

*Short Communication*

# Determining Kinetic Constants and Transport Efficiencies at Membrane Interfaces to Optimize the Removal/Recovery of Cu(II) through Bulk Liquid Membranes Containing Benzoylacetone as Carrier

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## Abstract

The removal, separation, and enrichment of heavy metals in aqueous solutions has become a prime concern over the last few decades because of both their adverse effects on the ecosystem and living organisms and their valuable resource character. This paper describes a study to optimize the simultaneous removal/recovery of Cu(II) from aqueous solutions by bulk liquid membranes, through a facilitated countertransport mechanism using benzoylacetone as a mobile carrier and hydrochloric acid as a stripping agent (protons as counter ions), by analyzing the effect of different operational variables (carrier concentration in membrane phase, stripping agent concentration in product phase, stirring rate, and membrane phase volume) on the removal/recovery kinetics constants and on the transport efficiencies through the feed/membrane and membrane/product interfaces.

**Keywords:** copper, removal/recovery, bulk liquid membranes, benzoylacetone, facilitated counter-transport

## Introduction

Copper is a naturally occurring metal, originating from the earth's crust, which is also found in both

industrial and domestic anthropogenic discharges [1-2]. Due to its properties and variety of uses, copper is one of the most important industrial metals, ranking after iron and aluminium in importance for infrastructure and technology [3]. It is considered an energy-critical element due to its conductive properties and is classified as a scarce mineral, with only 60 years of expected

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availability at current production levels [4]. Though at low concentrations copper is an essential element for virtually all plants and animals, including humans, it is considered a hazardous pollutant when it cannot be maintained at an appropriate physiological concentration due to its non-biodegradability and tendency to accumulate in living organisms, resulting in several diseases and disorders that damage proteins, lipids, and DNA as well as affect the liver, kidney, and pancreas [5-6]. Therefore, the removal/recovery of copper from raw materials and secondary sources can be considered an interesting research field from both economical and environmental viewpoints.

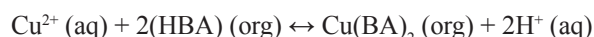
Several approaches have been studied and developed for the effective removal/recovery of Cu(II) from aqueous solutions, including chemical precipitation [7], cementation [8], adsorption [9], biosorption [10], ion exchange [11], chelation [12], electrocoagulation [13], electrodialysis [14], pressure-driven membrane processes [15], liquid membranes [16-17], and combined methods [18].

Liquid membranes have shown great potential for use in removal/recovery processes since they combine the extraction and stripping processes into a single unit operation [19]. In a liquid membrane, two miscible liquids (feed and product phases) are separated by a third immiscible liquid, which constitutes the membrane phase. In order to improve the effectiveness of the separation process, facilitated transport mechanisms that maximize both the extraction velocity and the reception capacity of the diffusing specie into the product phase have been described [20]. In carrier-facilitated transport, the transport of the diffusing species in the liquid membrane system is facilitated by an ion exchange reagent, which 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 from the product to the feed phase. This carrier-facilitated counter-transport mechanism is interesting because it offers the possibility of transporting a component against its own concentration gradient [21].

In this paper we study the optimization of the simultaneous removal/recovery of Cu(II) by bulk

liquid membranes containing benzoylacetone (mobile carrier) solved in kerosene in the membrane phase, and hydrochloric acid as stripping agent (protons as counter ions) in the product phase, by analyzing the effect of different operational variables (carrier concentration in membrane phase, stripping agent concentration in product phase, stirring rate and organic phase volume) on the removal/recovery kinetic constants and on the transport efficiencies through the feed/membrane and membrane/product interfaces.

A carrier counter transport mechanism is involved (Fig. 1a). The carrier benzoylacetone (HBA) diffuses from the bulk membrane phase to the feed membrane interface, where it undergoes acid dissociation and reaction with Cu(II) according to the chemical equation:



The Cu(II)-BA complex formed ( $\text{Cu}(\text{BA})_2$ ) diffuses through the membrane to the membrane product interface where, by reversing the above reaction, protons are exchanged for Cu(II) ions, which are released into the product phase. HBA is regenerated, thus initiating a new separation cycle. The Cu(II) transport mechanism is therefore a coupled counter-transport mechanism with Cu(II) and  $\text{H}^+$  travelling in the opposite direction.

## Material and Methods

Experimental studies were carried out by applying the bulk liquid membrane technique using a stirred transfer Lewis-type cell with bulk liquid membrane layered over feed and product phases (Fig. 1b). The feed phase contained a 0.025M Cu(II) chloride solution in acetate buffer (pH 4.0), the membrane phase consisted in solutions of different concentrations of BAH (1-8%) in kerosene, and the product phase comprised hydrochloric acid solutions of different concentrations (0.05 to 2.00 M). The effect of stirring rate of the three phases (50-250 rpm) and membrane phase volume (12.5-50  $\text{cm}^3$ ) were also analyzed. The feed and product phases were sampled periodically for Cu(II) concen-

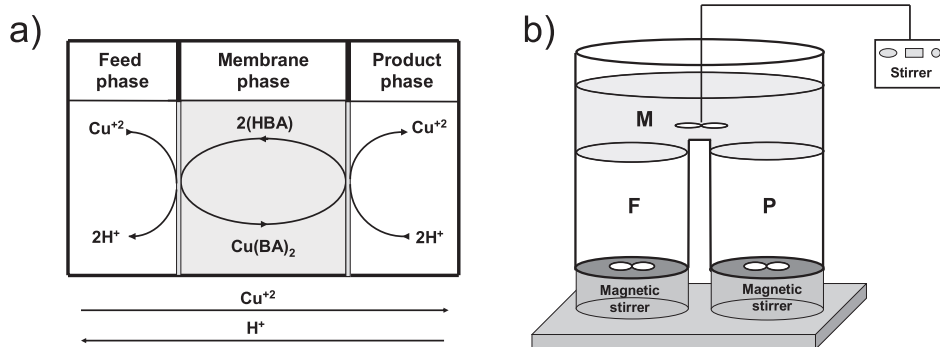


Fig. 1. a) Diagram of the facilitated countertransport of Cu(II) ions using HBA as carrier and  $\text{H}^+$  as counter ions, b) Schematic representation of the experimental cell (F, feed phase; M, membrane phase; P, product phase).

tration determination by atomic absorption spectrometry using a Shimadzu AA-6200 instrument at a wavelength of 324.8 nm. The corresponding concentration of Cu(II) in the membrane phase was calculated from material balance. All experiments were carried out in duplicate and the relative standard deviation between replicate samples was less than 3%.

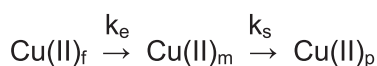
Efficiency percentages of Cu(II) transported through the feed/membrane (F/M) and membrane/product (M/P) interfaces (at 24 hours) were calculated from the following equations [22]:

$$F / M = \frac{C_{f0} - C_{ft}}{C_{f0}} \times 100 \quad (1)$$

$$M / P = \frac{C_{pt}}{C_{f0} - C_{ft}} \times 100 \quad (2)$$

... where  $C_{f0}$  is the initial concentration of Cu(II) ions in the feed phase and  $C_{ft}$  and  $C_{pt}$  are the concentrations of Cu(II) in the feed and product phases, respectively, at 24 hours.

The carrier-facilitated countertransport of Cu(II) through bulk liquid membranes can be explained by the kinetic laws of two consecutive irreversible first-order reactions, the removal or extraction reaction (rate constant,  $k_e$ ) and the recovery or stripping reaction (rate constant,  $k_s$ ).



This kinetic behaviour can be described by equations (3) to (5) [23-25].

$$R_f = \exp(-k_e t) \quad (3)$$

$$R_m = \frac{k_e}{k_s - k_e} [\exp(-k_e t) - \exp(-k_s t)] \quad (4)$$

$$R_p = 1 - \frac{1}{k_s - k_e} [k_s \exp(-k_e t) - k_e \exp(-k_s t)] \quad (5)$$

Dimensionless reduced concentrations of Cu(II) in the feed ( $R_f$ ), membrane ( $R_m$ ), and product phases ( $R_p$ ) were calculated ( $R_f = C_{ft}/C_0$ ,  $R_m = C_{mt}/C_0$  and  $R_p = C_{pt}/C_0$ ; the sum of  $R_f + R_m + R_p$  being unity). In the experiments with different membrane volumes, a "corrected concentration" related to feed volume was defined in the membrane phase ( $C_{mt}' = V_m \cdot C_{mt} / V_f$ ) in order to use the relationship  $R_f + R_m' + R_p = 1$ .

Numerical analysis of the variation with time of Cu(II) reduced concentration in the feed, in the membrane, and in the product phase by non-linear curve fitting, permitting

the rate constants of the kinetic process to be determined from those equations.

## Results and Discussion

The influence of carrier concentration in the membrane phase on Cu(II) removal/recovery is shown in Fig. 2a). The increase in carrier concentration in the membrane phase leads to an increase in the removal of kinetic constant, but to a slight decrease in the recovery kinetic constant, which produces an increase in transport efficiency though the feed/membrane interface without any significant variation in transport efficiency through the membrane/product interface. Higher values of carrier concentration in the membrane phase facilitate the formation of the  $\text{Cu(BA)}_2$  complex, that is, the extraction of Cu(II) from the feed to the membrane phase, but also increase the mass transfer resistance due to the increase in membrane phase viscosity, which causes a reduction on the diffusivity of  $\text{Cu(BA)}_2$  complex through the membrane phase. This leads to a non-significant variation in the percentage of Cu(II) transported through the membrane/product interface. As the number of Cu(II)-complex molecules increases with the increase in carrier concentration, the global result is the increase in Cu(II) recovered in the product phase.

The influence of the stripping agent concentration in the product phase on Cu(II) removal/recovery is shown in Fig. 2b). The increase in HCl concentration in the product phase (increase in counter-ion concentration) from 0.05M to 1.00M leads to an increase in both the removal and the recovery of kinetic constants (being the latter much more significant), which produces a slight increase in transport efficiency though the feed/membrane interface, but an important increase in transport efficiency though the membrane/product interface because the acidity of the product phase enhanced the stripping reaction in that interface and, consequently, the driving force for the transport of Cu(II) ions through the membrane phase. A further increase in HCl concentration to 2.00 M has no so significant effect on Cu(II) removal/recovery due to the saturation of the membrane/product interface by the stripping agent and the increase in product phase viscosity.

The influence of the stirring rate on Cu(II) removal/recovery is shown in Fig. 2c). A higher stirring rate leads to a noticeable increase in Cu(II) removal/recovery. The increase in the stirring rate leads to the increase in the removal and the recovery kinetic constants, producing obviously an increase in the transport efficiencies through the feed/membrane and the membrane/product interfaces. These results can be explained by the decrease in the size of the boundary layers at both sides of the interfaces (with no alteration of their hydrodynamic stability), resulting from the increase in stirring speed, which enhanced the effectiveness and the speediness of the Cu(II) transport through the liquid membrane. These variations are important between 50 and 200 rpm, but they are much less significant between 200 and 250 rpm.

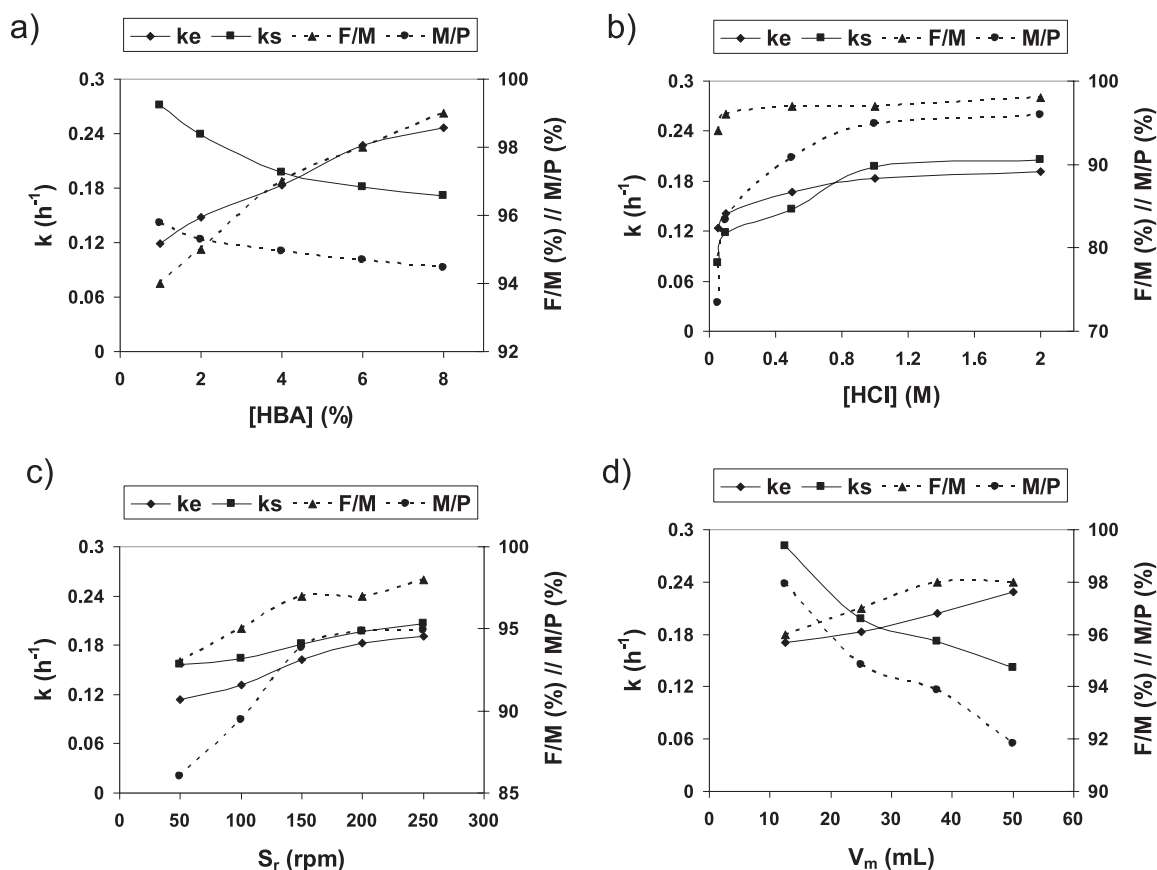


Fig. 2. Influence of different parameters on the removal/recovery kinetic constants ( $k_e$ ,  $k_s$ ) and on the transport efficiencies through feed/membrane (F/M) and membrane/product (M/P) interfaces: a) benzoylacetone concentration in membrane phase, b) hydrochloric acid concentration in product phase, c) stirring rate, d) membrane phase volume.

The influence of the membrane phase volume on Cu(II) removal/recovery is shown in Fig. 2d). The increase in the volume of membrane phase, without modifying cobalt concentration in the feed phase and carrier concentration in the membrane phase, leads to an increase in the removal kinetic constant due to the higher mass of carrier present in the membrane phase, but to an important decrease in the recovery kinetic constant due to the diminution of Cu(II)-carrier complex concentration in the membrane phase, which leads to a diminution of its diffusivity through that membrane phase and, consequently, to a diminution of both the effectiveness and the speediness of the Cu(II) stripping reaction at the membrane/product interface. The global result of these effects is a slight increase in transport efficiency through the feed/membrane interface, but an important decrease in transport efficiency through the membrane/product interface.

According to the described results, optimal experimental/economical conditions for Cu(II) removal/recovery by bulk liquid membranes using benzoylacetone as carrier are as follows: 8% benzoylacetone concentration in membrane phase, 1M hydrochloric acid concentration in product phase, 200 rpm stirring speed, and 12.5 mL volume of membrane phase.

## Conclusions

This paper describes a study to optimize the recovery of Cu(II) from aqueous solutions by bulk liquid membranes through a carrier facilitated countertransport mechanism using benzoylacetone as a mobile carrier and hydrochloric acid as a stripping agent (protons as counter ions), by analyzing the effect of different operational variables (carrier concentration in membrane phase, stripping agent concentration in product phase, stirring rate, and organic phase volume) on both the extraction/stripping kinetic constants and the transport efficiencies through feed/membrane and membrane/product interfaces. The increase in benzoylacetone concentration in the membrane phase, in hydrochloric acid concentration in the product phase, and in stirring rate in the three phases, and the decrease in the volume of the membrane phase leads to an increase in the global simultaneous removal/recovery of Cu(II) in the product phase. Optimal experimental/economical conditions for Cu(II) recovery by bulk liquid membranes using benzoylacetone as carrier are as follows: 8% benzoylacetone concentration in membrane phase, 1M hydrochloric acid concentration in product phase, 200 rpm stirring speed, and 12.5 mL volume of membrane phase.

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