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# Facilitated transport of cobalt through bulk liquid membranes containing D2EHPA as carrier. Kinetic study of the influence of some operational variables

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## ABSTRACT

The presence of heavy metals in aqueous solutions beyond certain limits creates serious threat to the environment due to their non-degradability and toxicity. So the search for techniques to remove those pollutants is of increasing interest. Liquid membranes have shown great potential in this way, especially in cases where pollutant concentrations are relatively low and other techniques cannot be applied efficiently. A kinetic study of the influence of some operational variables (organic phase volume, emulsifier concentration in the membrane phase and stirring rate) on the transport of cobalt (II) through bulk liquid membrane containing di(2-ethylhexyl) phosphoric acid (D2EHPA), as mobile carrier, in kerosene and protons, as counter ions, in the product phase ($H_2SO_4$), is carried out is this paper. The transport kinetic was analysed by means of a kinetic model involving two consecutive irreversible first order reactions. The rate constants of the extraction and stripping reactions were determined for all the experimental conditions studied. Maximum transport fluxes of cobalt (II) through the bulk liquid membrane were also calculated.

*Keywords***:** Membrane processes; Bulk liquid membranes; Cobalt; D2EHPA; Kinetics

## 1. Introduction

Heavy metal contamination of industrial effluents and wastewaters is a very important environmental problem. As heavy metals are not biodegradable they tend to accumulate in living organisms causing various diseases and disorders.

Cobalt is one of the heavy metals associated to industrial activities being present in effluents and wastewaters of a wide range of industries, such as mining, hydrometallurgy, electroplating, painting, etc. The permissible limits of cobalt in the irrigation water and livestock watering are 0.05 and 1.0 $mg·dm^{-3}$ respectively [1]. The effects of acute cobalt poisoning in humans are very serious, among them are asthma like allergy, damage to the heart, causing heart failure, and damage to the thyroid and liver. Cobalt may also cause genetic changes in living cells.

Different techniques have been described for cobalt removal from wastewater, including chemical precipitation [2], adsorption on activated carbon [3,4], biosorption [5] ion exchange [6–9], pressure driven membrane processes [10] and combined methods (sorption or complexation plus pressure driven membranes processes) [11–13]. Recently, the use of liquid membranes for the removal of

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cobalt from aqueous solutions has been described [14–18]. Liquid membranes have shown great potential, 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 [19]. 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, it is governed by a non-equilibrium mass transfer.

Metal ion extraction in the liquid membrane system can be facilitated by carrier mediated transport, in which an ion exchange reagent is incorporated in the membrane phase to carry the diffusing specie across the membrane to the product phase, a process that is usually accompanied by the transport of other chemical specie from the product to the feed phase (facilitated counter transport). This coupled transport mechanism is interesting because it offers the possibility of transporting a component against its own concentration gradient [20].

The kinetics of the effect of some operational variables (organic phase volume, emulsifier concentration in the membrane phase and stirring rate) on the transport of cobalt (II) through bulk liquid membrane containing di(2-ethylhexyl) phosphoric acid (D2EHPA), as mobile carrier, in kerosene and protons, as counter ions, in the product phase ($H_2SO_4$), is studied in this paper.

## 2. Theory

The facilitated transport of Co(II) ions through a liquid membrane using D2EHPA as carrier and $H^+$ as counter ions is illustrated in Fig. 1. The carrier diffuses from the bulk membrane phase to the feed membrane interface, where cobalt (II) ions are exchanged for protons. Due to the high interfacial reactivity of D2EHPA [21], a dimerized molecule undergoes acid dissociation [22] and reaction with cobalt (II), according to the equation:

$$Co^{2+}(aq) + 2(HR)_2(org) \Leftrightarrow CoR_2(HR)_2(org) + 2H^+(aq) \quad (1)$$

The cobalt (II) carrier complex formed diffuses through the membrane to the membrane product interface, where, by reversing the described reaction, protons are exchanged for cobalt (II) ions, which are released into the product phase. The carrier is regenerated, thus beginning a new separation cycle.

The cobalt (II) transport mechanism is therefore a coupled counter ion transport mechanism, with Co (II) and $H^+$ travelling in the opposite direction.

The mechanism of that facilitated transport of cobalt has been explained by the kinetic laws of two consecutive irreversible first-order reactions, the extraction (rate constant, $k_1$) and the stripping (rate constant, $k_2$) reactions [15]. This mechanism has been used to describe the transport of some divalent ions through bulk liquid membranes [23–26].

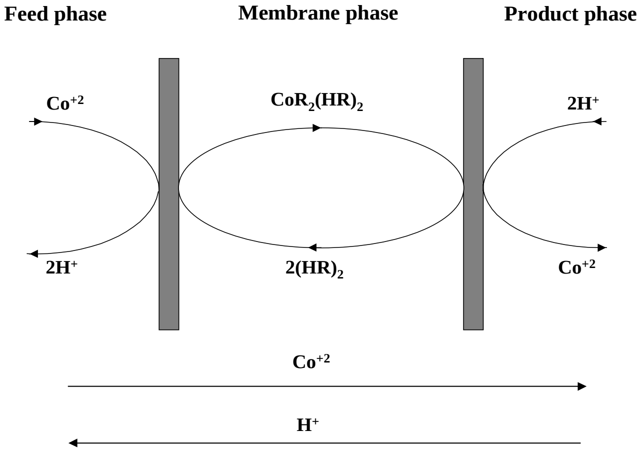

Fig. 1. Diagram of the facilitated transport of Co(II) ions using D2EHPA as carrier and $H^+$ as counter ions.

This kinetic behaviour can be described according to the following equations [23]:

$$\frac{dR_f}{dt} = -k_1 R_f \equiv J_{f/m} \quad (2)$$

$$\frac{dR_m}{dt} = k_1 R_f - k_2 R_m \quad (3)$$

$$\frac{dR_p}{dt} = k_2 R_m \equiv J_{m/p} \quad (4)$$

Integration of those differential equations gives [23]:

$$R_f = \exp(-k_1 t) \quad (5)$$

$$R_m = \frac{k_1}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] \quad (6)$$

$$R_p = 1 - \frac{1}{k_2 - k_1}\left[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)\right] \quad (7)$$

These equations show that the time dependence of $R_f$ is monoexponential and the time dependence of both $R_m$ and $R_p$ is biexponential.

$R_m$ has a maximum, the time at which it occurs being obtained from $dR_m/dt = 0$.

$$t_{\max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2} \quad (8)$$

The value of $R_m$ at that time being [23]

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

Combining Eqs. (8) and (9) the following relationship can be obtained.

$$k_2 = \frac{\ln\left(\frac{1}{R_m^{\max}}\right)}{t_{\max}} \tag{10}$$

First-order time differentiation of Eqs. (5)–(7) leads to the final form of the flux equations [26].

$$\frac{\mathrm{d}R_f}{\mathrm{d}t} = -k_1 \exp\left(-k_1 t\right) \tag{11}$$

$$\frac{\mathrm{d}R_m}{\mathrm{d}t} = \frac{k_1}{k_2 - k_1}\left[k_2 \exp\left(-k_2 t\right) - \exp\left(-k_1 t\right)\right] \tag{12}$$

$$\frac{\mathrm{d}R_p}{\mathrm{d}t} = \frac{k_1 k_2}{k_2 - k_1}\left[\exp\left(-k_1 t\right) - \exp\left(-k_2 t\right)\right] \tag{13}$$

By substituting the expression of $t_{\max}$ given for Eq. (8) in Eqs. (11)–(13), maximum fluxes can be obtained [26].

$$\left[\frac{\mathrm{d}R_f}{\mathrm{d}t}\right]_{\max} = -k_1\left(\frac{k_1}{k_2}\right)^{-\frac{k_1}{k_1 - k_2}} = J_f^{\max} \tag{14}$$

$$\left[\frac{\mathrm{d}R_m}{\mathrm{d}t}\right]_{\max} = 0 \tag{15}$$

$$\left[\frac{\mathrm{d}R_p}{\mathrm{d}t}\right]_{\max} = k_2\left(\frac{k_1}{k_2}\right)^{-\frac{k_2}{k_1 - k_2}} = J_p^{\max} \tag{16}$$

$$-\left[\frac{\mathrm{d}R_f}{\mathrm{d}t}\right]_{\max} = +\left[\frac{\mathrm{d}R_p}{\mathrm{d}t}\right]_{\max} \Rightarrow -J_f^{\max} = +J_p^{\max} \tag{17}$$

## 3. Experimental equipment and procedure

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).

0.0025 M cobaltous sulphate solutions in 0.05 M formic acid, adjusted to pH 4.0 with sodium hydroxide, were used as feed phase. Use of formate buffer prevented the pH in the feed solution from varying by more than 0.1 pH units, as has been described [27]. The membrane phase was constituted by solutions of di-2-ethylhexyl phosphoric acid in kerosene (6% weight) with varying proportions of Span. 1 M aqueous sulphuric acid solutions were used as product phase. The volumes of feed and product phases were 25 cm$^3$. The areas of both feed–membrane and membrane–product interfaces were 3.2 cm$^2$. In the different experiments volumes of membrane phase of 12.5 cm$^3$, 25.0 cm$^3$, 37.5 cm$^3$ and 50.0 cm$^3$, Span concentrations in the membrane phase of 0.0%, 0.5%, 2.0% and 5.0% and stirring speeds of 50 rpm, 100 rpm, 150 rpm and 200 rpm were used.

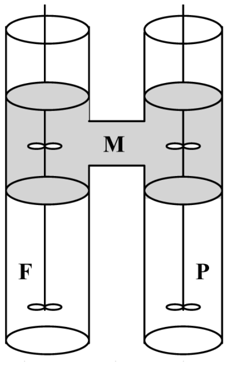

Fig. 2. Schematic representation of the experimental transfer cell (F, feed phase; M, membrane phase; P, product phase)

Cobalt (II) ion concentrations in both feed and product phases were determined by UV spectrophotometry using an Unicam UV2 instrument, measuring the absorbance of the colour developed by the product of the reaction between cobalt (II) and xylenol orange [28]. Cobalt (II) ion concentration in the membrane phase was established from the material balance. For practical reasons, dimensionless reduced concentrations of cobalt (II) in the feed ($R_f$), membrane ($R_{m,}$) and product phases ($R_p$) were used ($R_f = C_{ft}/C_0$, $R_m = C_{mt}/C_0$ and $R_p = C_{pt}/C_0$, the sum of $R_f + R_m + R_p$ obviously 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 relation $R_f + R'_m + R_p = 1$.

## 4. Results and discussion

The influence of membrane phase volume, Span concentration in membrane phase and stirring speed on cobalt transport are represented in Figs. 3, 4 and 5, respectively. An increase in the membrane phase volume leads to a slight decrease in total cobalt transport, and an increase in the cobalt mass in the membrane. An increase in Span concentration in the membrane phase leads to a substantial decrease in the total cobalt transport, and an increased amount of cobalt retained in the membrane phase. A higher stirring speed leads to a noticeable increase in cobalt transport.

Numerical analysis of experimental results by nonlinear curve fitting permits the rate constants of the kinetic process to be determined (Table 1). The values of $k_1$ are directly obtained by iteration from Eq. (5). This value is introduced as a constant value in Eqs. (6) and (7). An initial value of $k_2$ is obtained in each case from Eq. (10), then introduced in Eqs. (6) and (7) and iterated. Two values of the rate constant $k_2$ are obtained in each

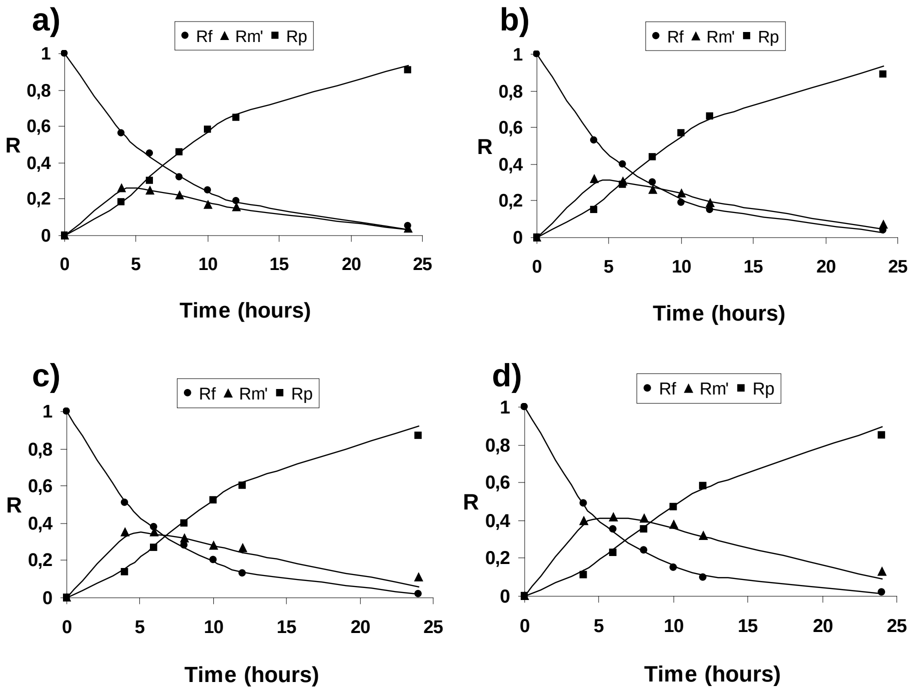

Fig. 3. Influence of membrane phase volume on Co (II). Membrane phase volume: a) 12.5 cm$^3$; b) 25.0 cm$^3$; c) 23.5 cm$^3$; d) 50.0 cm$^3$. (Points, experimental values; lines, model values).

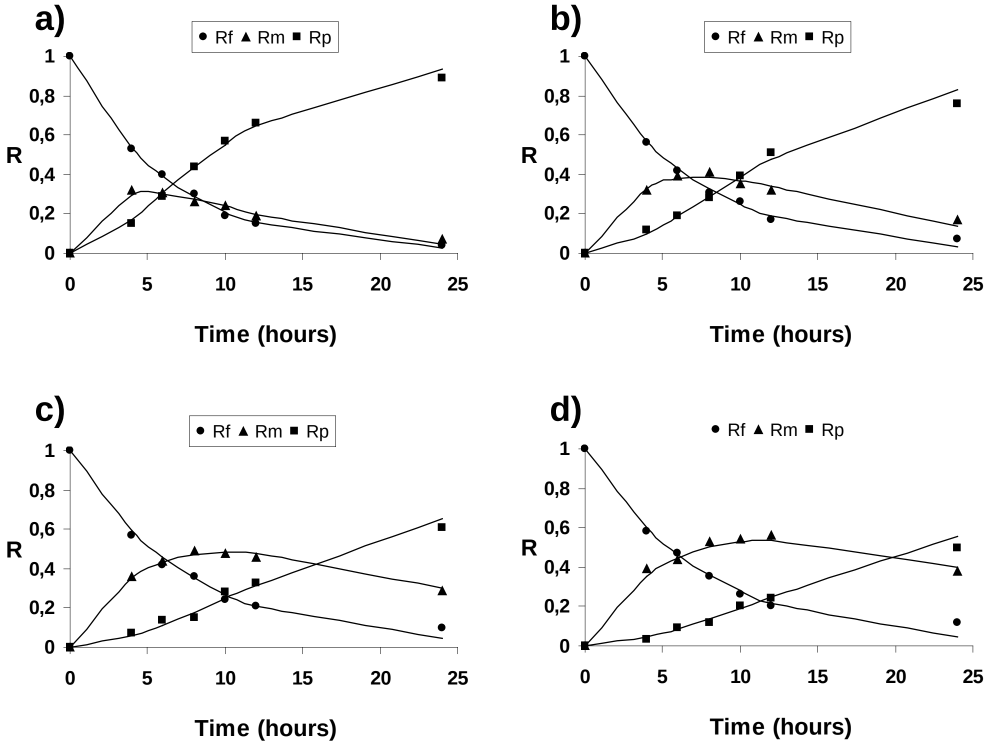

Fig. 4. Influence of Span concentration in the membrane phase on Co (II) transport. Span concentration in the membrane phase: a) 0.0%; b) 0.2%; c) 0.5%; d) 2%. (Points, experimental values; lines, model values).

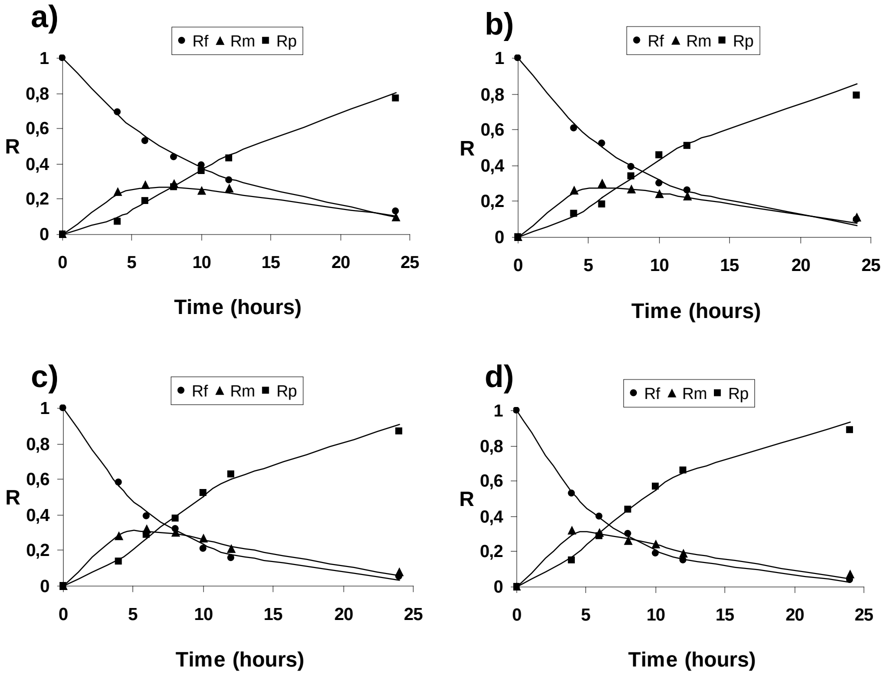

Fig. 5. Influence of stirring speed on Co (II) transport. Stirring speed: a) 50 rpm; b) 100 rpm; c) 150 rpm; d) 200 rpm. (Points, experimental values; lines, model values).

Table 1
Rate constants for extraction ($k_1$) and stripping ($k_2$) processes and maximum flux ($J_{max}$) of cobalt (II) transport at different membrane phase volumes, Span concentrations in membrane phase and stirring speeds (feed phase cobalt (II) 0.0025 M, product phase sulphuric acid 1 M, membrane phase D2EHPA 6% in kerosene)

| | Membrane phase volume (cm$^3$) | | | |
|---|---|---|---|---|
| | 12.5 | 25.0 | 37.5 | 50.0 |
| $k_1$ (h$^{-1}$) | 0.141 | 0.156 | 0.164 | 0.181 |
| $k_2$ (h$^{-1}$) (average value) | 0.281 | 0.223 | 0.188 | 0.142 |
| $J_{max}$ (h$^{-1}$) | 0.070 | 0.068 | 0.064 | 0.059 |
| | Span concentration in membrane phase (%) | | | |
| | 0.0 | 0.5 | 2.0 | 5.0 |
| $k_1$ (h$^{-1}$) | 0.156 | 0.140 | 0.131 | 0.127 |
| $k_2$ (h$^{-1}$) (average value) | 0.223 | 0.127 | 0.071 | 0.053 |
| $J_{max}$ (h$^{-1}$) | 0.068 | 0.049 | 0.034 | 0.028 |
| | Stirring speed (rpm) | | | |
| | 50 | 100 | 150 | 200 |
| $k_1$ (h$^{-1}$) | 0.097 | 0.114 | 0.144 | 0.156 |
| $k_2$ (h$^{-1}$) (average value) | 0.176 | 0.195 | 0.201 | 0.223 |
| $J_{max}$ (h$^{-1}$) | 0.047 | 0.054 | 0.062 | 0.068 |

case, one derived from Eq. (6), $k_{2m}$, and the other derived from Eq. (7), $k_{2p}$. Good agreement between $k_{2m}$ and $k_{2p}$ constants was observed in all experimental conditions. Maximum fluxes calculated from Eqs. (14) and (16) are also included in Table 1.

Model curves of time dependence of $R_f$, $R_m$ and $R_p$, for the different experimental conditions, calculated from Eqs. (5)–(7) are also shown in Figs. 3, 4 and 5. Good agreement between experimental and model data can be observed.

An increase in the membrane phase volume leads to a slight increase in the extraction constant and to a decrease of stripping constant, the result being a decrease in maximum cobalt flux. An increase in the volume of membrane phase, while not modifying cobalt concentration in feed phase, diminishes the concentration of cobalt (II)-carrier complex in membrane phase and decreases the total cobalt transport.

An increase of Span concentration in membrane phase leads to a decrease of both the extraction and the stripping constants (especially the latter), and, accordingly, to a significant decrease of maximum cobalt flux. An increase in surfactant concentration of the membrane phase leads to an increase of mass transfer resistance due to both the increase of the viscosity of membrane phase, which causes a reduction on the difusivity of carrier and cobalt (II)–carrier complex in the membrane phase [29], and the presence of more surfactant at the feed–membrane and membrane–product interfaces [30].

The higher stirring speed leads the higher both, the extraction and the stripping constants, and, consequently, accompanied by an increase in maximum cobalt flux. These results suggest that a decrease of the size of the limit layers at both sides of the feed–membrane and membrane–product interfaces results from the increase of stirring speed, leading to an increase of transport rates [31] with no alteration of the hydrodinamic stability of the two interfaces.

## 5. Conclusions

The effect the membrane phase volume, Span concentration in the membrane phase and stirring speed on the kinetics of the transport of cobalt (II) ions through bulk liquid membrane containing di(2-ethylhexyl) phosphoric acid (D2EHPA) as mobile carrier in kerosene and protons ($H_2SO_4$), as counter ions, in the product phase was studied in this paper. The transport kinetics was analysed by means of a kinetic model involving two consecutive irreversible first order reactions. The rate constants of the extraction and stripping reactions were determined by numerical analysis of the experimental results in all the experimental conditions studied. Good agreement between model and experimental data is observed.

An increase in the membrane phase volume leads to an increase of the extraction constant and a higher decrease of stripping constant, resulting in a decrease of maximum cobalt flux. An increase of Span concentration in the membrane phase leads to a decrease of both the extraction and the stripping constants (being the latter more significant), leading to a significant decrease of maximum cobalt flux. An increase of stirring speed leads to an increase of both the extraction and the stripping constants, resulting in an increase of maximum cobalt flux

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