

## Research Paper

## Oriented Processes for Extraction and Recovery of Blue P3R Dye across Hybrid Polymer Membranes: Parameters and Mechanism

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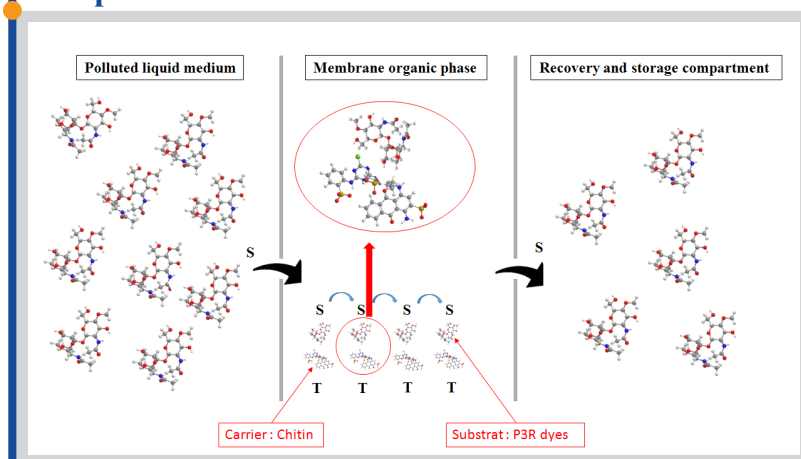
Facilitated extraction

Oriented processes

## Highlights

- The extraction and recovery of dyes across new affinity polymer membranes.
- Chitin and Chitosan, effective extractive agents for the facilitated extraction and recovery of reactive blue P3R dye.
- Determination of parameters: macroscopic ( $P$  and  $J_0$ ) and microscopic ( $K_{ass}$  and  $D^*$ ).
- Mechanisms by successive jumps on fixed sites.

## Graphical abstract



## Abstract

In the present work, two asymmetric polymer membranes based on polyvinylidene fluoride (PVDF) and polyvinylpyrrolidone (PVP) with chitin and chitosan (as extractive agents) were synthesized through the phase inversion technique. The mechanisms of oriented process for the facilitated extraction of blue P3R dye across the as-prepared membranes were elucidated through different experiments. Further, kinetic and thermodynamic models based on Fick's first law were used to determine the macroscopic (permeability ( $P$ ) and initial flux ( $J_0$ )) and the microscopic (association constant ( $K_{ass}$ ) and apparent diffusion coefficient ( $D^*$ )) parameters of the membranes. Finally, the values of different activation parameters (energy ( $E_a$ ), enthalpy ( $\Delta H^\ddagger$ ), and entropy ( $\Delta S^\ddagger$ )) were determined using theoretical models, and the analytical results revealed a kinetic control through the PVDF/PVP-chitin membrane and an energetic control through its PVDF/PVP-chitosan counterpart.

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## 1. Introduction

Textile manufacturing processes consume large volumes of water mainly in dyeing and finishing operations. Textile wastewater is considered one of the most toxic mediums among all industrial effluents [1–3]. Water is used as the main medium to remove impurities and also to apply dyes and chemical compounds during dry- and wet-processing step [2,4]. The commonly observed pollutants in textile effluents include suspended solids, recalcitrant organic colored compounds, surfactants, chlorinated compounds, toxic metals, and salts [3].

In addition, due to the presence of aromatic groups in their chemical

structures, textile dyes reduce the penetration of light and cause oxygen deficiency [5–9].

In recent years, liquid membranes, such as bulk liquid membranes [10,11], emulsion liquid membranes [12], and supported liquid membranes [13,14], have attracted considerable attention due to their applications in separation and purification of colored effluents [15]. However, polymer inclusion membranes (PIMs) are found to be more stable and efficient as compared to liquid membranes. Aitali et al. [15] synthesized a PIM with di-(ethyl hexyl) phosphoric acid (D2EHPA) as the carrier to remove methylene

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blue dye from aqueous solutions and achieved an extraction efficiency of more than 93% at pH = 6.0. Ling and Suah [16] prepared a poly-(vinyl) chloride (PVC)-based PIM with bis-(2-ethylhexyl) phosphate (B2EHP) as the carrier in order to extract malachite green (MG) from wastewater solutions and obtained an average extraction efficiency of >98% for MG concentrations of 20–80 mg L<sup>-1</sup>. Mahmoudian et al. [17] mixed the as-prepared PIM with hydrolyzed polymethylmethacrylate (PMMAhyd) grafted graphene oxide (GO-PMMAhyd) to improve its extraction performance of salts, dyes and heavy metal ions.

In the current research, two PIMs based on polyvinylidene fluoride (PVDF) and polyvinylpyrrolidone (PVP) with chitin and chitosan (as extractive agents) were synthesized through the phase inversion technique. The as-prepared membranes were characterized by both Fourier-transform infrared-attenuated total reflection (FTIR-ATR) and scanning electron microscopy (SEM) to confirm the grafting of extractive agents on the polymeric support. Kinetic and thermodynamic models based on the interactions between the substrate (S; blue P3R dye) and extractive agents (T; chitin or chitosan) were developed to determine the macroscopic (permeability (*P*) and initial flux (*J*<sub>0</sub>)) and the microscopic (association constant (*K*<sub>ass</sub>) and apparent diffusion coefficient (*D*<sup>\*</sup>)) parameters of the membranes.

## 2. Theoretical models

In the present research, kinetic and thermodynamic models were adopted to determine different macroscopic, microscopic, and activation parameters of the studied processes. Macroscopic parameters, permeability (*P*) and initial flux (*J*<sub>0</sub>), were calculated by Eqs. (1) and (2) [18–22].

$$P(t - tL) = (\ell^*V/2*S) \ln(C_0/C_0 - 2C_T) \quad (1)$$

$$P = a*V*\ell/2*S \text{ and } J_0 = P*C_0/\ell \quad (2)$$

where *a* represents the slope of the straight line  $-\ln(C_0 - 2C_T) = f(t)$ ,  $\ell$  is membrane thickness, *S* is the membrane active area in contact with aqueous solution, and *V* denotes receiving phase volume.

Similarly, microscopic parameters, association constant (*K*<sub>ass</sub>), and apparent diffusion coefficient (*D*<sup>\*</sup>), were determined by Eqs. (3) and (4).

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

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

where *p* and *oo*, respectively, are the slope and the intercept values of the straight line  $1/J_0 = f(1/C_0)$ ,  $[T]_0$  is the concentration of extractive agent in the membrane phase.

Previous studies [23–25] on the facilitated extraction process of organic compounds across membranes indicate that initial flow (*J*<sub>0</sub>) is related to temperature according to the Arrhenius law.

$$J_0(T) = A_j e^{(E_a/RT)} \quad (5)$$

where *R* is the perfect gas constant, *A<sub>j</sub>* is the pre-exponential factor, and *E<sub>a</sub>* represents activation energy. These parameters are related to the transition state of the formed entity (ST) or to dissociation reactions occurring during the migration of a substrate (S) through the membrane.

Now, after linearization,

$$\ln J_0 = ((-E_a/R)*1/T) + \ln A_j \quad (6)$$

Therefore, the values of *E<sub>a</sub>* and *A<sub>j</sub>* were calculated from the slope and the intercept of the linear function  $\ln(J_0) = f(1/T)$ , respectively.

Further, the activation parameters, enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ), were determined according to the activated complex theory (Eyring theory).

$$\Delta H^\ddagger = E_a - 2500 \quad (7)$$

$$\Delta S^\ddagger = R (\ln A_j - 30.46) \quad (8)$$

## 3. Material and methods

### 3.1. Materials

All analytical-grade chemicals, reagents, and solvents were procured from Aldrich, Fluka. The reactive blue P3R dye solution was prepared by

dissolving the as-supplied dye in distilled water at a concentration of 0.0011 M without adding any auxiliary compounds. Polyvinylidene fluoride (purchased from Alfa Aesar) was used as the polymeric support.

### 3.2. Experimental section

In the present research, the facilitated transport and extraction of the reactive blue P3R dye were carried out in a cell with two glass compartments (Figure 1) [22,25]. The membrane was inserted between the compartments using two Teflon rings, and the effective membrane area for diffusion was 14.5 cm<sup>2</sup>. The receiving and the feed compartments were, respectively, filled with pure water (130 cm<sup>3</sup>) and an aqueous solution (130 cm<sup>3</sup>) of the dye. Further, aqueous solutions of NaOH and H<sub>2</sub>SO<sub>4</sub> were used to set the pH values in the compartments. The cell was immersed into a thermostatic bath (298 K), and the solutions in both compartments were stirred with magnetic bars using a Variomag apparatus. The aforesaid procedure was repeated four times with different dye concentrations (0.0011 M to 0.00014 M). An aliquot of 1.0 cm<sup>3</sup> was withdrawn from the receiving phase after a known interval. The concentrations of the substrate (reactive blue P3R dye) against time were determined by ultraviolet–visible spectroscopy. The oriented process was terminated after a dynamic equilibrium (*C<sub>s</sub>* = *C<sub>r</sub>* = *C<sub>0</sub>*/2) was established between the compartments [20].

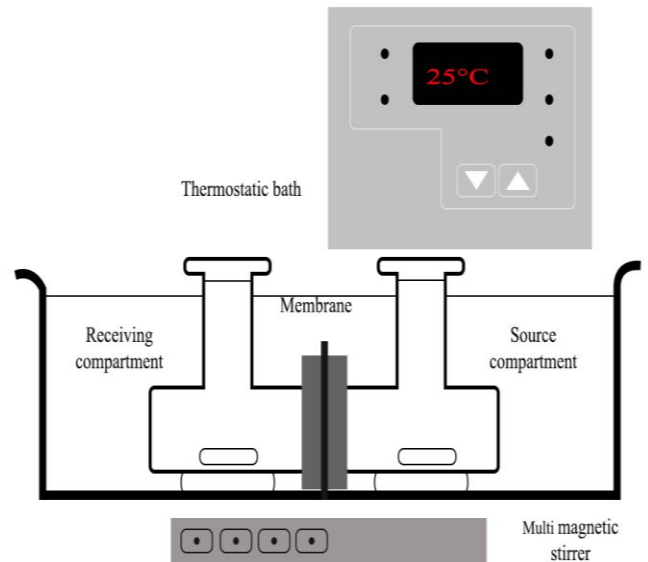


Fig. 1. The experimental device for the facilitated extraction process.

#### 2.2.1. Preparation of affinity polymer membranes

Affinity polymer membranes were prepared by the phase inversion technique. A mixture of polyvinylidene fluoride (PVDF) and polyvinylpyrrolidone (PVP) was first completely dissolved in dimethylformamide (25 cm<sup>3</sup>) for 24 h at room temperature, and then chitin or chitosan (as an extractive agent) was added to the prepared solution of PVDF.

Further, the obtained solution of polymer-extractive agents was spread on a glass plate using a glass rod at room temperature. The as-prepared casting (liquid-film) was allowed to evaporate in the air for 20 sec prior to the immersion in a water bath (20 °C).

After a few seconds of immersion, a white solid film was stripped on the glass, and the coagulated membranes were washed with water and then stored in Milli-Q water for 48 h [26,27]. The thicknesses of the as-prepared membranes were determined by an electronic palmer (Mitutoyo Corporation Takatsu-ku, Kawasaki-shi, Kanagawa Japan; ±0.001 mm accuracy).

#### 3.2.2. Characterization of the prepared membranes

All membranes, before and after adsorption, were lyophilized to remove water from their pores. The lyophilization process was carried out in

Labcomco equipment (Freeze dry system/Freezone 4.5, Brazil) under a vacuum of  $35 \times 10^{-3}$  bar and at a temperature of  $-65$  °C.

The morphologies of the lyophilized membranes were evaluated by a scanning electron microscope (SEM; SEMJEOL NeoScope JCM-5000; JEOL Ltd. Akishima, Tokyo, Japan).

FTIR spectra were analyzed in the ATR mode by a Nicolet 6700 Fourier-transform infrared spectrometer (Thermo Scientific, Madison, USA) equipped with a smart omni-sampler. Spectral scanning was performed in the range of  $4000$   $\text{cm}^{-1}$  to  $675$   $\text{cm}^{-1}$  at a resolution of  $4$   $\text{cm}^{-1}$ .

## 4. Results and discussion

### 4.1. Characterization of the developed membranes by FTIR

Figure 2 illustrates the FTIR spectra of the PVDF/PVP polymeric support before and after the incorporation of extractive agents.

The characteristic peaks (C-F) of PVDF were noticed at  $1071$ – $1277$   $\text{cm}^{-1}$ . The PVDF/PVP-Chitin membrane yielded two new peaks at  $1653$   $\text{cm}^{-1}$  (associated with the vibration of C=O carbonyl group) and at  $3396$   $\text{cm}^{-1}$  (associated with the vibration of O-H group), whereas the PVDF/PVP-Chitosan membrane manifested two new peaks at  $1655$   $\text{cm}^{-1}$  due to the vibration of N-H group and at  $3385$   $\text{cm}^{-1}$  (associated with the vibration of O-H group). Hence, these new peaks indicated that chitin and chitosan were well grafted to PVDF/PVP.

### 4.2. Characterization of the prepared membranes by SEM

Two mechanisms, i.e., liquid-liquid demixing and crystallization, governed the formation of PVDF/PVP membranes during phase inversion. Coagulation medium is considered one of the key elements to determine the effects of liquid-liquid demixing and crystallization on PVDF/PVP membranes produced by immersion precipitation [28].

The wet inversion phase separation process (using water as the non-solvent) was carried out to prepare the grafted membranes, and the surface morphologies of the PIMs are displayed in Figure 3. Figure 3(a) indicates that

the skin layer surfaces of PVDF/PVP membranes were smooth, dense, and porous. Moreover, the incorporation of chitin and chitosan yielded smaller pores beneath the skin layers of the prepared PIMs (Figures 3 (b) and (c)). The cross-sectional views of the membranes (Figures 3 (e) and (f)) reveal that the synthesized PIMs consisted of finger-like macrovoids. The thicknesses of PVDF/PVP-chitin and PVDF/PVP-chitosan membranes were measured as  $290$   $\mu\text{m}$  and  $142$   $\mu\text{m}$ , respectively.

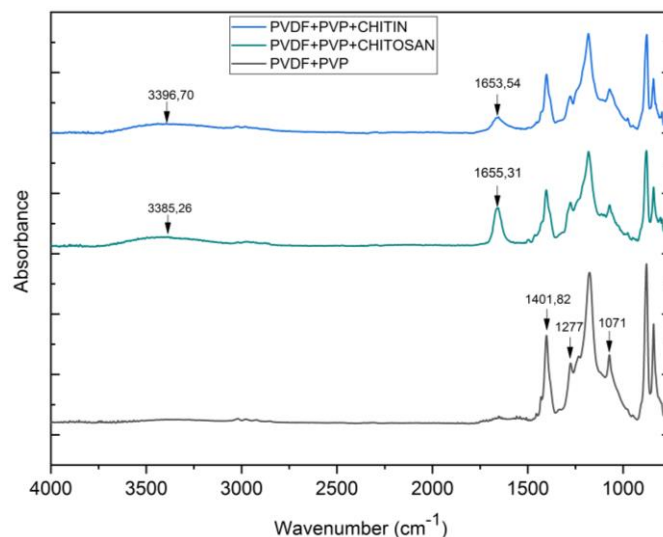


Fig. 2. Fourier transform infrared-attenuated total reflection spectra of the membranes: PVDF/PVP support, PVDF/PVP-Chitin and PVDF/PVP-Chitosan.

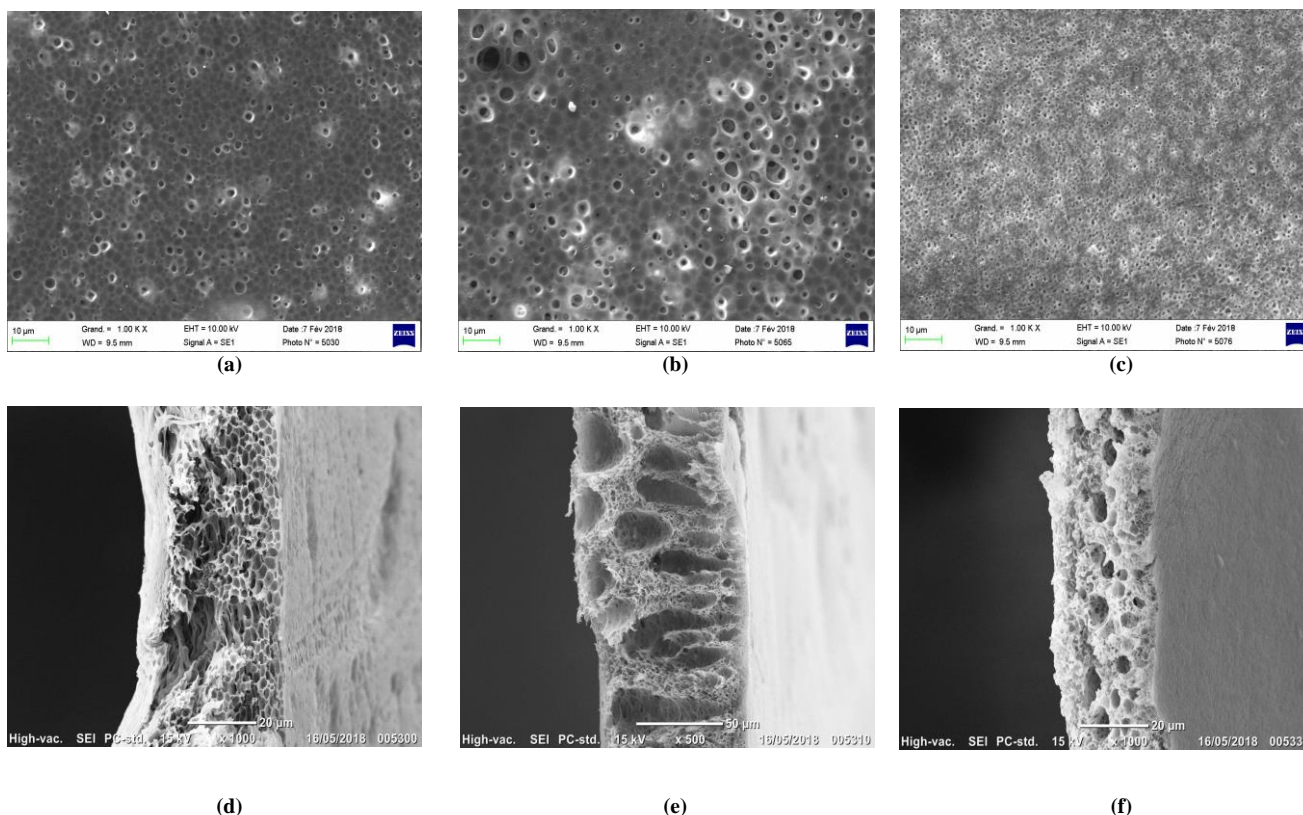
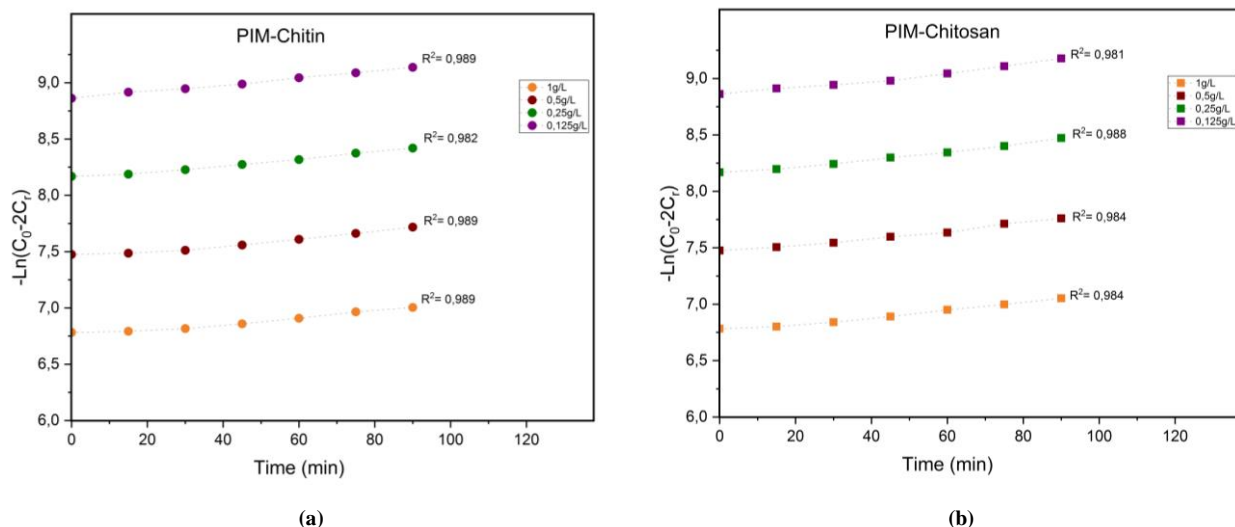


Fig. 3. SEM images: (a) PVDF/PVP surface, (b) PVDF/PVP-Chitin surface, (c) PVDF/PVP-Chitosan surface, (d) PVDF/PVP cross-section, (e) PVDF/PVP-Chitin cross-section, (f) PVDF/PVP-Chitosan cross-section.



**Figure 4.** Evolution of the kinetic function  $-\ln(C_0-2C_t) = f(t)$  for the facilitated extraction of Blue P3R dye at different initial substrate concentrations: (a) PVDF/PVP-Chitin and (b) PVDF/PVP-Chitosan;  $[\text{Chitin}]_0 = 0.0007035 \text{ M}$ ,  $[\text{Chitosan}]_0 = 0.000887 \text{ M}$ ,  $\text{pH} = 4$ , and  $T = 298 \text{ K}$ .

### 4.3. Oriented process for the facilitated extraction of blue P3R dye

#### 4.3.1. Influences of extractive agents and initial substrate concentration

The effects of chitin and chitosan on facilitated extraction of blue P3R dye across PIMs based on PVDF/PVP (percentage of extractive agents was 5% (w/w)) was analyzed in the current section. The influences of substrate concentrations ( $C_0 = 0.125\sim 1 \text{ g/L}$ ) under the operating conditions of  $\text{pH} = 4$  and  $T = 298 \text{ K}$  were also considered.

Figure 4 depicts the kinetic term  $-\ln(C_0-2C_t)$  as a function of time, and straight lines were obtained for both chitin and chitosan. The obtained values of  $P$  and  $J_0$  for both PVDF/PVP-chitin and PVDF/PVP-chitosan membranes are presented in Table 1. It is evident from the results in Table 1 that as compared to the initial substrate concentration, extractive agents had profound effects on facilitated extraction of blue dye P3R. It was found that the PIM-chitin membrane performed relatively better in comparison to its PIM-chitosan counterpart under the adopted conditions.

In order to elucidate the mechanism of facilitated extraction of P3R blue dye, the Lineweaver-Burk plots of the function  $1/J_0 = f(1/C_0)$  were studied (Figure 5). Straight lines with positive slopes confirm the validity of the proposed thermodynamic model, thus ascertaining the formation of a pseudo-complex with (1/1) composition due to the interactions between the substrate (blue P3R dye) and extractive agents.

**Table 1**

The influence of the nature of extractive agent and initial substrate concentration  $C_0$  on the evolution of microscopic parameters  $P$  and  $J_0$ .

Extractive agent	$C_0 = [\text{Blue P3R dye}]$ ( $\text{mol L}^{-1}$ )	$P \times 10^{-7}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	$J_0 \times 10^{-5}$ ( $\text{mmol cm}^2 \text{ s}^{-1}$ )
Chitin	0.00113	56.68	0.022
	0.00056	60.68	0.011
	0.00028	62.79	0.006
	0.00014	65.26	0.003
Chitosan	0.00113	30.10	0.024
	0.00056	31.60	0.012
	0.00028	32.04	0.006
	0.00014	34.67	0.003

$[\text{Chitin}]_0 = 0.0007035 \text{ M}$ ,  $[\text{Chitosan}]_0 = 0.000887 \text{ M}$ ,  $\text{pH} = 4$ , and  $T = 298 \text{ K}$

The slope and the intercept values of the obtained line segments were used to determine the microscopic parameters ( $K_{\text{ass}}$  and  $D^*$ ) of the membranes

(Table 2).

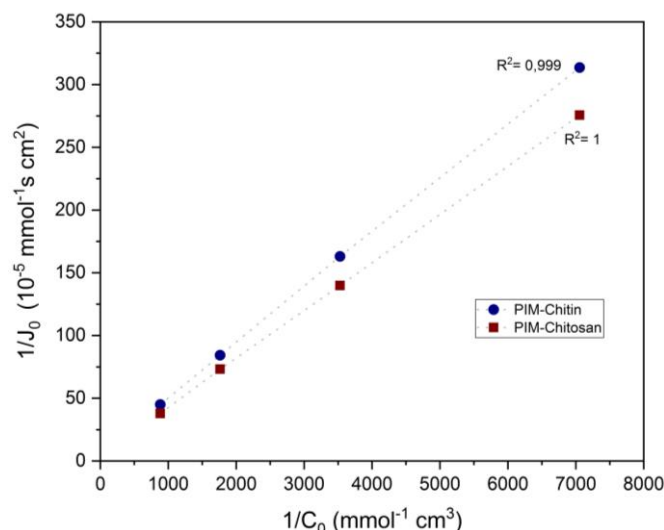
The results, shown in Table 2, also confirm that the PIM-chitin membrane was more efficient than its PIM-chitosan counterpart for the facilitated extraction of blue P3R dye. It was found that chitin possessed several interaction sites to form more stable pseudo-entities (as compared to its chitosan counterpart) with the extracted molecules of the dye. Hence, the diffusion of the substrate across the membrane was more favorable in the presence of chitin.

**Table 2**

Evolution of  $K_{\text{ass}}$  and  $D^*$  parameters according to the nature of the used extractive agents.

Extractive agent	$D^* \times 10^{-5}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	$K_{\text{ass}}$ ( $\text{L. mol}^{-1}$ )
Chitin	5.35	177.07
Chitosan	3.53	117.81

$[\text{Chitin}]_0 = 0.0007035 \text{ M}$ ,  $[\text{Chitosan}]_0 = 0.000887 \text{ M}$ ,  $\text{pH} = 4$ , and  $T = 298 \text{ K}$



**Fig. 5.** Lineweaver-Burk plots for the facilitated extraction phenomenon of Blue P3R dye by the membranes: PVDF/PVP-Chitin and PVDF/PVP-Chitosan;  $[\text{Chitin}]_0 = 0.0007035 \text{ M}$ ,  $[\text{Chitosan}]_0 = 0.000887 \text{ M}$ ,  $\text{pH} = 4$ , and  $T = 298 \text{ K}$ .

#### 4.3.2. Influence of acidity of feed and receiving aqueous phases

In order to examine the effects of pH of feed and receiving phases on  $P$  and  $J_0$ , the facilitated extraction of blue P3R dye ( $C_0 = 0.125\text{--}1\text{ g/L}$ ) was carried out in acid solutions of pH 3, 4, and 5. It is noticeable that the kinetic model yielded straight lines for the function  $-\ln(C_0 - 2C_t) = f(t)$  for all three studied acidity levels. The slopes of the straight lines were used to determine the values of  $P$  and  $J_0$  (Table 3). It is discernible that in the PIM-Chitin membrane,  $P$  and  $J_0$  were inversely proportional to the acidity of the medium; hence, with the increasing pH values,  $P$  and  $J_0$  started to decrease. However, a weak influence of acidity factor on facilitated extraction of P3R dye across the PIM-chitosan membrane was observed.

In order to better understand the influences of acidity factor on facilitated extraction of P3R dye, microscopic parameters ( $K_{\text{ass}}$  and  $D^*$ ) were determined

by the Lineweaver-Burk plots of the function  $1/J_0 = f(1/C_0)$ . The obtained slopes and intercepts were used to calculate the values of  $K_{\text{ass}}$  and  $D^*$  (Table 4).

It is evident from the results in Table 4 that a better membrane performance was achieved at pH = 3.

#### 4.3.3. Evolution of different parameters as a function of temperature

Under the same experimental conditions, the facilitated extraction of blue P3R dye was conducted at pH = 4 and at different temperatures (298 K, 303 K, and 308 K). The kinetic model with the function  $-\ln(C_0 - 2C_t) = f(t)$  yielded straight lines in all cases. The calculated values of  $P$  and  $J_0$  for both PVDF/PVP-Chitin and PVDF/PVP-Chitosan are presented in Table 5.

**Table 3**

Influence of acidity factor on the evolution of  $P$  and  $J_0$  parameters related to the facilitated extraction process of Blue P3R dye.

Extractive agent	$C_0 = [\text{Blue P3R}]$ (mol L <sup>-1</sup> )	$P \times 10^{-7}$ (cm <sup>2</sup> s <sup>-1</sup> )			$J_0 \times 10^{-5}$ (mmol cm <sup>2</sup> s <sup>-1</sup> )		
		pH=3	pH=4	pH=5	pH=3	pH=4	pH=5
Chitin	0.00113	57.44	56.68	49.92	0.0224	0.0220	0.0195
	0.00056	62.88	60.68	58.62	0.0122	0.0118	0.0114
	0.00028	64.97	62.79	61.58	0.0063	0.0061	0.0060
	0.00014	66.99	65.26	63.74	0.0033	0.0032	0.0031
Chitosan	0.00113	33.09	30.10	29.17	0.0264	0.024	0.0232
	0.00056	34.25	31.60	29.65	0.0136	0.0126	0.0118
	0.00028	35.83	32.04	30.38	0.0071	0.0063	0.0060
	0.00014	36.35	34.67	30.97	0.0036	0.0034	0.0030

[Chitin]<sub>0</sub> = 0.0007035 M, [Chitosan]<sub>0</sub> = 0.000887 M, T = 298 K.

**Table 4**

The influence of acidity factor on the parameters  $K_{\text{ass}}$  and  $D^*$  for the facilitated extraction process of Blue P3R dye by the membranes: PVDF/PVP-Chitin and PVDF/PVP-Chitosan.

Extractive agent	$D^* \times 10^{-5}$ (cm <sup>2</sup> s <sup>-1</sup> )			$K_{\text{ass}}$ (L. mol <sup>-1</sup> )		
	pH=3	pH=4	pH=5	pH=3	pH=4	pH=5
Chitin	5.66	5.35	3.63	171.98	177.07	258.37
Chitosan	4.07	3.53	1.72	86.54	117.83	231.97

[Chitin]<sub>0</sub> = 0.0007035 M, [Chitosan]<sub>0</sub> = 0.000887 M, T = 298 K.

**Table 5**

The temperature factor influence on the evolution of  $P$  and  $J_0$  parameters for the facilitated extraction process of Blue P3R dye.

Extractive agents	$C_0 = [\text{Blue P3R}]$ (mol L <sup>-1</sup> )	$P \times 10^{-7}$ (cm <sup>2</sup> s <sup>-1</sup> )			$J_0 \times 10^{-5}$ (mmol cm <sup>2</sup> s <sup>-1</sup> )		
		298 K	303 K	308 K	298 K	303 K	308 K
Chitin	0.00113	56.68	57.64	61.71	0.0220	0.0225	0.0241
	0.00056	60.68	61.57	64.84	0.0118	0.0120	0.0126
	0.00028	62.79	63.83	65.50	0.0061	0.0062	0.0064
	0.00014	65.26	66.15	69.31	0.0032	0.0033	0.0034
Chitosan	0.00113	30.10	35.74	38.15	0.0240	0.0301	0.0304
	0.00056	31.60	36.23	38.86	0.0126	0.0144	0.0155
	0.00028	32.04	36.82	39.14	0.0063	0.0075	0.0078
	0.00014	34.67	38.73	40.35	0.0034	0.0038	0.0040

[Chitin]<sub>0</sub> = 0.0007035 M, [Chitosan]<sub>0</sub> = 0.000887 M, pH = 4.

The results in Table 5 indicate that temperature had moderate influences on macroscopic parameters ( $P$  and  $J_0$ ) related to the facilitated extraction of blue P3R dye. It was found that  $P$  and  $J_0$  were directly proportional to the variation in temperature, thus with the increasing aqueous solution temperatures, the values of these two parameters became larger.

In order to further explain the macroscopic results of the oriented process, the Lineweaver-Burk plots of the ( $1/J_0 = f(1/C_0)$ ) function were studied. The adopted thermodynamic model yielded straight lines for all three temperatures. The obtained slopes and intercepts of the straight lines were used to determine the values of  $K_{ass}$  and  $D^*$  (Table 6).

It was found that an increase in the temperature of the source and receiving aqueous phases resulted in the formation of unstable pseudo-entities "substrate-extractive agents" (decrease in  $K_{ass}$ ) with a better substrate diffusion through the organic membrane phase (increase in  $D^*$ ). Consequently, the improvements in macroscopic parameters ( $P$  and  $J_0$ ) yielded better membrane performances at higher temperatures.

It is clear that the movements of substrate molecules across PIMs were governed by reversible reactions (association/dissociation) of substrate molecules with each extractive agent. Therefore, the migration of blue P3R dye from the feed phase to the receiving phase cannot be a simple diffusion process, it occurs due to successive jumps of substrate molecules from a fixed site to another of the extractive agents [29–32].

**Table 6**

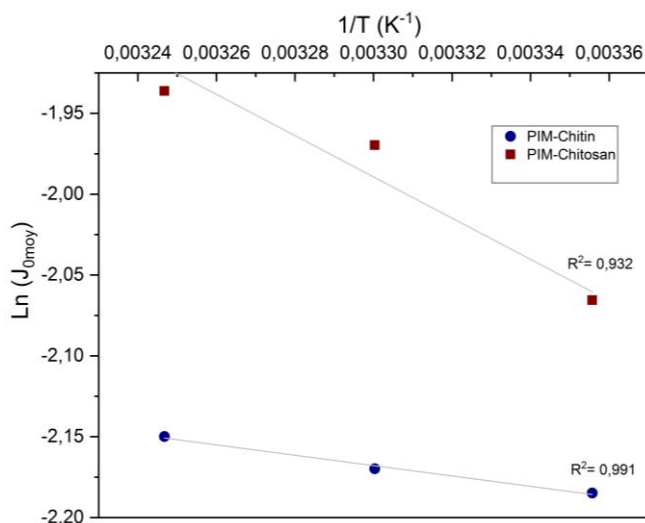
The influence of temperature factor on the evolution of  $K_{ass}$  and  $D^*$  parameters for the facilitated extraction process of Blue P3R dye across the elaborated PIM membranes.

Extractive agent	$D^* \times 10^{-5} \text{ (cm}^2 \text{ s}^{-1}\text{)}$			$K_{ass} \text{ (L. mol}^{-1}\text{)}$		
	298 K	303 K	308 K	298 K	303 K	308 K
Chitin	5.35	5.54	5.82	177.07	173.45	172.18
Chitosan	3.53	5.17	5.23	117.83	87.79	84.77

[Chitin] $_0 = 0.0007035 \text{ M}$ , [Chitosan] $_0 = 0.000887 \text{ M}$ , pH = 4.

In order to elucidate the mechanism of the oriented process for the facilitated extraction of P3R dye, reversible reactions (association/dissociation) between the substrate and extractive agents were studied by the kinetic model with the function  $\text{Ln}(J_0 \text{ moy}) = f(1/T)$  (Figure 6).

The obtained slope and intercept values were used to determine activation energy ( $E_a$ ), activation enthalpy ( $\Delta H^\ddagger$ ), and activation entropy ( $\Delta S^\ddagger$ ) (Table 7).



**Fig. 6.** Representation of the function  $\text{Ln}(J_0 \text{ moy}) = f(1/T)$  related to the facilitated extraction process of Blue P3R dye across the elaborated PIM membranes.

**Table 7**

Activation parameter values for the facilitated extraction process of Blue P3R dye by elaborated membranes: PVDF/PVP-Chitin and PVDF/PVP-Chitosan

Extractive agent	$E_a$ (kJ.mol $^{-1}$ )	$\Delta H^\ddagger$ (kJ.mol $^{-1}$ )	$\Delta S^\ddagger$ (J.K $^{-1}$ .mol $^{-1}$ )
Chitin	2.66	0.16	-262.47
Chitosan	9.89	7.39	-237.13

[Chitin] $_0 = 0.0007035 \text{ M}$ , [Chitosan] $_0 = 0.000887 \text{ M}$ , pH = 4.

It is noticeable that the facilitated extraction of blue P3R dye through PIMs membranes required a small amount of activation energy ( $E_a$  or  $\Delta H^\ddagger$ ), whereas the negative values of  $\Delta S^\ddagger$  indicate that transition states were well ordered in the association of dye-extractive agents. Further, transition states were also depended on the nature and the structures of substrate molecules and extractive agents. Hence, when the transition occurred early, reversible reactions (association/dissociation) became fast and ensured a better diffusion of substrate molecules through PIMs. The analysis of the facilitated extraction process of blue P3R dye reveals a kinetic control through the PVDF/PVP-chitin membrane and an energetic control through its PVDF/PVP-chitosan counterpart.

## 5. Conclusions

In this study, two PIMs based on PVDF and PVP with chitin and chitosan (as extractive agents) were synthesized and characterized. Further, the mechanism of the oriented process for the facilitated extraction and recovery of blue P3R dye across the prepared membrane were elucidated through different experiments, and the related macroscopic and microscopic parameters (permeability, flux, the association constant, and apparent diffusion coefficient) were determined.

The influences of initial substrate concentration, pH, and temperature on macroscopic and microscopic parameters were analyzed. It was found that the PVDF/PVP-chitin membrane manifested the most favorable dye extraction performance as compared to its counterpart PVDF/PVP-Chitosan.

Further, the effects of temperature on activation parameters ( $E_a$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$ ) were evaluated. It was found that the facilitated extraction of blue P3R dye across PIMs was governed by the activation entropy ( $\Delta S^\ddagger$ ) of the formed entity (ST) "substrate-extractive agent". Therefore, the interaction sites engaged between the substrate and extractive agent molecules are important factors to ensure proper migration of the substrate through PIMs.

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## Symbols

[T] $_0$	Concentration of the extractive agent in the membrane, mol.l $^{-1}$
[TS]	Concentration of the complex TS, mol.l $^{-1}$
a	Slope of the plot: $-\ln(C_0 - 2Cr) = f(t)$ , s $^{-1}$
$C_0$	Initial concentration of P3R Dye in the feed phase, mol.l $^{-1}$
$C_r$	Concentration of P3R Dye in the receiving phase, mol.l $^{-1}$
$D^*$	Apparent diffusion coefficient, cm $^2$ .s $^{-1}$
$J_0$	Initial flux of the substrate, mmol.cm $^{-2}$ .s $^{-1}$
$J_0 \text{ moy}$	Average initial flux of the substrate, mmol.cm $^{-2}$ .s $^{-1}$
$K_{ass}$	Association constants
L	Membrane thickness, cm
P	Permeability, cm $^2$ .s $^{-1}$
PIM	Polymer Inclusion Membrane
PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
S	Active area of the membrane, cm $^2$
T	Temperature, K or $^\circ\text{C}$
t	Time, s
V	Volume of the receiving compartment, cm $^3$
$E_a$	Activation energy, j.mole $^{-1}$
$\Delta H^\ddagger$	Activation enthalpy of association, j.mole $^{-1}$
$\Delta S^\ddagger$	Entropy, j.mole $^{-1}$

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