

Communication

# Kinetic Study of Copper(II) Simultaneous Extraction/Stripping from Aqueous Solutions by Bulk Liquid Membranes Using Coupled Transport Mechanisms

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**Abstract:** Heavy metals removal/recovery from industrial wastewater has become a prime concern for both economic and environmental reasons. This paper describes a comparative kinetic study of the removal/recovery of copper(II) from aqueous solutions by bulk liquid membrane using two types of coupled facilitated transport mechanisms and three carriers of different chemical nature: benzoylacetone, 8-hydroxyquinoline, and tri-*n*-octylamine. The results are analyzed by means of a kinetic model involving two consecutive irreversible first-order reactions (extraction and stripping). Rate constants and efficiencies of the extraction ( $k_1$ , EE) and the stripping ( $k_2$ , SE) reactions, and maximum fluxes through the membrane, were determined for the three carriers to compare their efficiency in the Cu(II) removal/recovery process. Counter-facilitated transport mechanism using benzoylacetone as carrier and protons as counterions led to higher maximum flux and higher extraction and stripping efficiencies due to the higher values of both the extraction and the stripping rate constants. Acceptable linear relationships between EE and  $k_1$ , and between SE and  $k_2$ , were found.

**Keywords:** copper(II); removal/recovery; bulk liquid membrane; kinetics; coupled facilitated transports

## 1. Introduction

In recent years, the removal and recovery of heavy metals from wastewaters of industrial effluents, water supplies, and mine waters have received much attention. Copper is one of the most widespread heavy metals, widely used in industrial processes such as mining, metallurgy, plating, steel manufacturing, paper and pulp, fertilizer, paint and pigments, petroleum refining, wood preservatives, and printing circuits [1,2], and it is often present in the wastewater of these industrial processes. It is a micronutrient, but it is also considered to be one of the most toxic metals by the World Health Organization [3] and as a priority pollutant by the US EPA [4]. As copper has been classified as a critical element, with only 60 years of expected availability at current production levels, its removal/recovery from raw materials and secondary sources is considered a valid hydrometallurgical research field for both economic and environmental reasons [5].

A wide variety of techniques has been developed for the removal/recovery of copper ions from wastewater including cementation [6], precipitation [7], solvent extraction [8], adsorption [9] reduction [10], biosorption [11], ion exchange [12], chelation [13], electrocoagulation [14],

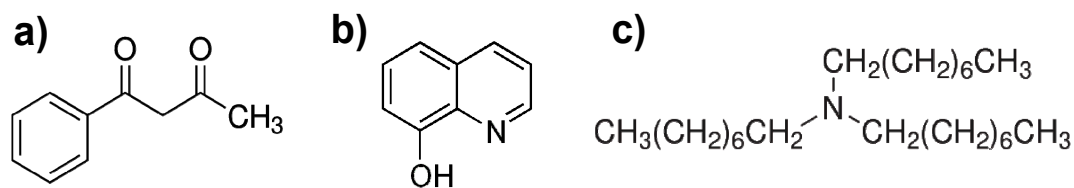
electrodialysis [15], pressure driven membrane processes [16], liquid membranes [17–20], and combined methods (chelation plus pressure-driven membranes processes) [21].

Liquid membranes have shown great potential for use in removal/recovery processes, especially in cases where solute concentrations are relatively low and other techniques cannot be applied efficiently, since they combine the processes of extraction and stripping in a single unit operation [22]. The extraction chemistry is basically the same as that found in liquid–liquid extraction, but the transport is governed by kinetic rather than equilibrium parameters, that is, by a non-equilibrium mass transfer.

In a liquid membrane, two miscible liquids (feed and product phases) are separated by a third immiscible liquid, which constitutes the membrane phase. If the feed and the product phases are aqueous, the membrane phase must be organic; however, if the feed and the product phases are organic, the membrane phase must be aqueous. Three basic kinds of liquid membranes have been described: bulk, supported, and emulsion liquid membranes [22]. In bulk liquid membranes, a thick layer of the liquid that constitutes the membrane phase directly separates the feed and the product phases. In supported liquid membranes, the membrane phase fills the pores of a rigid porous support that separates the feed and the product phases. Emulsion liquid membranes are obtained by forming an emulsion between the membrane and the product phases and then dispersing this emulsion in the feed phase via stirring; the membrane separates the encapsulated internal droplets of the product phase in the emulsion from the external feed phase.

Transport of the diffusing species in the liquid membrane system, may be facilitated by carrier mediated transport. In such a transport mechanism, an ion exchange reagent is incorporated in the membrane phase to carry the diffusing species from the feed to the product phase across the membrane phase, a process that is usually accompanied by the transport of other chemical species (coupled transport), either from the feed to the product phase (coupled co-transport) or from the product to the feed phase (coupled counter-transport). These coupled facilitated transport mechanisms are interesting because they offer the possibility of transporting a component against its own concentration gradient [23].

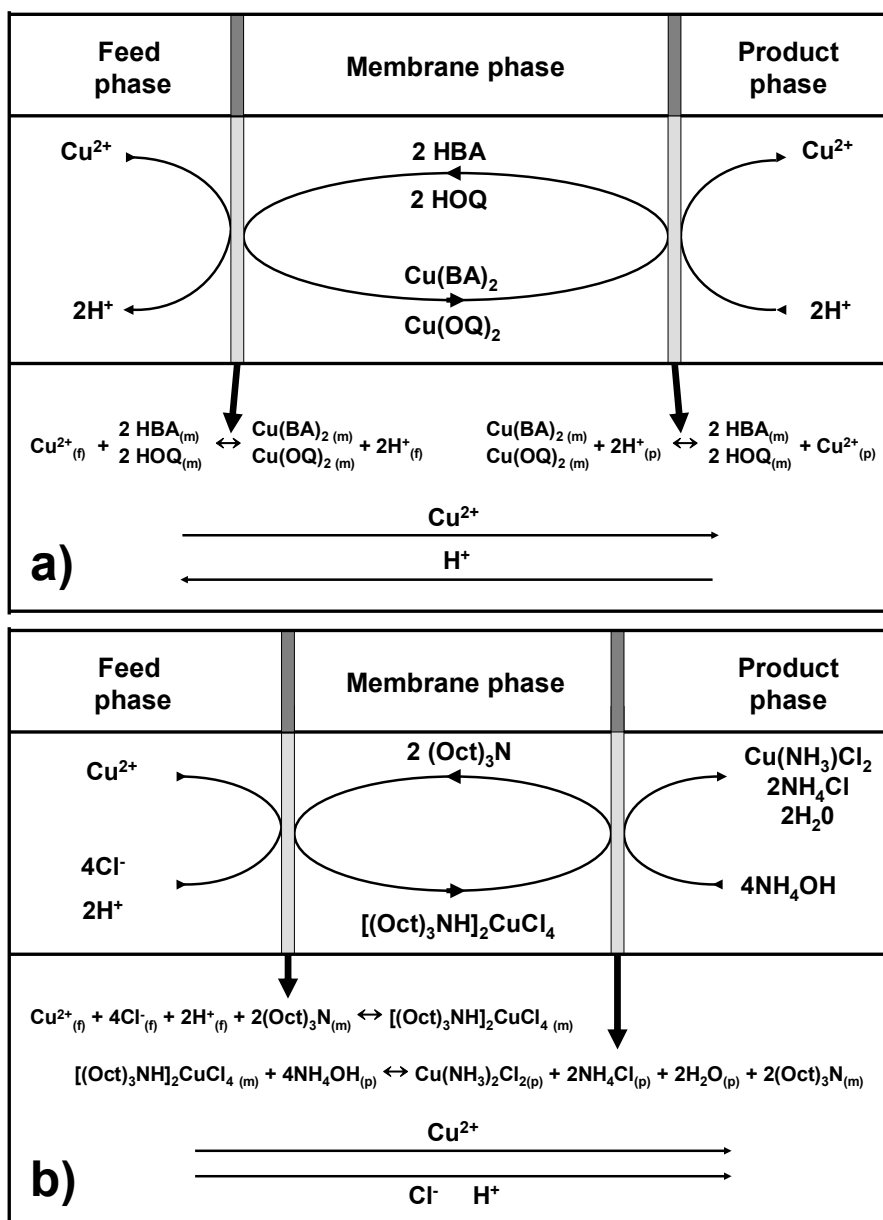
A comparative kinetic study of the carrier mediated transport of copper through bulk liquid membranes containing three carriers of different chemical nature:—benzoyl acetone (HBA), 8-hydroxy quinoline (HOQ), and tri-*n*-octyl amine (Oct<sub>3</sub>N)—is carried out in this paper. The chemical structure of the different carriers is shown in Figure 1.



**Figure 1.** Chemical structure of carriers used in this study (a) benzoylacetone; (b) 8-hydroxyquinoline; (c) tri-*n*-octylamine.

Two types of facilitated transport mechanisms are involved: a carrier-mediated counter-transport mechanism, which uses HBA or HOQ as carriers and protons as counter-ions (Figure 2a), and a carrier-mediated co-transport mechanism, which uses (Oct<sub>3</sub>N) as carrier and chloride and protons as co-ions (Figure 2b).

In the counter-transport mechanism (Figure 2a), the carrier (HBA or HOQ) diffuses from the bulk membrane phase to the feed/membrane interface where it reacts with copper(II). The copper(II)-carrier complex formed diffuses through the membrane to the membrane/product interface where, by reversing the reaction, protons are exchanged for copper(II) ions, which are released into the product phase. The carrier is regenerated, thus initiating a new separation cycle. The copper(II) transport mechanism is therefore a coupled counter-transport mechanism, with Cu(II) and H<sup>+</sup> travelling in the opposite direction.



**Figure 2.** Facilitated transport of Cu(II) through bulk liquid membranes using (a) a carrier-mediated counter-transport mechanism and (b) a carrier-mediated co-transport mechanism.

In the co-transport mechanism (Figure 2b), the carrier ( $\text{Oct}_3\text{N}$ ) diffuses from the bulk membrane phase to the feed/membrane interface where it reacts with copper(II), which forms  $\text{CuCl}_4^{2-}$  in HCl media. The chloro-copper(II)-carrier complex formed ( $(\text{Oct}_3\text{NH})_2\text{CuCl}_4$ ) diffuses through the membrane to the membrane/product interface where it reacts with the  $\text{NH}_4\text{OH}$ , present in product phase, breaking the complex and leading to the stripping of Cu(II) in that product phase. The copper(II) transport mechanism is therefore a coupled co-transport mechanism, with Cu(II),  $\text{Cl}^-$ , and  $\text{H}^+$  travelling in the same direction.

## 2. Materials and Methods

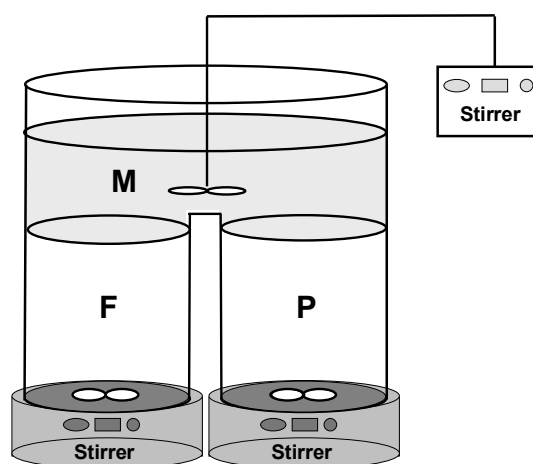
### 2.1. Chemicals

Analytical grade copper(II) chloride, 8-hydroxyquinoline, sodium acetate and glacial acetic acid, hydrochloric acid (37%), and sulphuric acid (96%) were purchased from Panreac. Benzoylacetone

(99%), tri-*n*-octylamine (98%), and ammonium hydroxide (25%) were obtained from Sigma-Aldrich (Madrid, Spain). Kerosene (99%) was supplied by BDH.

## 2.2. Transport Experiments

Transport experiments were carried out using a stirred transfer Lewis type cell with the organic phase layered over the feed and the product aqueous phases, bridging the feed and the product aqueous phases (Figure 3). When carrier-facilitated coupled co-transport was studied (using Oct<sub>3</sub>N as carrier), a 0.025 M copper(II) chloride solution in 0.5 M HCl was used as feed phase. The membrane phase comprised a 3% solution of Oct<sub>3</sub>N in kerosene, while a 0.5 M aqueous NH<sub>4</sub>OH solution was used as product phase. In the experiments of carrier-facilitated coupled counter-transport (using HBA or HOQ as carriers), a 0.025 M copper(II) chloride solution in acetate buffer, pH 4.0, was used as feed phase, 3% solutions of carrier in kerosene as membrane phase, and 1M solution of sulphuric acid as product phase. The volumes of feed, membrane, and product phases were 25 mL, and the areas of both feed/membrane and membrane/product interfaces were 3.2 cm<sup>2</sup>. The three phases were stirred at 200 rpm, and all the experiments were carried out at 25 °C.



**Figure 3.** Schematic representation of the experimental cell (F: feed phase; M: membrane phase; P: product phase).

## 2.3. Analytical Methods and Calculations

Samples of feed and product phases were taken at intervals, and the copper(II) ion concentration was determined by atomic absorption spectrometry using a Shimadzu AA-6200 instrument (IZASA, Madrid, Spain) at a wavelength of 324.8 nm. Copper(II) ion concentration in the membrane phase was established from the material balance. Experiments were carried out in duplicate with a maximum standard deviation of 2%. For practical reasons, dimensionless reduced concentrations of copper(II) in the feed ( $R_f = C_{ft}/C_{f0}$ ), membrane ( $R_m = C_{mt}/C_{f0}$ ), and product ( $R_p = C_{pt}/C_{f0}$ ) phases were used (the sum of  $R_f + R_m + R_p$  obviously being unity). In addition, the efficiency of Cu(II) extraction from the feed phase (EE) and of Cu(II) stripping in the product phase (SE), were calculated, at 24 h, from the following equations [24]:

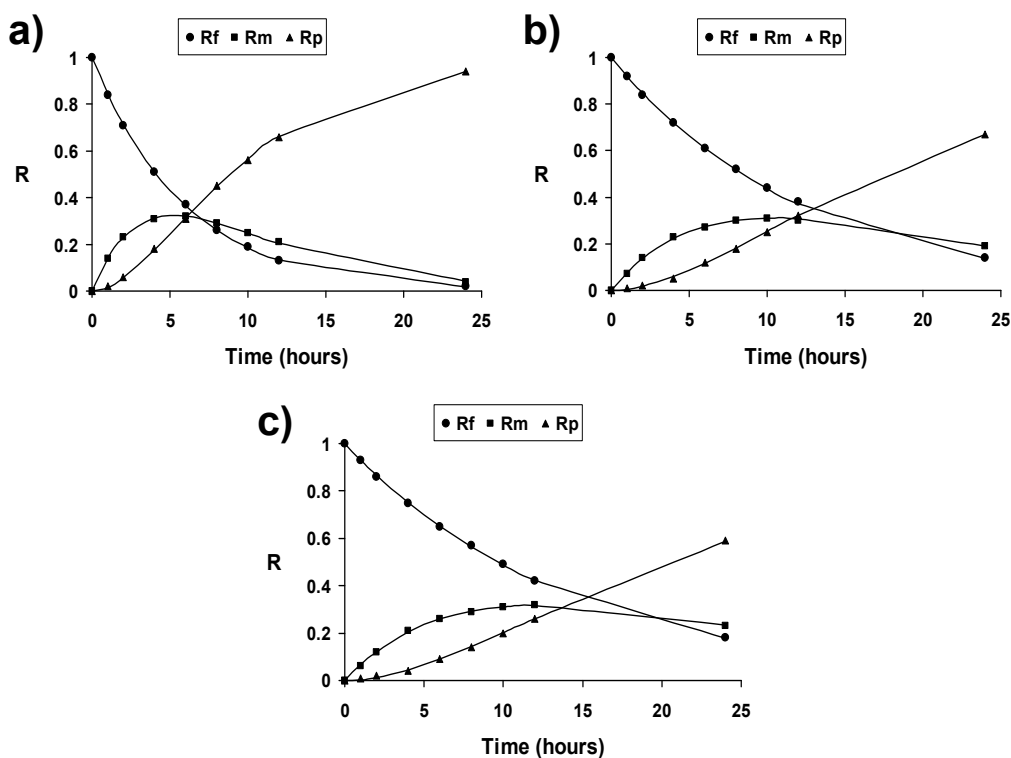
$$EE (\%) = \frac{C_{f0} - C_{ft}}{C_{f0}} \times 100 \quad (1)$$

$$SE (\%) = \frac{C_{pt}}{C_{f0} - C_{ft}} \times 100 \quad (2)$$

where  $C_{f0}$  is the initial concentration of Cu(II) in the feed phase, and  $C_{ft}$ ,  $C_{mt}$ , and  $C_{pt}$  are the concentrations of Cu(II) in the feed, membrane, and product phase, respectively, at time  $t$ .

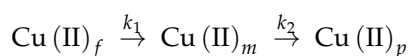
### 3. Results and Discussion

Variation with time of feed, membrane, and product copper(II)-reduced concentrations, for the three studied carriers, is shown in Figure 4. It can be appreciated that, in all three cases,  $R_f$  decreases monoexponentially with time,  $R_p$  follows an increasing sigmoided type curve, and  $R_m$  time dependence presents a maximum.



**Figure 4.** Time dependence of  $R_f$  in feed phase,  $R_m$  in membrane phase, and  $R_p$  in product phase in the facilitated counter transport of Cu(II) using benzoylacetone (a), 8-hydroxyquinoline (b), and tri-*n*-octylamine (c) as carriers. (Points, experimental values; line, model values).

The results suggest that copper(II) transport follows the kinetic laws of two consecutive irreversible first-order reactions, the extraction (rate constant,  $k_1$ ), and the stripping (rate constant,  $k_2$ ) reactions:



The irreversibility must be expected by the fact that  $R_f$  and  $R_m$  tend to zero, while  $R_p$  tends to one, that is, the copper(II) transport from the feed phase to the product phase seems to be virtually complete.

In this kinetic behaviour, the variation rate of the metal reduced concentration in each phase can be described by the following equations [25–27]:

$$\frac{dR_f}{dt} = -k_1 R_f \equiv J_{f/m} \quad (3)$$

$$\frac{dR_m}{dt} = k_1 R_f - k_2 R_m \equiv J_m \quad (4)$$

$$\frac{dR_p}{dt} = k_2 R_m \equiv J_{m/p} \quad (5)$$

where  $J_f$ ,  $J_m$ , and  $J_p$  represent the instantaneous metal flux in each of the three phases.

Integration of these differential equations, leads to expressions of variation of  $R_f$ ,  $R_m$ , and  $R_p$  with time:

$$R_f = \exp(-k_1 t) \quad (6)$$

$$R_m = \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (7)$$

$$R_p = 1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \quad (8)$$

The time leading to the maximum value of  $R_m$  can be obtained from  $dR_m/dt = 0$ .

$$t_{\max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2} \quad (9)$$

Substitution of this time value in Equations (3)–(5) allows the maximum flux expressions to be obtained:

$$\left[\frac{dR_f}{dt}\right]_{\max} = -k_1 \left(\frac{k_1}{k_2}\right)^{-\frac{k_1}{k_1 - k_2}} = J_f^{\max} \quad (10)$$

$$\left[\frac{dR_p}{dt}\right]_{\max} = k_2 \left(\frac{k_1}{k_2}\right)^{-\frac{k_2}{k_1 - k_2}} = J_p^{\max} \quad (11)$$

$$-\left[\frac{dR_f}{dt}\right]_{\max} = +\left[\frac{dR_p}{dt}\right]_{\max} \Rightarrow -J_f^{\max} = +J_p^{\max} \quad (12)$$

Numerical analysis of the experimental results by non-linear curve fitting permits the rate constants of the extraction and stripping processes to be determined (Table 1) and the model curves for the time dependence of  $R_f$ ,  $R_m$ , and  $R_p$ , (calculated from Equations (4)–(6)) to be obtained (Figure 4). Good agreement between experimental and model data can be observed. Maximum fluxes, extraction efficiencies, and stripping efficiencies for the three studied carriers are also shown in Table 1.

**Table 1.** Rate constants for extraction ( $k_1$ ) and stripping ( $k_2$ ) processes, maximum flux ( $J_{\max}$ ) extraction efficiency (EE), and stripping efficiency (SE) for the coupled transport of Cu(II) using different carriers.

Mechanism	Carrier	$k_1$ (h <sup>-1</sup> )	$k_2$ (h <sup>-1</sup> )	$J_{\max}$ (h <sup>-1</sup> )	EE (%)	SE (%)
Counter-transport	HBA	0.1679	0.2151	0.0696	98.1	96.1
Counter-transport	HOQ	0.0825	0.1143	0.0354	85.9	77.9
Co-transport	(Oct <sub>3</sub> N)	0.0716	0.0961	0.0303	81.8	71.8

As can be seen, Cu(II) ion extraction/stripping is greater with the counter-facilitated transport mechanism using benzoylacetone as carrier and protons as counterions (higher maximum flux and higher extraction and stripping efficiencies). This is due to the higher values of both the extraction and the stripping rate constants. The lower values of these rate constants in the counter-facilitated transport mechanism that uses 8-hydroxy quinoline as carrier and protons as counterions lead to much lower maximum fluxes and extraction and stripping efficiencies. The values of the extraction and stripping rate constants obtained when a co-transport mechanism is used (trioctylamine as carrier) show this process to be the worst for the removal/recovery of copper(II) because of the low maximum flux and extraction and stripping efficiencies obtained. Differences in the observed efficiencies of the different carriers should be the result of differences in the diffusion coefficient of the different Cu(II)-carrier complexes in the membrane phase and of differences in the formation constants of those complexes (also in the breaking constant in the case of co-transport mechanism, where formation and breaking reactions are different).

Extraction and stripping efficiencies (98.1% and 96.1%, respectively) obtained with benzoylacetone as a carrier are similar (or higher in some cases) to those described in the literature using the bulk liquid membrane technique with other carriers [25], using other liquid membrane techniques with other carriers [19,20], and using extraction processes [8,28,29].

Acceptable linear relationships between EE(%) and  $k_1$  ( $R^2 = 0.98$ ) and between SE(%) and  $k_2$  ( $R^2 = 0.99$ ) have been obtained from the values of these parameters in the studied carriers.

#### 4. Conclusion

This paper describes a comparative kinetic study of the removal/recovery of copper(II) from aqueous solutions by bulk liquid membrane using two types of coupled facilitated transport mechanisms and three carriers of different chemical nature: benzoylacetone, 8-hydroxyquinoline and tri-*n*-octylamine. Both carrier mediated transport mechanisms follow the kinetic laws of two irreversible consecutive first-order reactions (extraction and stripping). Rate constants and efficiencies of the extraction and the stripping reactions, and maximum fluxes through the membrane have been determined for the three carriers. Counter-facilitated transport mechanism using benzoylacetone as carrier and protons as counterions leads to higher maximum flux and higher extraction and stripping efficiencies due to the higher values of both the extraction and the stripping rate constants. An acceptable linear relationship between both extraction efficiency and extraction rate constant and stripping efficiency and stripping rate constant has been found.

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**Author Contributions:** G. León, L. León, and M.A. Guzmán conceived and designed the experiments; G. León, L. León, and M.A. Guzmán performed the experiments; G. León, L. León, and J. Senent analyzed the data; G. León and J. Senent contributed reagents/materials/analysis tools; G. León wrote the paper.

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

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