Oriented membranes processes for facilitated extraction and recovery of some industrial dyes across polymer inclusion membranes containing Chitin as new extractive agent

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Abstract. In this study, we developed a polymer inclusion membrane (PIM) using the phase inversion technique, based on polymer supports polyvinylidene fluoride (PVDF) and polyvinylpyrrolidone (PVP), with chitin as extractive agent (EA). This PIM was used to study facilitated extraction and recovery processes of Astrazon Red FBL 200%, Blue P3R, Direct Turquoise FBL 400% and BEMACID Yellow N-TF dyes from simulated aqueous textile solutions. To explore the composition, structure and morphology of the developed PIM, both FTIR and SEM techniques were used. To explain the performance of the PIM and describe the mechanism of the process studied for the recovery of dyes from simulated wastewater, kinetic and thermodynamic models were also adopted, which are based on Fick's laws and the saturation law of EA by the substrate (dyes). The overall data indicate that the used EA is effective for these orriented processes, and the facilitated extraction of dyes is not depending on the pore size but on structures and interactions between the molecules of the EA and the dye.

1. Introduction
To solve the problems related to textile effluents, several studies have investigated the origin of pollution (integrated approach) [1-7] and at the treatment of the final effluents (end-of-pipe approach) [8–10].

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].

In the current study, we have elaborated polymer inclusion membranes (PIM) based on polymer supports polyvinylidene fluoride (PVDF) and polyvinyl pyrrolidone (PVP), according to the phase inversion technique, with chitin as extractive agent (EA). These PIM have been used to study facilitated extraction and recovery processes of Astrazon Red FBL 200%, Blue P3R, Direct Turquoise FBL 400% and BEMACID Yellow N-TF dyes from simulated aqueous textile solutions. To explore the composition, structure and morphology of the developed PIM, both FTIR and SEM techniques were used. Kinetic and thermodynamic models were applied [13–18], based on the formation of unstable
entity (TS) by the low interactions of the substrate S (dyes) with the immobilized EA (chitin), necessary for the diffusion of the substrate molecules through the membrane phase. These models were used to determine the macroscopic parameters, respectively: initial flux $J_0$ and permeability $P$ in relation to the performance of the PIM membrane developed for the facilitated extraction process of the dye. Next, we calculated the microscopic parameters, namely the Kass association constants related to the formed entities (S-EA), and the apparent diffusion coefficients $D^*$ relating to the diffusion of the substrate S through the membrane phase of the adopted PIM.

2. Materials and methods
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.

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:
The Figure 1 shows the infrared spectra of the PVDF/PVP polymer substrate, before/after the addition of EA, the appearance of 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 membranes, PVDF support and PIM-Chitin.](image)

The SEM image in figure 2 show an asymmetric membranes, and there are homogeneous and contain cavities of different sizes, communicative through pores.
3.2 Macroscopic and microscopic parameters:
To optimize dyes extraction conditions, various factors affecting the facilitated extraction of the dyes from wastewater, such as the polymer support, the nature and the concentration of the extractive agent (AE), the initial concentration of the substrate, the pH and the temperature of the aqueous phase. All macroscopic \( P \) and \( J_0 \) and microscopic \( K_{ass} \) and \( D^* \) parameters are calculated with the thermodynamic model developed by our laboratory [13-18].

![Figure 2. SEM image: PVDF/PVP-Chitin surface.](image)

![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)

\[\text{[Chitin]}_0 = 0.0007035 \text{ M, pH = 4, and T = 298 K}\]
Table 1. Effect of initial concentration $C_0$ on the evolution of $P$ and $J_0$ parameters for the facilitated extraction process of 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  | 0.00113              | 5.66                             | 0.022                            |
| Direct Turquoise FBL 400% | 0.00132              | 0.26                             | 0.0073                           |
| BEMACID Yellow N-TF     | 0.00132              | 0.103                            | 0.0029                           |
| Astrazon Red FBL 200%, pH = 4, and T = 298 K, PIM=PVDF/PVP+Chitin | 0.0025              | 1.09                             | 0.0028                           |

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

4. Conclusion
In this work, we prepared by phase inversion method a 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 textile effluents.

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