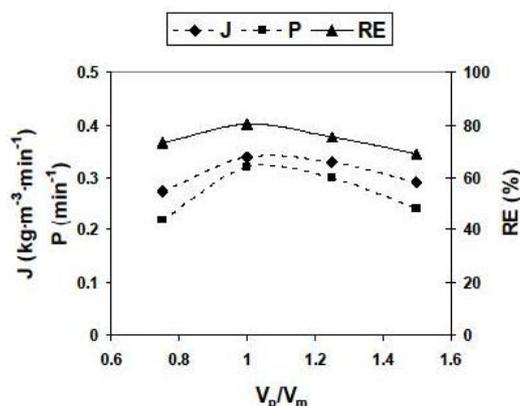


Figure 9. Effect of permeate phase/membrane phase volume ratio on Cu(II) flux (J), permeability (P) and removal efficiency (RE). Value of other parameters: typical experimental conditions.

The emulsification time and emulsification rate had no significant effect on the removal of Cu(II), as can be seen in Figure 10. This can be explained if we assume that the expected decrease in Cu(II) removal caused by the slight increase in the emulsion breakage when the emulsification time and emulsification rate are increased is counteracted by a slight increase in the removal efficiency, the result being no significant effect on Cu(II) removal. Whatever the case, the removal was slightly higher for a 5 min emulsification time and a 2700 rpm emulsification rate.

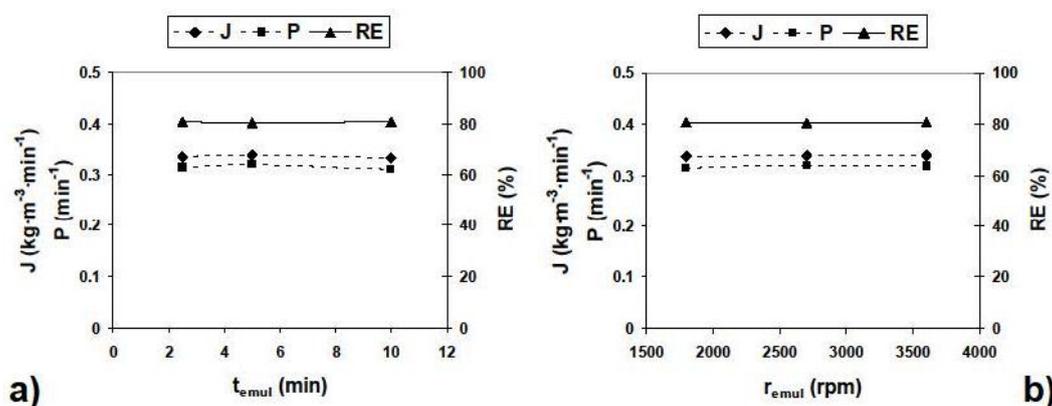


Figure 10. Effect of emulsification time (a) and emulsification rate (b) on Cu(II) flux (J), permeability (P) and removal efficiency (RE). Value of other parameters: typical experimental conditions.

3.2.3. Optimal Removal Conditions

From the results shown in Figures 3–10 and Table 2, it can be concluded that the optimal experimental conditions for Cu(II) removal from aqueous acetate buffer solutions by emulsion liquid membranes using a facilitated counter-transport mechanism with HBA as the carrier, protons as counter-ions (HCl as the stripping agent), Span 80 as the emulsifier and kerosene as the organic diluent are: 5.5 feed pH, 10 kg/m³ HBA concentration in the membrane phase, 18.250 kg/m³ HCl concentration in the permeate phase, 50 kg/m³ Span concentration in the membrane phase, 200 rpm stirring rate, 5 min emulsification time, 2700 rpm emulsification rate, 2:1 feed:emulsion volume ratio and 1:1 permeate:membrane volume ratio. In these optimal conditions, 80.3% of Cu(II) was removed in 15 min with an apparent initial flux and permeability of 0.3384 kg·m⁻³·min⁻¹ and 0.3208 min⁻¹, respectively.

4. Conclusions

We have described the removal of Cu(II) from aqueous acetate buffered solutions by emulsion liquid membranes using a facilitated counter-transport mechanism with benzoyl acetone as the carrier, HCl as the stripping agent, Span 80 as the emulsifier and kerosene as the organic diluent. The effects of different experimental conditions on the Cu(II) removal were studied in order to obtain the optimal removal conditions. Cu(II) removal increased by increasing the HCl concentration in the internal aqueous phase from 0.1 to 1.0 M, the surfactant concentration in the membrane phase from 0.5% to 5.0%, the stirring speed from 50 to 200 rpm, and the treatment and phase ratios up to one. Removal was slightly affected by changes in the emulsification time and emulsification speed. The initial apparent fluxes and permeabilities of Cu(II) through the liquid membrane in the different experimental conditions were also determined and were seen, in general, to follow a similar variation as that of Cu(II) removal. Optimal Cu(II) experimental/economical removal conditions were: 5.5 feed pH, 10 kg/m³ HBA concentration in the membrane phase, 18.250 kg/m³ HCl concentration in the permeate phase, 50 kg/m³ Span concentration in the membrane phase, 200 rpm stirring rate, 5 min emulsification time, 2700 rpm emulsification rate, 2:1 feed:emulsion volume ratio and 1:1 permeate:membrane volume ratio. In these optimal conditions, 80.3% of Cu(II) removal was attained in 15 min with an apparent initial flux and permeability of 0.3384 kg·m⁻³·min⁻¹ and 0.3208 min⁻¹, respectively.

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Author Contributions: Gerardo León and Loreto León conceived and designed the experiments; Gerardo León and Loreto León performed the experiments; Gerardo León, Carmen Pérez-Sirvent and Javier Senent analyzed the data; Gerardo León, Javier Senent and Carmen Pérez-Sirvent contributed reagents/materials/analysis tools; Gerardo León wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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