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Optimization of Cu(II) removal/recovery by bulk liquid membranes containing benzoylacetone as mobile carrier

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ABSTRACT

The effective treatment of wastewater containing heavy metal ions has grown into an important research area in the last decades due to both environmental and economic point of view. In this paper we study the removal/recovery of Cu(II) by bulk liquid membranes, through a facilitated counter transport mechanism, using benzoylacetone as carrier and hydrochloric acid as striping agent (protons as counter-ions). The influence of different experimental conditions (carrier concentration in the membrane, stripping agent concentration in the product phase, stirring rate and membrane phase volume) on transport parameters (flux and permeability through feed/membrane and membrane/product interfaces) and on the percentages of Cu(II) removed from feed phase, recovered in the product phase and accumulated in the membrane phase, are analyzed in order to optimize the conditions of the removal/recovery process. Cu(II) recovery increases with the increase in carrier concentration in the membrane phase, in stripping agent (counter-ion) concentration in the product phase and in stirring rate in the three phases, and decreases with the increase in the volume of that membrane phase.

Keywords: Copper; Removal/recovery; Bulk liquid membranes; Benzoylacetone; Facilitated counter transport

1. Introduction

The release of heavy metals into the environment in the effluents of many industries has led their removal/recovery from wastewater becoming a major topic of research in recent decades due to their toxicity and non-degradability, and to their potential importance as valuable resource [1].

One of the most commonly used and valuable metals in industry is copper, which ranks after iron and aluminium in importance for infrastructure and technology [2]. It is considered an energy critical element, due to its conductive properties, and is classified as a scarce mineral, with only sixty year of expected availability at current production levels [3]. Cu(II) is present in the wastewater of many industrial processes involved in mining, metallurgy, plating, steel-making, paper and pulp, fertilizer, petroleum refining, wood preservatives, and printing circuits [4,5]. Though copper is a micronutrient element, it is a hazardous pollutant when it cannot be maintained at an appropriate physiological concentration, leading to disorders in animals and humans [6,7]. For this reason, Cu(II) is considered as one of the most toxic metals by the World Health Organization [8] and as a priority pollutant by US EPA [9]. Therefore, the removal/recovery of Cu(II) from raw materials and secondary sources may be considered as an interesting research field from both economic and environmental view points.

Several methods have been described for the effective removal/recovery of Cu(II) from wastewater, including

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cementation [10], chemical precipitation [11], adsorption [5,12–14], biosorption [15,16], ion exchange [17] chelation [18], electrocoagulation [19], electrodialysis [20], pressure driven membrane processes [21–26], liquid membranes [1,27,28] and combined methods [29]. Advantages and disadvantages of some of these processes have been analyzed recently [30].

Liquid membranes have shown great potential as a removal/recovery process, since they combine the processes of extraction and stripping in a single unit operation [31]. Liquid membranes involve a liquid (membrane phase) which is immiscible and separates two miscible liquids (feed and product phases) and serves as a semipermeable barrier between them. In bulk liquid membranes, a bulky layer of the liquid that constitutes the membrane phase directly separates the feed and the product phases.

In order to increase both the selectivity and the mass transfer rates of the removal/recovery process, the transport of the diffusing species through the liquid membrane system, can be facilitated by carrier mediated transport [32,33], whereby a carrier reagent is incorporated in the membrane phase to transport the diffusing species from the feed to 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 [34].

Taking as starting point the results of a previous paper comparing the efficiency of different carriers and different transport mechanisms for Cu(II) removal/recovery [35], this paper represents an optimizing study of the removal/recovery of Cu(II) by bulk liquid membrane containing benzoylacetone as mobile carrier in the membrane phase and hydrochloric acid as stripping agent (protons as counter ions) in the product phase. The effect of different operational variables (carrier concentration in the membrane phase, stripping agent concentration in the product phase, stirring rate and organic phase volume) on Cu(II) flux and permeability through the feed/membrane and membrane/product interfaces is studied, along with the effect on the percentages of Cu(II) removed from the feed phase, recovered in the product phase and accumulated in the membrane phase, in order to optimize the efficiency of the removal/recovery process.

2. Experimental

2.1. Materials

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

2.2. Methods

Experimental studies were carried out applying the bulk liquid membrane technique, using a stirred transfer Lewis type cell with bulk liquid membrane layered over feed and product phases (Fig. 2). A 3.3625 kg/m^3 copper (II) chloride solution in acetate buffer, pH 4.0, was used as feed phase. The membrane phase comprised solutions of different concentrations of HBA (10–100 kg/m^3) in kerosene, while hydrochloric acid solutions of different concentrations (1.825–73.000 kg/m^3) were used as product phase. The effect of stirring speed of the three phases (50–250 rpm) and membrane phase volume (12.5–50 cm^3) were also analyzed. Typical experimental conditions were: 40 kg/m^3 benzoyl acetone, 36.500 kg/m^3 HCl, 200 rpm stirring speed, 25 mL membrane phase volume, time 12 h.

Samples of feed and product phases were taken at intervals and Cu(II) concentration was determined by atomic absorption spectrometry, using a Shimadzu AA-6200 instrument at a wavelength of 324.8 nm. The Cu(II) concentration in the membrane phase was established from the material balance. All experiments were carried out in duplicate (the relative standard deviation between replicate samples was less than 3%) and the average concentration value was used to obtain the transport parameters.

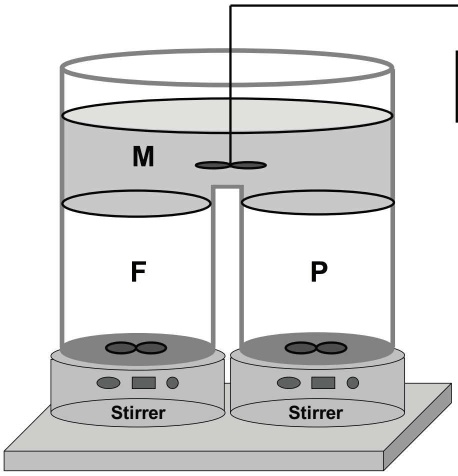

Fig. 1. Schematic representation of the experimental cell (F, feed phase; M, membrane phase; P, product phase).

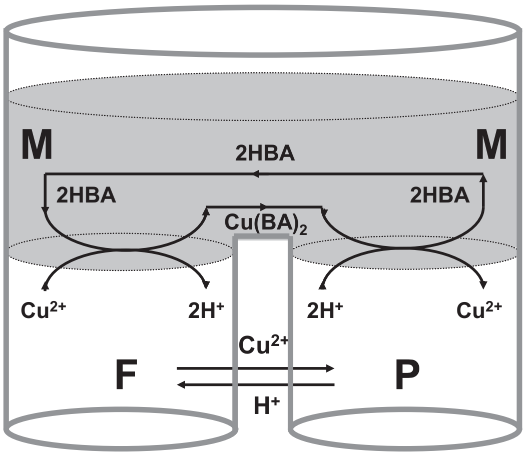

Fig. 2. Illustration of the facilitated transport of Cu(II) ions using HBA as carrier and H$^+$ as counter ion.

Fluxes through the feed/membrane ($J_{f/m}$) and membrane/product ($J_{m/p}$) interfaces were determined by monitoring Cu(II) concentrations in the feed and product phases as a function of time, based on the following equations [36,37]:

$$J_{f/m} = -\frac{V}{A}\frac{dC_{ft}}{dt} \tag{1}$$

$$J_{m/p} = \frac{V}{A}\frac{dC_{pt}}{dt} \tag{2}$$

where C_{ft} and C_{pt} are the concentrations of Cu(II) in the feed and product phases, respectively, at time t, V is the volume of feed and product phases and A is the area of the feed/membrane and membrane/product interfaces.

Permeabilities through the feed/membrane ($P_{f/m}$) and membrane/product ($P_{m/p}$) interfaces were obtained, respectively, from the expressions [38]:

$$\ln\frac{C_{ft}}{C_{fo}} = -\frac{A}{V}P_{f/m}t \tag{3}$$

$$\ln\frac{C_{fo}-C_{pt}}{C_{fo}} = -\frac{A}{V}P_{m/p}t \tag{4}$$

where C_{fo} is the initial concentration of Cu(II) in the feed phase.

The percentages of Cu(II) removed from the feed phase (RF) and recovered in the product phase (RP) were determined by the equations:

$$RF = 100\cdot\frac{C_{fo}-C_{ft}}{C_{fo}} \tag{5}$$

$$RP = 100\cdot\frac{C_{pt}}{C_{fo}} \tag{6}$$

Cu(II) percentage accumulated in the organic membrane phase (AM) was calculated through a material balance.

3. Results and discussion

3.1. Transport mechanism

The transport of Cu(II) through bulk liquid membranes containing benzoylacetone as mobile carrier and hydrochloric acid as stripping agent (protons as counter ions) involves a carrier facilitated counter transport mechanism (Fig. 2). 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:

$$Cu^{+2}\ (aq) + 2(HBA)\ (org) \leftrightarrow Cu(BA)_2\ (org) + 2H^+\ (aq)$$

The Cu(II)-BA complex formed ($Cu(BA)_2$) 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 H^+ travelling in the opposite direction.

3.2. Influence of different experimental parameters on Cu(II) removal

3.2.1. Effect of carrier concentration in the membrane phase

Fig. 3 shows the influence of carrier concentration (HBA) on Cu(II) removal/recovery. The increase in HBA concentration in the membrane phase up to 40 kg/m³ leads to an increase in both the fluxes and permeabilities through the feed/membrane and membrane/product interfaces (slightly higher at the feed/membrane interface) (Fig. 3a), due to the presence of a higher number of carrier molecules, which improves Cu(II) transport from the feed to the product phase. A further increase in carrier concentration has no significant effect on flux and permeability due to both, the saturation of the feed membrane interface by the carrier and the increase in membrane phase viscosity. These results explain the observed increase in the percentages of Cu(II) removed from the feed phase, recovered in the product phase and accumulated in the membrane phase (Fig. 3b).

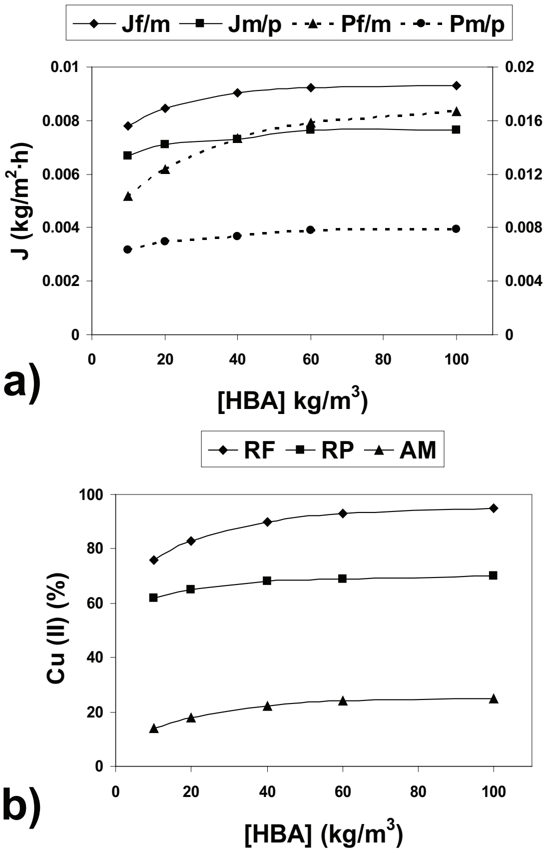

Fig. 3. Influence of carrier concentration in membrane phase on Cu(II) removal/recovery: a) interfaces transport parameters, b) Cu(II) removed, recovered and accumulated percentages.

3.2.2. Effect of hydrochloric acid concentration in the product phase

The influence of the stripping agent (HCl) concentration on Cu(II) removal/recovery is shown in Fig. 4. Increasing the HCl concentration in the product phase (increase in counter-ion concentration) from 1.825 to 36.500 kg/m^3 leads to a slight increase in flux and permeability through the feed/membrane interface but to a substantial increase in flux and permeability through the membrane/product interface (Fig. 4a), due to the improvement of the stripping process. This leads to a large fall in Cu(II) accumulation in the membrane phase and a pronounced increase in Cu(II) recovery in the product phase (Fig. 4b). A further increase in HCl concentration to 73.000 kg/m^3 had no significant effect on Cu(II) removal or recovery due to the saturation of the membrane/product interface by the stripping agent and the increase in product phase viscosity.

3.2.3. Effect of stirring rate in the three phases

Fig. 5 shows the influence of stirring rate in the three phases on Cu(II) removal/recovery. An increase in the stirring rate leads to an increase in flux and permeability through both feed/membrane and membrane/product interfaces (Fig. 5a) due to a diminution in the boundary layers thickness with the increased stirring rate. This leads to an increase in both, Cu(II) removal from the feed phase and its recovery in the product phase, and to a decrease in the Cu(II) accumulation in the membrane phase (Fig. 5b). Such variations are substantial between 50 and 200 rpm but much less so between 200 and 250 rpm.

3.2.4. Effect of membrane phase volume

The influence of the membrane phase volume on Cu(II) removal/recovery is shown in Fig. 6. The increase in membrane volume (without modifying Cu(II) concentration in the feed phase or carrier concentration in the membrane phase), leads to increased flux and permeability through the feed/membrane interface, due to the higher mass of carrier present in that membrane phase, but to a decrease in the same through the membrane/product interface (Fig. 6a), due to a diminution of the copper(II)-carrier complex concentration in the membrane phase, which leads to a diminution of the driving force of Cu(II) transport. The results is a decrease in Cu(II) recovery in the product phase, because the increase in Cu(II) removal from the feed phase is accompanied by its increased accumulation in the

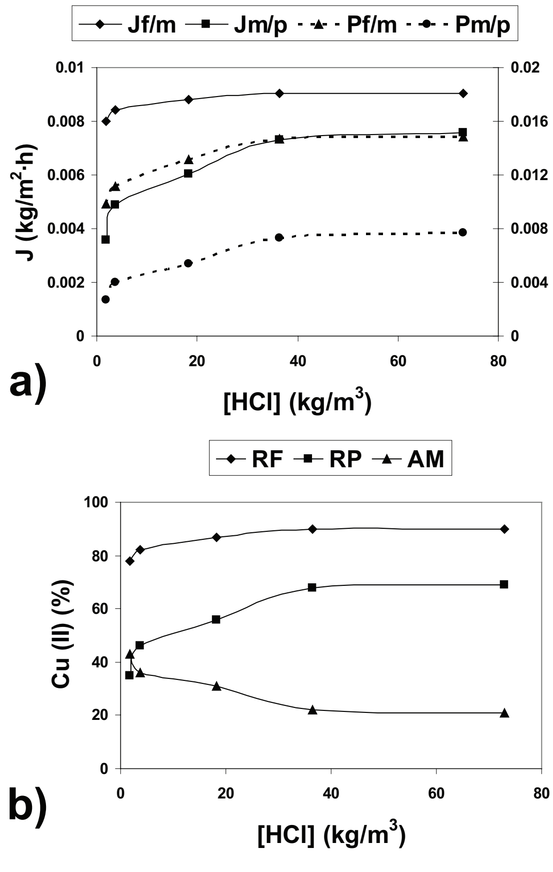

Fig. 4. Influence of hydrochloric acid concentration in product phase on Cu(II) removal/recovery: a) interfaces transport parameters; b) Cu(II) removed, recovered and accumulated percentages.

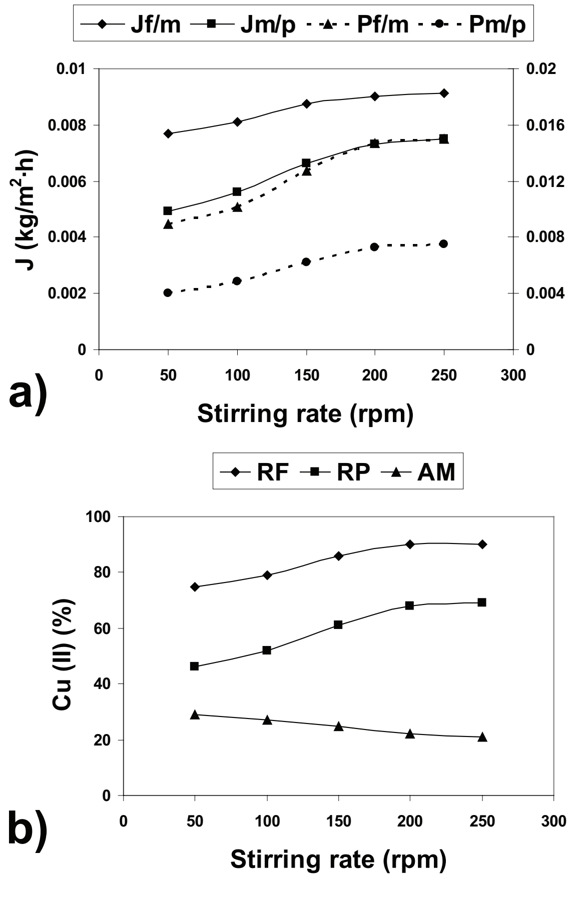

Fig. 5. Influence of stirring rate in the three phases on Cu(II) removal/recovery: a) interfaces transport parameters; b) Cu(II) removed, recovered and accumulated percentages.

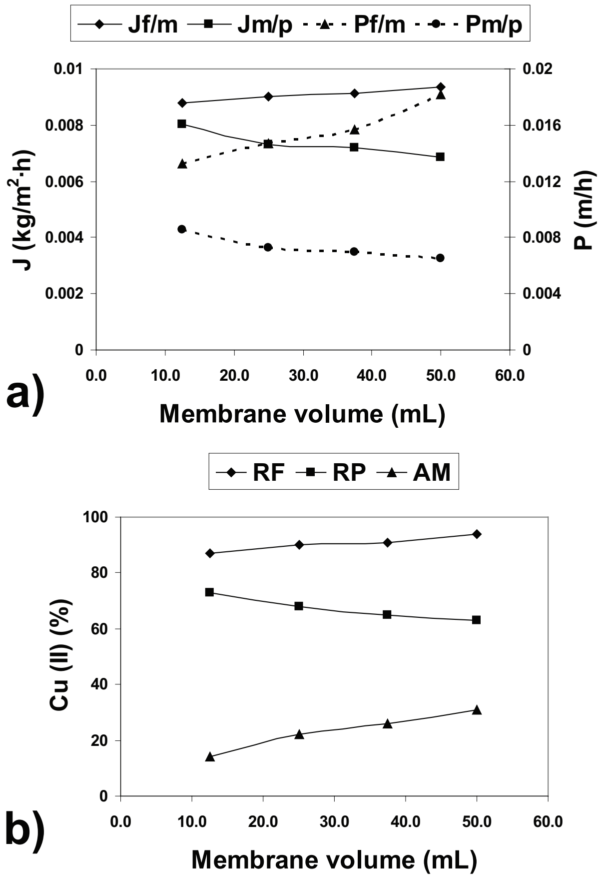

Fig. 6. Influence of membrane phase volume (12.5 cm^3 to 50 cm^3) on Cu(II) removal/recovery: a) interfaces transport parameters; b) Cu(II) removed, recovered and accumulated percentages.

membrane phase due to the presence of a higher volume of membrane (Fig. 6b).

3.3. Optimal experimental conditions

According to the results obtained, the optimal experimental/economic conditions for Cu(II) removal/recovery from aqueous solutions by bulk liquid membranes using benzoylacetone as carrier are as follows: 40 kg/m^3 benzoylacetone concentration in the membrane phase, 36.5 kg/m^3 hydrochloric acid concentration in the product phase, 200 rpm stirring speed and 12.5 mL membrane phase volume. In these optimal experimental conditions, the values of flux and permeability through the feed membrane and membrane product interfaces were 0.00878 kg/m^2·h, 0.01327 m/h and 0.00802 kg/m^2·h, 0.00859 m/h, respectively, and the percentages of Cu(II) removed from the feed phase, recovered in the product phase and accumulated in the membrane phase were 87%, 73% and 14%, receptively.

4. Conclusion

This paper describes the optimization of Cu(II) removal/recovery from aqueous solutions by bulk liquid membranes, through a facilitated counter transport mechanism, using benzoylacetone as carrier and hydrochloric acid as stripping agent (protons as counter ions). An increase in the benzoylacetone concentration in the membrane phase, in the hydrochloric acid concentration in the product phase and in the stirring rate in all three phases leads to an increase in Cu(II) recovery in the product phase due to increased fluxes and permeabilities through both the feed/membrane and the membrane/product interfaces. In contrast, an increase in the volume of the membrane phase leads to a decrease in Cu(II) recovery in the product phase due to diminished fluxes and permeabilities through both the feed/membrane and the membrane/product interfaces. Optimal Cu(II) removal/recovery conditions are: 40 kg/m^3 benzoylacetone concentration in the membrane phase, 36.5 kg/m^3 hydrochloric acid concentration in the product phase, 200 rpm stirring speed and 12.5 mL volume of membrane phase. In these optimal experimental conditions, 87% of Cu(II) was removed from the feed phase, 73% was recovered in the product phase and 14% was accumulated in the membrane phase, while the values of flux and permeability through the feed/membrane and membrane/ product interfaces were, 0.00878 kg/m^2·h, 0.01327 m/h and 0.00802 kg/m^2·h, 0.00859 m/h, respectively.

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