ORIENTED MEMBRANE PROCESSES FOR EXTRACTION OF METHYLENE BLUE AND BLUE P3R DYSES ACROSS POLYMER INCLUSION MEMBRANEs CONTAINING CHITIN AS NEW EXTRACTIVE AGENT

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Abstract: In the present work, according to the phase inversion technique, we have developed polymer inclusion membranes (PIMs) based on polymer supports polyvinylidene fluoride (PVDF) and polyvinyl pyrrolidone (PVP), with chitin as extractive agent (EA). These PIMs have been used to study the facilitated extraction and recovery of the Methylene Blue (MB) and Blue P3R dyes from simulated aqueous textile solutions. FT-IR spectra and SEM micrographs of these membranes were recorded to explore composition, structure and morphology of the elaborated PIMs. The adoption of the kinetic and thermodynamic models based on the Fick’s laws, and the saturation law of the EA by the substrate (dyes) were tested to explain the performance of each membrane and the mechanism of the studied process for the recovery of dyes from water. The overall data indicate that the used extractive agent is effective for this oriented process, and the adopted membranes can remove about 87% of dyes from wastewater, without applying any external pressure on the polluted aqueous medium.

Keywords: Textile industry, polymer inclusion membranes, Methylene Blue, Bleu P3R dye, facilitated extraction process.

1. Introduction

Dyes are widely used in various industries such as textile, paper, leather and plastic. Textile industries produce large amounts of liquid wastes that contain organic and inorganic compounds. At present, 100000 different types of dyes exist, with an annual production of 735 new species. Among them textile industries consume about 36000 ton/year, 10 to 20 percent of which remains in wastewater [1].

During the dyeing process it has been estimated that the losses of colorants to the environment can reach 10–50% [2,3]. In addition, the effects caused by other pollutants, it is noteworthy that some dyes are highly toxic and mutagenic, and also decrease light penetration and photosynthetic activity, causing oxygen deficiency and limiting downstream beneficial uses such as recreation, drinking water and irrigation [4,5].

To solve the problems related to textile effluents, several studies have focused on the origin of pollution (integrated approach) [6,7] and at the treatment of the final effluents (end-of-pipe approach) [8–10].
The Membrane separation was selected as an appropriate treatment tool, characterized by their ability to clarify, concentrate, and continuously separate, are potentially interesting for effluent treatment through recycling. In the last few years, the treatment of industrial waste effluents by membrane processes has gained more and more interest because of technical, economical, and political reasons. Technically, the basic technology of process engineering has been developed. Economically, the shortage of water and the increasing cost of auxiliary chemicals and energy have pushed this technology. Politically, the increasing interest of government and people to environmental problems has forced industries to observe severe environmentally safe procedures [11,12].

The goal of this work is to adopt polymer inclusion membrane type (PIM) for the extraction and recovery of Methylene Blue and Blue P3R dyes from simulated aqueous textile solutions. The PIM membrane based on polymers Polyvinylidene fluoride (PVDF) and polyvinylpyrrolidone (PVP), containing chitin as a new extractive agent was prepared by phase inversion method. Elaborated PIM has been characterized by two methods (Fourier transform infrared attenuated total reflection and SEM), to confirm the inclusion of the extractive agent (carrier) into polymeric support. Kinetic and thermodynamic models were developed, based on the formation of unstable entity ($T\text{S}$) by the low interactions of the substrate $S$ (dyes) with the immobilized extractive agent $T$ (chitin), necessary for the diffusion of the substrate molecules through the membrane phase. These models were used to determine the macroscopic and microscopic parameters, respectively: the permeability $P$ and the initial flux $J_0$ related to the performance of elaborated PIM membrane for the facilitated extraction process of the dyes. Then the association constants $K_{\text{ass}}$ related to the formed entities (Chitin-EA), and the apparent diffusion coefficients $D^*$ related to the diffusion of the substrate $S$ through the membrane phase of the adopted PIM.

2. Materials and methods

2.1 Chemicals:
All chemicals, reagents, and solvents were pure commercial products (Aldrich, Fluka) of analytical grade. The dye solutions were prepared by dissolving dye (as supplied) in distilled water without adding any auxiliary compounds. The used polymeric support is “Poly(vinyllidene fluoride” supplied by Alfa Aesar.

2.2 Membrane preparation:
The membrane was prepared by phase inversion method, the mixture of PVDF/PVP was completely dissolved in Dimethylformamide as solvent and Chitin as extractive agent and as the water bath step of phase inversion at room temperature.

2.3 IR and SEM observations:
The Fourier transform infrared spectroscopy was used to characterize the elaborated PIM membrane. The prepared membrane was previously dried in vacuum desiccators at room temperature. Samples shaped square were cut from the PIM. The samples were fractured in liquid nitrogen and coated with gold–palladium and then observed by a scanning electron microscope (ZEISS EVO40EP).

2.4 Facilitated extraction experiments:
Extraction experiments were carried out in a cell that contains two compartments, the source phase and the receiving phase, the system is immersed in a thermostatic bath and agitation provided by a multi station magnetic stirring, to follow the extraction evolution of dyes substrate, we took samples from the receiving phase as a function of time, and we used THERMO SCIENTIFIC UV adsorption spectroscopy to analyze the samples [13,14].

3. Results and discussion

3.1 Characterization of the membrane:
We developed under the same conditions two PIMs membranes PVDF/PVP without and with Chitin as extractive agent, and we made the characterization of these prepared membranes:

3.1.1 Fourier transforms infrared-attenuated total reflection:
For the developed support and PIM membrane, the following Figure 1 illustrate the infrared spectra of polymeric support PVDF/PVP, before and after the addition of extractive agent. The two new peaks at 1653 cm\(^{-1}\) and at 3996 cm\(^{-1}\) in the spectrum of the PVDF+PVP+Chitin membrane are attributed respectively to the vibration of C =O carbonyl group of the ester function, and the vibration of O-H groups. Those new peaks indicate that the Chitin extractive agent is inserted correctly in the PVDF+PVP support.

![Figure 1. Fourier transform infrared-attenuated total reflection spectra of the PVDF/PVP and PVDF/PVP/Chitin membranes.](image)

3.1.3 Membrane morphology:
The SEM images in Figure 2 show that has asymmetric membranes, and there are homogeneous and contain cavities of different sizes, communicative through pores.

![Figure 2. Micrographs SEM of the surface of polymer support and PVDF/PVP/Chitin PIM membrane](image)

3.2 Facilitated extraction of Bleu P3R dye:
We have conducted the facilitated extraction process of dyes using the PIM membrane PVDF+PVP+Chitin at T = 298 K and pH = 4 for initial concentration \(C_0\) (0.00014 M to 0.0011 M) for Blue P3R dye, and \(C_0\) (0.00078 M to 0.00009 M) for Methylene Blue dye. Several studies conducted
by Hlaibi et al. [15], indicated that the macroscopic parameters, permeability $P$ and initial flux $J_0$ are calculated from the following equations (1) and (2):

$$P(t-t_L) = \left( \frac{\ell \times V}{2S} \right) \ln \left( \frac{C_0}{C_0 - 2C_r} \right)$$  
(1)

$$P = a \times V \times \ell / 2 \times S$$  
and

$$J_0 = P \times C_0 / \ell$$  
(2)

$a$: the slope experimental values of the straight lines $-\ln(C_0-2C_r) = f(t)$. $\ell$: the membrane thickness. $S$: the membrane active area in contact with the aqueous solutions. $V$: the receiving phase volume.

### 3.2.1 Macroscopic parameters $P$ and $J_0$:

Initially we studied the influence of the substrate (Blue P3R dye) initial concentration $C_0$ on the evolution of the parameters for this facilitated extraction process. Our experimental results for the facilitated extraction process of Blue P3R dye, verify the developed kinetic model. The study of the function $-\ln(C_0-2C_r) = f(t)$ for the different studied concentrations $C_0$, provides straight lines shown by the graph in the Figure 3, then we can calculate the macroscopic parameters $P$ and $J_0$, from the slopes of these straight line and the obtained values are grouped in table 1.

![Figure 3: Evolution of the kinetic function $-\ln(C_0-2C_r) = f(t)$ for the facilitated extraction of Blue P3R dye at different initial substrate concentrations.](image)

Table 1: Influence of initial concentration $C_0$ on the evolution of $P$ and $J_0$ parameters for the facilitated extraction process of the dyes

| Substrate            | $C_0$ (mol L$^{-1}$) | $P \times 10^6$ (cm$^2$ s$^{-1}$) | $J_0 \times 10^5$ (mmol cm$^{-2}$ s$^{-1}$) |
|----------------------|-----------------------|-----------------------------------|------------------------------------------|
| Blue P3R dye         | 0.00113               | 5.66                              | 0.022                                    |
|                      | 0.00056               | 6.06                              | 0.011                                    |
|                      | 0.00028               | 6.27                              | 0.006                                    |
|                      | 0.00014               | 6.52                              | 0.003                                    |
| Methylene Blue dye   | 0.00078               | 12.60                             | 0.685                                    |
|                      | 0.00039               | 13.83                             | 0.298                                    |
|                      | 0.00019               | 15.15                             | 0.163                                    |
|                      | 0.00009               | 16.20                             | 0.087                                    |

$[\text{Chitin}]_0 = 0.0007035 \text{ M, pH = 4, and T = 298 K}$

The results show a very good performance of the developed membrane for the oriented process of the facilitated extraction of studied dyes.

### 3.2.1 Microscopic parameters $D^*$ and $K_{\text{m}}$:
The same studies conducted by Hlaibi et al. [15–17], and the developed thermodynamic model, based on a saturation law of the extractive agent by the substrate, show that the microscopic parameters are determined from the expressions in the following relationships.

\[
\frac{1}{J_0} = \frac{1}{D^*} \left( \frac{1}{[T]_0} * K_{ass} * C_0 \right) + \frac{1}{[T]_0} \quad (3)
\]

\[
K_{ass} = \text{intercept (oo) } / \text{ slope (p)} \quad \text{and} \quad D^* = \left( \frac{1}{\text{oo}} \right) \left( \frac{1}{[T]_0} \right) \quad (4)
\]

The experimental results verify the thermodynamic model, and make it possible to obtain the line segments presented by the graph of the figure 4 for the presentation of function \( \frac{1}{J_0} = f\left(\frac{1}{C_0}\right) \). The intercepts and the slopes of these segments make it possible to calculate \( K_{ass} \) and \( D^* \) parameters according to the expressions in equation (4).

![Figure 4: Line weaver - Burk straights for the facilitated extraction phenomenon of Bleu P3R dye by the membranes: PVDF+PVP+Chitin.](image)

[Chitin]_0 = 0.0007035 M, pH = 4, and T = 298 K

**Table 2:** Evolution of the parameters \( K_{ass} \) and \( D^* \) according to the nature of the used substrate

| Substrate         | \( D \times 10^5 \) (cm\(^2\) s\(^{-1}\)) | \( K_{ass} \) (L. mol\(^{-1}\)) |
|-------------------|------------------------------------------|-------------------------------|
| Blue P3R dye      | 4.15                                     | 242.42                        |
| Methylene Blue dye| 22.49                                    | 7.74                          |

[Chitin]_0 = 0.0007035 M, pH = 4, and T = 298 K

All obtained results in Table 2 show an inverse evolution of these parameters with low values of the association constant \( K_{ass} \), which suggests a *jumping mechanism on fixed-sites* for the facilitated diffusion process of the studied dyes through this PIM membrane type.

### 4. Conclusions

In this work, we prepared by phase inversion method new PIM membrane based on PVDF+PVP as supports and Chitin as extractive agent. We characterized the obtained membrane by SEM and IR, and we found that insertion of the extractive agent Chitin in the membrane phase of the PIM allows the passage of dyes. On the other hand, we have verified our models and we were able to calculate all parameters related to facilitated extraction process of dyes through the elaborated PIM membrane.

Finally, we have elucidated a mechanism by successive jumps on fixed sites for the studied process through this PIM membrane type, and we can conclude that the elaborated membrane is efficient for a
possible application relating to the extraction and the recovery of the studied dyes from the waters waste.

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