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New supported liquid membranes containing TBP and MC as carriers for the facilitated transport of cadmium ions from acidic mediums: Parameters and mechanism

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Abstract
In this work, we have developed two new supported liquid membranes (**SLMs**) for the recovery of cadmium ions **Cd(II)** from acidic mediums. To prepare this type of membrane, we have used the PVDF polymer as support, the compounds methyl Cholate (**MC**), Tri-butyl phosphate (**TBP**) as carriers, and toluene solvent as the organic phase. We have developed a kinetic model to calculate the macroscopic parameters (permeability **P** and the initial flux $\mathbf{J_0}$) relating to each membrane prepared, and we have also developed a thermodynamic model to determine the microscopic parameters $\mathbf{K_{ass}}$ (association constant) and D***** (apparent diffusion coefficient) that are specific to the diffusion of the complex (TS) formed between the substrate and the carrier used through the organic phase. The proposed models are verified by the experimental results found, and we have studied the influence of the nature of the carrier, and the initial concentration of the substrate Cadmium ions. Furthermore, these results indicate that the migration of cadmium ions through the organic phase of the SLM, is not a pure diffusion, but this migration corresponds to successive jumps of the substrate from one site to the other of the carrier.

Keywords: facilitated transport supported liquid membrane (SLM), cadmium, permeability, flux, diffusion

1. Introduction
The world has experienced a strong demographic evolution, which has imposed an increase of polluting due to industrial activities to satisfy the needs of market, but this evolution affects natural resources, which are limited. A large population of our planet does not have access to the drinking water because it exists in small amounts and it is polluted by toxic substances such as heavy metals (cadmium, copper,..). Cadmium is a highly toxic element that is located in the industrial discharges such as the manufacture of cadmium-nickel batteries [1], phosphatic fertilisers [2], pigments [3], stabilizers [4], alloys and electroplating industries [5] . Several methods have been proposed to eliminate cadmium from wastewater as methods of precipitation [6], the ion exchange [7], clays or zeolites [8], the adsorption on the surface of materials such as carbon [9] and membrane processes [10,11].

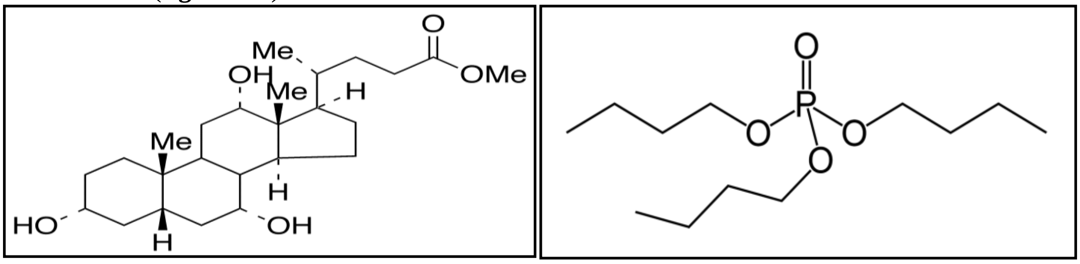
Membrane processes have techno-economic and environmental advantages, compared with other techniques. Several types of membranes have been used to recover cadmium like bulk liquid membranes (**BLM**) [12], emulsion liquid membranes (**ELM**)[13] and supported liquid membrane (**SLM**)[10,14]. This latter type of membranes is easy to elaborate at a laboratory scale, the SLM are developed by immobilizing a solution containing an amphiphilic molecule (**carrier**) and an organic solvent using a porous polymer support. In general, the carriers are organic acids, esters, amines, antibiotics, phosphoric compounds...

In this work, we have prepared two types of supported liquid membranes using the PVDF polymer as support, toluene as organic solvent and the methyl Cholate (**MC**) (**figure 1-A**) as a new carrier and we have also used the Tri-butyl phosphate (**TBP**)(**figure 1-B**) as a classic carrier, we have developed a kinetic model to calculate the parameters relating to the transport of Cd (II) through the membrane. This model is verified and we have determined the macroscopic parameters (permeability P and initial flux J_0). We have also used a thermodynamic model to determine the macroscopic parameters (association constant K_{ass} and apparent diffusion coefficient (D*) related to the association between the substrate and the carrier.

2. Transport mechanism:

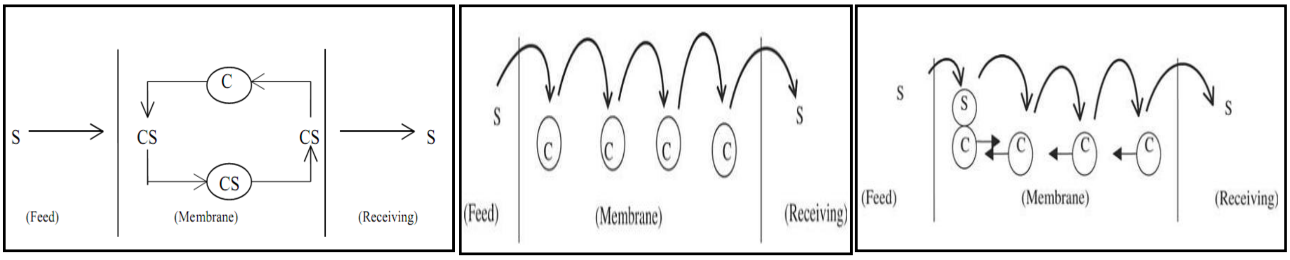
Several models have been proposed to describe the process of facilitated transport, the theory is useful to interpret the current transport systems and to design others systems more selective and effective in the future [15]. Three mechanisms of the facilitated transport phenomena are known:

- The first mechanism: a solution-diffusion mechanism, in which the carrier and the complex are mobile in the membrane phase and they migrate in the opposite direction (**figure 2-a**).
- The second mechanism: a mechanism by jumping on fixed sites, in which the carrier is fixed in the pores of the membrane and the substrate moves successively by an association with several carriers, this mechanism is well known in polymer inclusion membranes (PIM) (**figure 2-b**).
- The third mechanism: a mechanism by jumping on mobile sites in which the substrate is moving in series by linking to multiple mobile carriers (**figure 2-c**).



A **B**

Figure 1: Structure of: **A**- Methyl Cholate (MC) **B**-Tri-Butyl Phosphate (TBP)



a **b** **c**

Figure 2: Mechanisms of facilitated transport through membrane.

3. Model of calculation:

The models used in this study, to calculate the different parameters related to the transport of cadmium through the membranes are described in detail in previous works [16][17].

To calculate the macroscopic parameters (permeability P and the initial flux J_0) we used the slope of the function *- Ln $(C_0 - 2C_R) = f$ (time)*, which should be a straight line. Then, we can calculate the permeability by the equation (1):

$$\mathbf{P = a \times V \times l / 2S} \qquad \mathbf{(1)}$$

Where: **a** is the slope, **V**: volume of the transport cell, **l**: thickness of the membrane and S: surface of the membrane.
We can determine the initial flux J_0 by the equation:

$$\mathbf{J_0 = P \times C_0 / l} \qquad \mathbf{(2)}$$

where **P**: is the permeability of the membrane, $\mathbf{C_0}$: the initial concentration of the substrate, **l** : the thickness of membrane.

To calculate the microscopic parameters: (apparent diffusion coefficient (D*) and association constant (K_{ass}), we have considered the following equilibrium:

$$\mathbf{T_{org} \quad + \quad S_{aq} \quad \Leftrightarrow \quad TS_{org}}$$

And we have used the law of mass action and the first Fick's law, to get following equation:

$$\mathbf{P = J_0 x\ l / C_0 = (D^*) \times ([T]_i \times K_{ass} / (1 + K_{ass} \times C_0))} \qquad \mathbf{(3)}$$

After linearization by Lineweaver-Burk method, the following equation is obtained:

$$\mathbf{1/J_0 = (l / D^*) \times [(1 / [T]_i \times K_{ass}) \times (1/C_0) + (1 / [T]_i)]} \qquad \mathbf{(4)}$$

The graphical representation of $1/J_0 = (1/C_0)$ must be a straight line. Then, we can use the slope (p) and the intercept (o, o) of this function to calculate the microscopic parameters D * and K_{ass} according to the equation (5):

$$\mathbf{K_{ass} = (oo) / (p) \quad et\ D^* = (l / OO) \times (1 / [T]_i)} \qquad \mathbf{(5)}$$

Where **l**: thickness of the membrane and $\mathbf{[T]_i}$ the initial concentration of the carrier.

4. Materials and methods:

4.1 Chemicals :

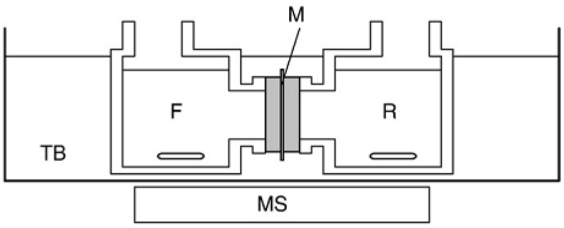
All reagents, solvents and chemicals used in this study are pure commercial products (Aldrich, Fluka and Alpha Aesar), the PVDF microporous support has a thickness of 100 µm, porosity of 69%, and with a pore diameter of 0.45 µm, the membrane diffusion surface is 20 cm^2). The Acidic solutions of Cd(II) ions are prepared from the hydrated salt of cadmium nitrate and the pH was adjusted using HCl and NaOH.

4.2. Preparation of the SLM:

The PVDF support must be impregnated for several hours by an organic solvent containing the carrier MC or TBP, the obtained membrane must be conditioned in distilled water before starting the extraction experiments, if the membrane is not conditioned, there is an induction time of several hours during which the extraction phenomenon is very slow. This operation is important in order to have a short experiment time and a better accuracy for the calculated parameters of this process[18].

4.3. Transport experiments of cadmium ions:

The transport cell contains two compartments glass, separated by the membrane M, the feed or source phase (S) and the receiving phase (R). The two compartments are placed in a thermostatic bath (TB) and the system is stirred by a multi-stirrer (MS) (**Figure 3**). Every 30 min, using a micropipette, we take a negligible sample volume compared to the total volume of each compartment, and then the samples are analyzed by atomic absorption spectrometry (AA-7000 Shimadzu) at a wavelength of 228.8 nm, (we have used a calibration curve in prior) (**figure 4**) :



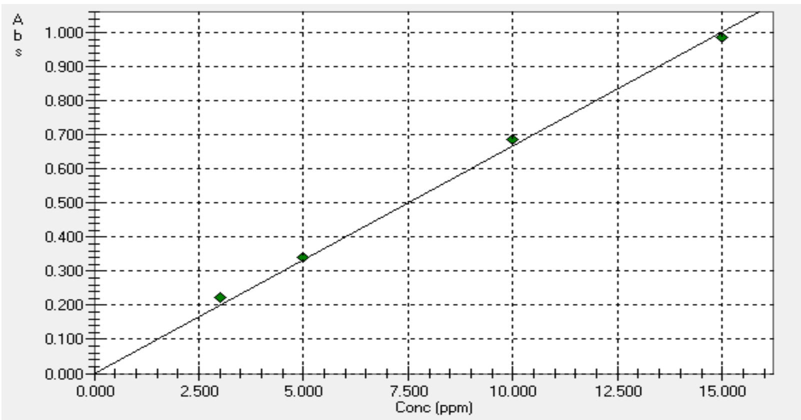
M: is the SLM. **F**: is the feed phase. **R**: is the receiving phase.
TB: is the thermostated bath. **MS**: is a multi-magnetic stirrer.

Figure 3: Transport cell

5. Results and discussion

5.1. The macroscopic parameters related to the facilitated transport of Cadmium ions :

The structure and nature of the carrier, have a very significant effect on selectivity and efficiency of the membrane, many studies were conducted to highlight this factor. Generally, the interactions are possible between charged metal ions and heteroatom of the carriers such as O, P...



Abs=0.06691Conc r=0.9996

Figure 4: Calibration curve

To study, this effect on the different macroscopic and microscopic parameters related to the facilitated transport of cadmium ions, we have prepared two supported liquid membranes using two different carriers (TBP and MC) by the same method. To realize the transport experiments, we have worked in the same conditions (T = 25 ° C, pH = 2, stirring speed...) with an initial concentration of cadmium varied from 0.0125 M to 0,1M. In a first time, we have represented the function *-ln* (C_0-2C_R) versus time for checking our model and, we have obtained the graphs represented in the Figure 5:

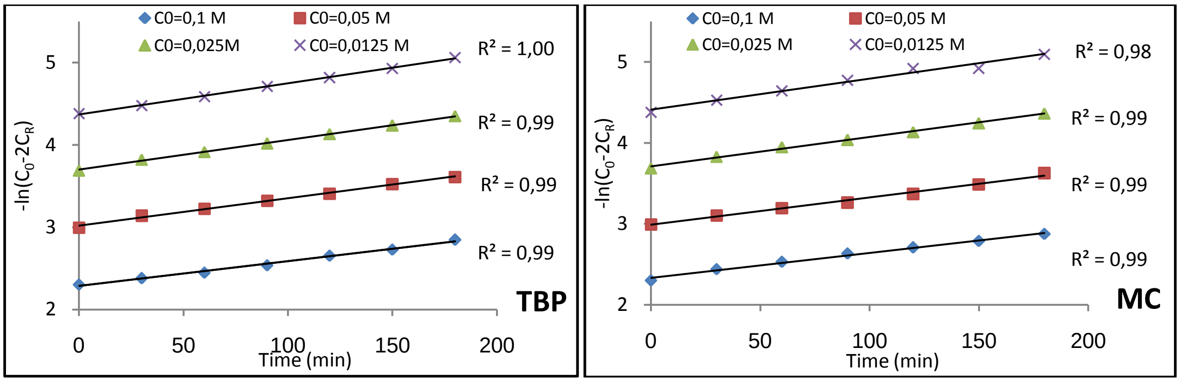


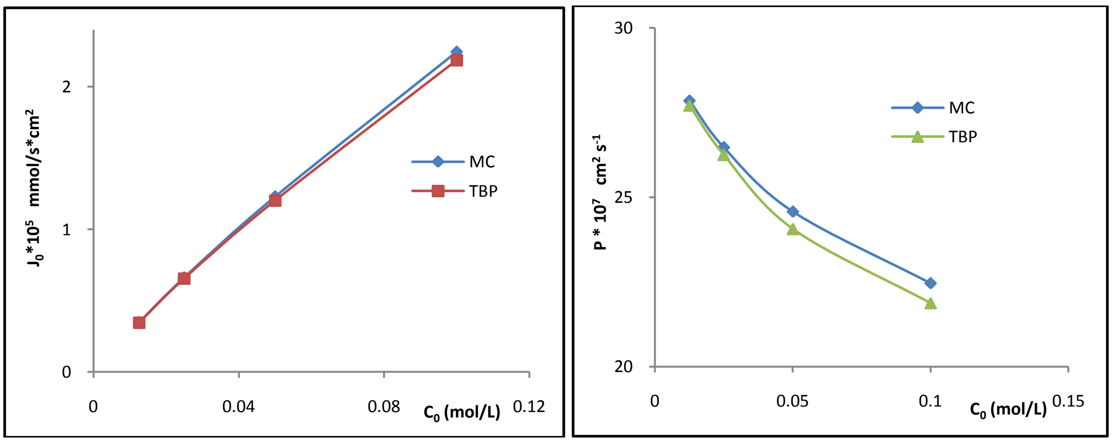
Figure 5: The evolution of the $-\ln(C_0-2C_R)$= f(time) related to the facilitated transport of cadmium ions

From the Figure 5, the representation of the term *-ln* (C_0-2C_R) versus time is a straight line for both membranes SLM-TBP and SLM-MC. This result verified our theoretical model and leads us to calculate the macroscopic parameters P and J_0 from the equations (1) and (2) of our model. The different values are grouped in the following table:

Table 1: Macroscopic parameters P and J_0 related to the facilitated transport of cadmium ions

Carrier	C_0 mol/l	P * 10^7 cm^2 s^{-1}	J_0*10^5 mmol/s*cm^2
MC	0.1	22.46	2.25
	0.05	24.57	1.23
	0.025	26.47	0.66
	0.0125	27.85	0.35
TBP	0.1	21.88	2.19
	0.05	24.06	1.20
	0.025	26.25	0.66
	0.0125	27.71	0.35

T=25°C, pH=2,[MC]=[TBP]=10^{-2}M in toulene ,PVDF as suuport



A **B**

Figure 6: Effect of the initial concentrations of cadmium ions on the macroscopic parameters:
A: initial flux, **B**: permeability

For the two types of supported liquid membranes (SLM-TBP and SLM-MC); the figure 6-A shows that the initial flux increases when the initial concentration of cadmium ions increases. In the opposite, the Figure 6-B shows that the permeability P of both membranes is reduced when the concentration of the cadmium ions increases for the two carriers used. These results have been found by other researchers for organic compounds (sugars) or for metal ions [19][20][21].

From table 1, we can remark that the values of permeability and initial flux for the membrane SLM-MC are relatively higher than the values of SLM-TBP, so MC is a new effective carrier to transport cadmium ions in these experimental conditions, the values of P and J_0 are comparable with the results found by Benjjar for Cr (III) and Cr (VI) [22][16] and they are more higher compared to sugars [20].

5.2. The microscopic parameters related to the facilitated transport of cadmium ions:

To explain these high values of P and J_0 for SLM-MC and SLM-TBP membranes, we have represented $1/J_0$ versus $1/C_0$ using the linearization method of Lineweaver-Burk for both membranes; this representation is a straight line (figure 7). We can conclude that the system follows a Michaelis-Menten mechanism type; moreover, we can also remark that our thermodynamic model is verified, and that the diffusion of the T-S complex is the rate-determining kinetic step for the reaction of the association between the carrier and the substrate. The microscopic parameters were calculated according to the equation (5) of our model, the values of these parameters are represented in the graph of the figure 8.

On the one hand, Figure 8 shows that the value of K_{ass} of the substrate-carrier complex of SLM-TBP membrane is relatively high compared to the value of K_{ass} of the substrate-carrier complex of SLM-MC, and that the Cd-TBP complex is relatively more stable than Cd-MC complex, but this latter has a value of D * more significant than the first complex, where the Cd-MC complex diffuses more than the Cd-TBP complex.

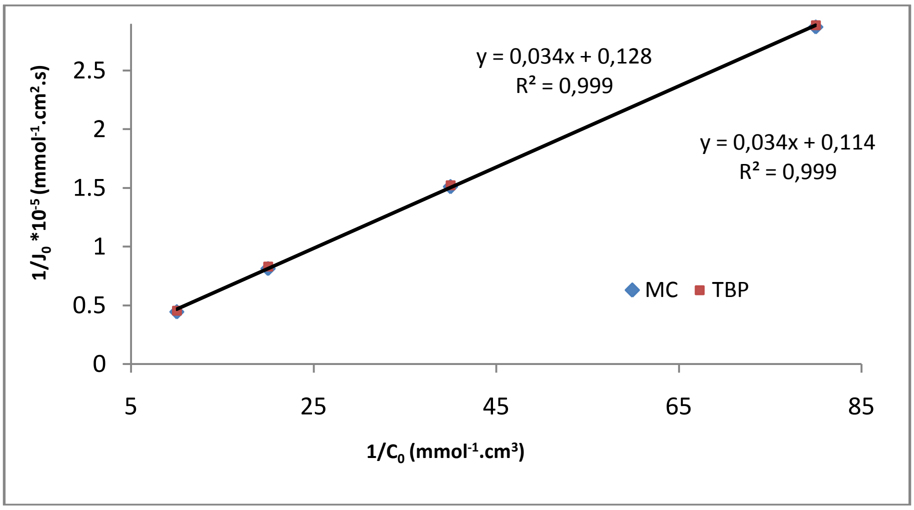


Figure 7: Lineweaver Burk representation of $1/J_0=f(1/C_0)$ for the facilitated transport of cadmium ions by SLM.

The Microscopic parameters K_{ass} and D* explain better the difference between the macroscopic parameters (P and J_0) of those two types of membranes, so an effective membrane (high permeability) corresponds to the formation of a less stable complex (small K_{ass} values) between the substrate and the carrier that can diffuse easily in the membrane phase (high D* values). So the efficiency of the membrane decreases when this complex is more stable and consequently its diffusion in the membrane phase became difficult.

On the other hand, researchers such as Smith et al [23] and Hor et al [21] have found that the apparent diffusion coefficient D * explains the mechanism of the transport, in our case, D* is in the range of 10^{-4}, therefore the moving mechanism of the substrate through the membrane phase is probably a jumping movement on the mobile sites because the carrier is movable in the organic phase.

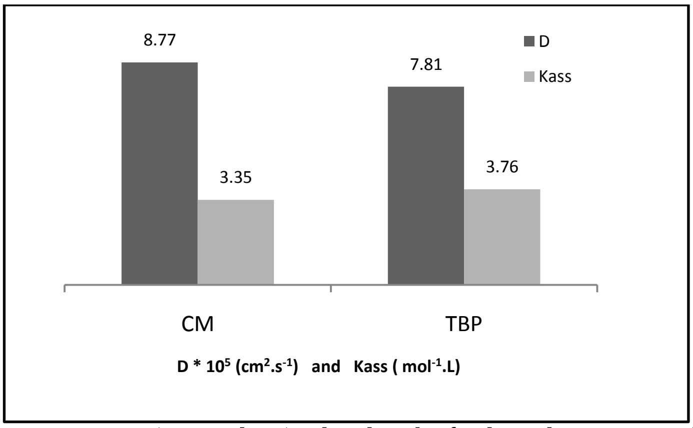


Figure 8: Microscopic parameters (K_{ass} and D*) related to the facilitated transport cadmium ions by SLM.

Conclusion

We have developed a new supported liquid membranes using the amphiphilic molecules (TBP and MC) as carriers, we have proposed and verified a theoretical model for calculating the macroscopic parameters (P and J_0) and the microscopic parameters (K_{ass} and D *) for the facilitated transport of cadmium ions from acidic mediums (pH = 2).
In this study, we have found that methyl Cholate is a new carrier which has the highest permeability, and efficiency. In perspective, further studies are needed to find the optimal parameters for the facilitated extraction of cadmium ions and to overcome the problem of instability of this type of membranes for the application on an industrial scale.

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