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Extraction and Transport of Methylene Blue Dye through a Plasticized Liquid Membrane containing Trioctyl Phosphine Oxide (TOPO) as the Carrier: Parametric Study

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Extraction and transport of Methylene Blue dye (MB) from synthetic waste water were investigated in this work, using a plasticized polymeric membrane (PPM) composed of the base polymer (PVC), the carrier trioctyl Phosphine Oxide (TOPO) and the plasticizer dioctyl phthalate (DOP). MB species extraction and transfer conditions from feed phase to the strip one through PVC/TOPO/DOP, were optimized (carrier mass, H_2SO_4 concentration in the strip solution...). The membrane was characterized by using SEM techniques.
Obtained results establish that PPM technique is suitable for discoloration of wastewater**.**

1. Introduction

Pollution from industrial wastewater has become a serious problem for many countries (Kümmerer, 2007). Some of the important pollutants are dyes which, once dissolved in water, will sometimes be difficult to treat, because they have a synthetic origin and a complex molecular structure which makes them more stable and difficult to be biodegraded (Forgacs et al., 2004) therefore they can constitute risk factors for human health and nuisance for environment (Rai et al., 2005).
Nowadays, there are more than 100,000 dyes belonging to various chemical classes with an annual production of $7x10^5$ tonnes (Yalkowski et al., 2010). Methylene blue, is the most common cationic (basic) dye used in dyeing cotton, wood and silk. Its inhalation can give rise to breathing difficulties and its ingestion by the mouth produces a burning sensation, causes nausea, vomiting, perspiration and profuse cold sweats (Djenouhat et al., 2018). It can cause eye burns that cause permanent injury to the eyes of humans and animals.
Different techniques have been applied for the treatment of industrial effluents containing dyes, such as biological reactions (Rai et al., 2005) and physicochemical processes, as adsorption (Boutemak et al., 2019) including the work of Rubio (2018) who used Cassava Bark residue (CBR) as adsorbent materials to remove methylene blue from aqueous solution and that of Kang (2020) who used a biomaterial prepared from Escherichia coli biomass, coagulation/flocculation (Bouyakoub et al., 2010), electrochemical oxidation (Dutta et al., 2001), nanofiltration, precipitation (Ben Mansour et al., 2011) and membrane separation processes such as liquid membranes (Hilmi et al., 2018) which have been used for the removal of organic and metallic pollutants from aqueous solutions, have shown great potential, especially in cases where solute concentrations are relatively low and other techniques cannot be applied effectively (Taoualit et al., 2016).
The extraction of chemical species in the liquid membrane system can be facilitated by a transporter (a carrier). In such transport, an ion exchange reagent or complexing agent (solvating agent) is incorporated into the membrane phase to transport the diffusing species from the feed phase through the membrane to the reception phase.
In this work, plasticized liquid membranes PPM is applied to study the extraction, recovery and transport of the Methylene Blue (MB) dye present in synthetic aqueous solutions. PPM is composed of i) polyvinyl chloride (PVC) as base polymer that provides mechanical strength, ii) trioctylphosphine oxide (TOPO) as carrier

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(solvating extractant, Figure1) which is responsible for the chemical species extraction and transport through PPM, iii) and dioctyl phthalate (DOP) as plasticizer which provides elasticity to the membrane (Benosmane et al., 2016) and increases the solubility of the extracted species in the membrane liquid phase (Nghiem et al., 2006).

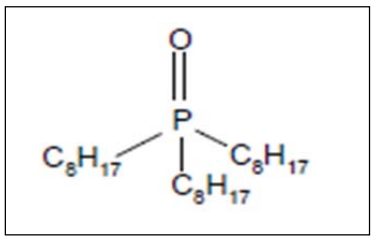

Figure 1: Structure of the organophosphorus carrier TOPO

2. Materials and Methods

2.1 Preparation of the plasticized liquid membrane PPM

PPM membranes were developed according to the protocol of Sugiura et al. (Sugiura, 1993; Sugiura et al., 1989) described by White et al. (Small, 1963).
In the present work, the used membrane was prepared from 1g of PVC dissolved in 30mL of tetrahydrofuran THF (99.9 % purchased from Carlo Erba Reagents), 0.1g of TOPO (97%, purchased from Fluka) and 1mL of DOP (99.5%, purchased from Yucheng Jinhe Industrial). The samples of obtained film were cut for duplication experiments. Aqueous solutions of MB were prepared by dissolving the corresponding reagent (dark blue crystals purchased from Merck Eurolab S.A) in bidistilled water. The chemical structure of MB or methylthioninium chloride is shown in Figure 2a.

2.2 Experimental device for Methylene Blue transport

The extraction and transport experiments were carried out in a two-compartment Teflon cell with a volume of 50 ml, respectively the source solution of $25\ \mathrm{ppm}$ of MB at pH solution of 2 and receiving phase containing a solution of H_2SO_4 0.05 M. The two compartments are separated by the membrane PVC/TOPO/DOP as shown in Figure 2b. Both the source and the receiving aqueous phases were stirred at 600 rpm. The active surface of PPM was S = 8.04 cm^2 and the thickness was e = 250-300 µm.

(a) **(b)**

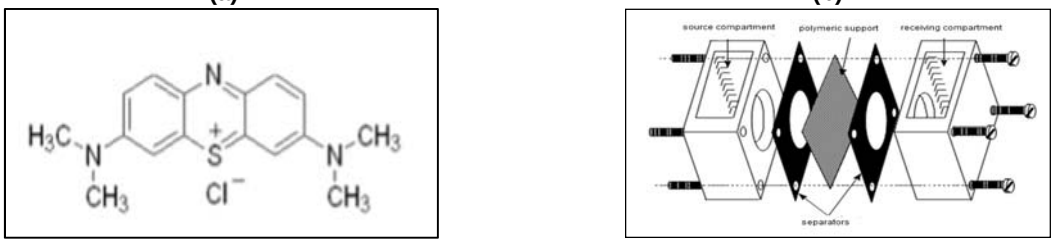

Figure 2 : (a) Chemical structure of MB : $C_{16}H_{18}ClN_3S$ (b) Experimental device of transport cell

Flux transport of MB species through PPM are determined by following the concentration variation of MB as function of time in both, source and receiving compartments, by removing successive samples of 0.5 mL in each compartment at defined time intervals, to be analyzed by spectrophotometry at 665 nm using a Shimadzu UV-1700 pharma spectrophotometer. The mass flux can be calculated using equation (1), (Arous et al., 2011), where J is the flux of the transported MB, V_R is the receiving phase volume, ΔC is the concentration variation of complexes species in the receiving phase, corresponding to time interval Δt (Yang et al., 2015):

$$J = \frac{V_R.\ \Delta C}{\Delta t\ .S} \tag{1}$$

Permeation coefficients P (Taoualit et al., 2016) were calculated by:

$$ln\frac{C_{ini}}{C_t} = P\frac{S.t}{V_A} \tag{2}$$

The flux can be calculated according to:

$$J = P.C_{ini} \quad (3)$$

The permeability is therefore determined by the slope of the curve:

$$ln\frac{C_{ini}}{C_t} = f\ (t) \quad (4)$$

Where C_t and C_{ini} are respectively the concentration of MB in the feed phase at given time and at the beginning of reaction, V_A is the feed solution volume and t is the process time. The extraction percentage of MB is calculated using the balance of the masses.

3. Results and Discussion

3.1 Effect of H_2SO_4 concentration in the strip solution

In order to avoid the accumulation of the MB-TOPO species in the membrane phase, reception solution must be used to facilitate the decomplexation and the release of MB species from the membrane phase at the second interface. In order to obtain the appropriate reception solution, two types of solutions were chosen; the sulphuric acid H_2SO_4 and water.

Obtained results show that H_2SO_4 solution is more effective than H_2O in improving the MB transport through PVC/TOPO/DOP which can be explained by the favoured decomplexions at the second interface (II) between membrane and aqueous phase (II) in the presence of H_2SO_4 (Figure 3a). Extraction and permeation of MB are higher, the extraction yields approach to 100 % (Figure 3b), those of diffusion do not exceed 1.03% (Figure 3c) and the diffusion coefficient about $7.82\ \mathrm{x}\ 10^{-4}\ \mathrm{cm}^2.\mathrm{s}^{-1}$. Therefore, sulphuric acid solution was chosen as the strip one for the rest of this work. Experimental results illustrated on Figure 3a show that the increase in the concentration of H_2SO_4 favours the increase of the MB permeability coefficient that becomes quasi-constant in the chosen range of H_2SO_4 concentration from 0 to 1.5M. A maximum permeability coefficient of $0.64\ \mathrm{m.s}^{-1}$ is observed at [H_2SO_4] = 0.05 M, which has therefore been chosen as optimal for the rest of this work.

3.2 Influence of the mass of the carrier

The mass range of the carrier TOPO is: 0.01, 0.02, 0.05, 0.1, 0.2, 0.3 and 0.5g. The coefficient of permeability increases until reaching a constant value slightly higher than $0.6\ \mathrm{m.s}^{-1}$ and a plateau is observed (Figure 3d). This result is probably explained by the maximization due to the saturation by the complexes formed and accumulated at the membrane interface, increasing the retention of the separation component on the entry side. Thus the coefficient of permeability is maintained at a constant value from 0.02 g of TOPO. Another reason is possible: it is a possible dimerization of TOPO at high concentrations in organic phase, which could make complexation of MB by TOPO at the first interface difficult (Kim et al., 2001). A mass of 0.02 g of TOPO is then maintained as the optimal value for the rest of the work.

3.3 Thermodynamic study of MB extraction-complexation by TOPO

Thermodynamic parameters of MB extraction and complexation by TOPO such as Gibbs free energy ΔG, enthalpy ΔH and entropy ΔS have been calculated using the following equations:

$$\Delta G\ =\ \Delta H\ -\ T\Delta S \quad (5)$$

$$\Delta G\ = -RT\ Ln\ K_{eq} \quad (6)$$

According to the following equilibrium (Taoualit et al., 2016):

$$MB +\ TOPO\ \leftrightarrow\ \overline{MBTOPO} \quad (7)$$

Taking into account the equation:

$$Ln\ K_{eq} = -\frac{\Delta H}{R.T} + \frac{\Delta S}{R} \quad (8)$$

ΔH and ΔS values have been determined from the slope and the original value of the line $Ln\ K_{eq} = f\ (\frac{1}{T})$ and the values of K_{eq} have been calculated from the equation 9. Table 1 groups the obtained results.

$$K_{eq} = \frac{\overline{[BMTOPO]}}{[BM]x[TOPO]} = \frac{D}{[TOPO]} \quad (9)$$

Table 1: Thermodynamic values of MB extraction by the PPM: PVC/TOPO/DOP

Temperature (K)	292.60	303.00	313.00
$\Delta H\ (kJ.mol^{-1})$	-15.750	-15.750	-15.750
$\Delta S\ (J.mol^{-1}.K^{-1})$	74.780	74.780	74.780
$\Delta G\ (kJ.mol^{-1})$	-21.864	-22.642	-23.390

Negative values of ΔH and ΔG and the positive values of ΔS indicate the exothermic and the spontaneous nature of MB complexation (extraction) by TOPO.

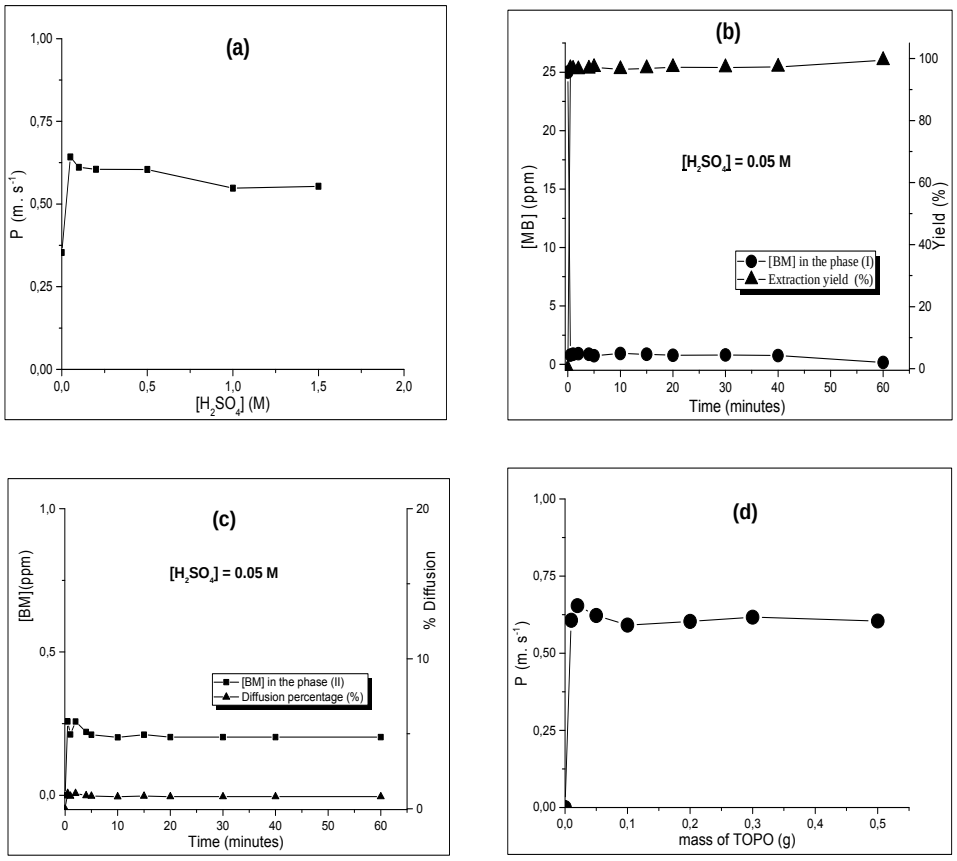

Figure 3: (a) Influence of H_2SO_4 concentration on MB permeability, (b)MB concentration in phase (I), (c) MB concentration in phase (II), (d) Influence of TOPO mass on MB permeability, T=20 °C, pH = 2, $[MB]_{init}$ = 25 ppm

4. Characterization of PPM by SEM technique

The images (a, b and c) of Figure 5, show clearly that the addition of the carrier TOPO confer to the membrane a porous appearance with many regular micro-pores or craters of different sizes that have been formed on the PPM surface due to the rapid evaporation of the THF solvent (Witt et al., 2018), comparing to the surface of PVC alone which is uniform and dense without porosity (Kebiche-Senhadji et al., 2008). The difference in pore size is related to the difference in the driving force for phase separation (Rajendran et al., 2008). Apparition of substances, probably, type of (MB TOPO) formed on the membrane surface filling an important number of pores, is shown on the SEM image of PPM loaded with MB (Figure 5d). There are some impurities due to the bad dissolution (distribution) of the extractant TOPO in the matrix, probably.

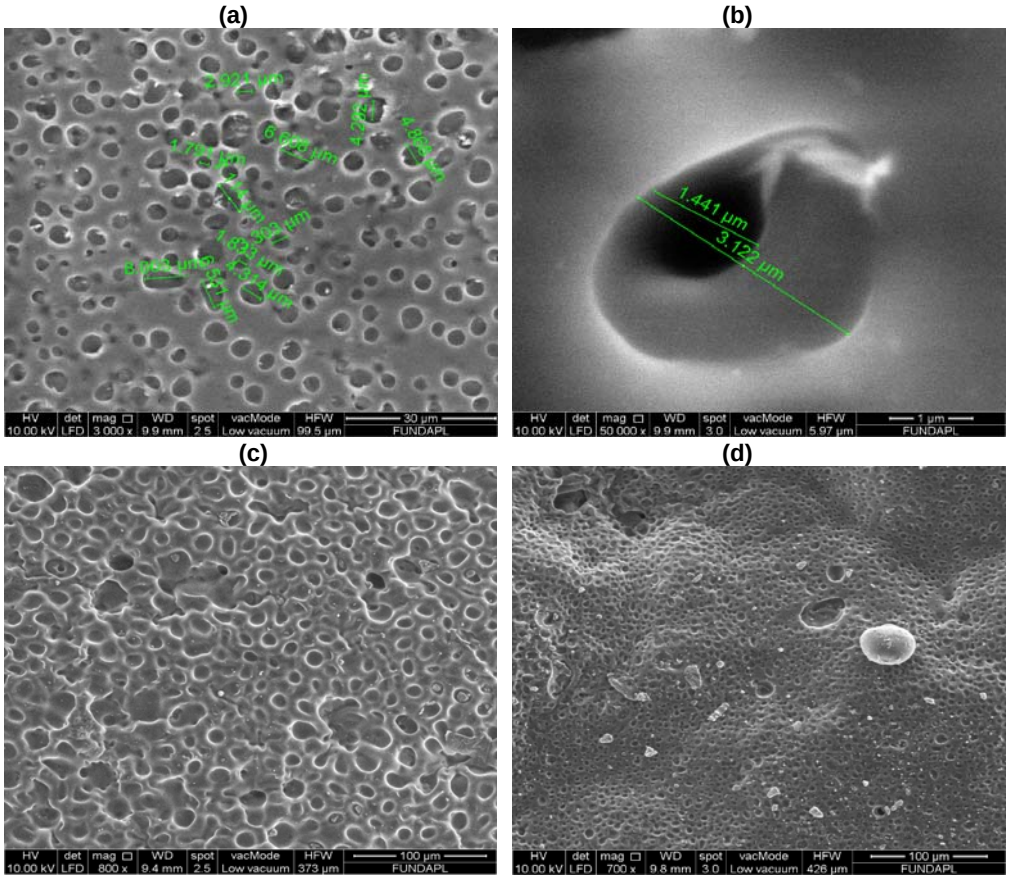

Figure 5: Membranes SEM images: (a) PVC/DOP, (b)micro-pore, (c)PVC/TOPO/DOP, (d)PVC/TOPO/DOP/ MB

5. Conclusions

Systematic parametric study of Methylene Blue transport from an aqueous feed solution through a plasticized liquid membrane (PPM) to a receiving solution of H_2SO_4 was carried out in order to optimize the operating conditions, such as the quantity of the carrier (extractant), composition of the strip aqueous phase as well as its H_2SO_4 concentration. Permeability experiments indicate that almost 100 % of a synthetic solution of 25 ppm of MB can be efficiently complexed with a permeability coefficient of 0.60 $m.s^{-1}$ during few minutes using 0.02 g of TOPO and 0.05 M of H_2SO_4 in the strip solution. Against only about 1.03% of MB who crossed PPM to the second compartment. The extraction-complexation of MB by TOPO is exothermic and spontaneous in aqueous solution. The diffusion coefficient is $7.82 \text{ x } 10^{-4}\ \text{cm}^2.\text{s}^{-1}$. SEM images show that the addition of the carrier creates inside the membrane a certain type of paths which facilitates the transport of complexes by diffusion. PPM technique is suitable for discoloration of wastewater. It is to consider to test this type of membrane also to treat other types of wastewater such as those of surface treatment workshops, olive oil mills, leachates, for desalination, etc., in order to protect the environment and recover the considered species.

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