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Optimization Study of Ultrafiltration Rate of a Membrane Based on Polysulfone Modified by Titanium Dioxide on Colored Water by Indigo

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Abstract

Textile dyeing processes are among the most dangerous and unfriendly industrial processes towards the environment because of the coloured wastewaters they produce and which are heavily polluted with textile auxiliaries and chemicals. The ultra-filtration method was studied as a wastewater treatment technique for the decolourization of residual dye bath effluents. The objective of this work is to study the removal rate of a vat dye used in the textile industry through an indigo solution, by the asymmetric organic membrane optimized polysulfone modified according to different weight percentages of titanium oxide.

1. Introduction

The uncontrolled discharge of dye-containing wastes in the environment creates a serious problem to the environment. Among the dyes, indigo, for example has been widely used in textile finishing, as hair colorant, paper colouring and paint production and as a sensitizer in photo-oxidation of organic pollutants [1-3]. Various methods are available for the removal of colored dyes from waste water such as adsorption [4-6], flocculation / coagulation method [7-9], and biodegradation [10-14]. The flocculation treatment process produces a large amount of sludge which causes disposal problems, thus increasing the operation cost. The separation processes based on membranes [15-17] have become an attractive alternative for the treatment of industrial wastewater containing dye due to their unique separation capability, easy scaling-up and low energy consumption during their optimized flow. The hydrophilic modification by TiO_2 particles embedded in collodion polysulfone improves the membrane permeability and restricts the fouling of the latter and imparts hydrophilicity to their surface [19-21].

In spite of these advantages, the incorporation of TiO_2 nano-particles could unavoidably alter the physical properties of the membrane which would affect its performance.

During this work, we treat the indigo dye by the ultrafiltration technique while using a new optimized membrane of polysulfone (PSU) modified by titanium dioxide TiO_2.

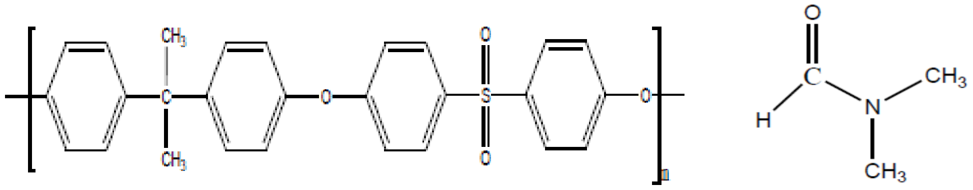
2. Experimental study

2.1. Characterizations of indigo

Indigo is a vat dye which was sold by Shanghai Yancui Import And Export Co., Ltd with the molecular formula $C_{16}H_{10}N_2O_2$ which is insoluble in water and the maximum wave languor λmax is equal to 662 nm. It is used in many fields, among which is the textile finishing industry.

2.2. The membrane used for ultrafiltration

The synthesized membranes were obtained by mixing at the same time of the masses of polysulfone (0,98 , 0,96 and 0,95), (0.02, 0.04 and 0.05) of the inorganic filler Titanium dioxide in 90% in the solvent N, N-dimethylformamide (DMF) whose chemical structure is shown below (Figures 1). The prepared mixtures were allowed to stir using a magnetic stirrer with a speed of 560 Tor/min for 120 minutes under normal temperature and pressure. The obtained collodions were spread on a glass plate using a glass rod. This plate was immediately immersed in a water bath serving as non-solvent to obtain an asymmetric membrane by the phase inversion. The synthesized membrane was characterized successively according to the microscopic properties (Fourier Transform Infrared (FTIR) and the nuclear magnetic resonance (NMR), and according to the macroscopic properties[22,23] .



(a) (b)

Figure 1: Chemical structures of polysulfone (PSU) (a) and of N, N-dimethylformamide (DMF) (b).

2.3. Structural analysis :

2.3.1. Fourier Transform Infrared analysis (FTIR)

The used IR spectrometer is a Fourier Transform Spectrometer (FTIR) BRUKER. The spectra were achieved in transmission on KBr pellets. The light beam passes through the sample with a thickness of about 2 microns. The analysis is carried out between 4000 cm^{-1} and 600 cm^{-1}.

2.3.2. Nuclear Magnetic Resonance (NMR)

The 1H NMR analyzes were obtained using an apparatus of Bruker AVANCE 300 by dissolving the product in DMSO. The chemical displacements are expressed in ppm. The letter s, d, t, q and m respectively mean singlet, doublet, triplet, quadruplet and multiplet.

2.4. Thickness measurement of the membrane by the micrometer:

The thickness of the membrane (E) has an influence on the flux and selectivity, and it can be modified by changing the characteristics of the rule used in their preparation. This size is determined by two steps L1 and L2 such as E = L2 - L1, with L1 = substrate's thickness = 2240 µm and L2 = the substrate's thickness plus the membrane (µm).

2.5. Scanning electron microscopy (SEM)

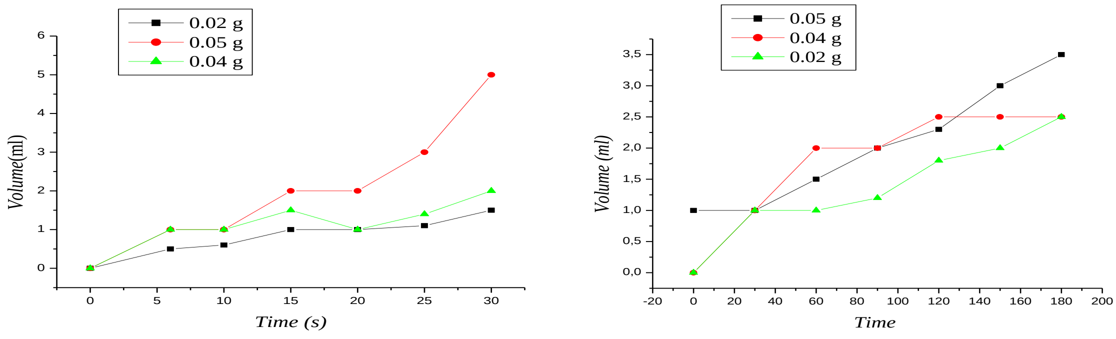
The images of the ultra-filtration's membranes were made with an electron microscope Zeiss Supra 55 FEG scanning VP-low voltage (2 or 3 keV). The sample of observations on the section were made after the immersion in liquid nitrogen and then broken. The samples were all plated with a thin gold layer.

3. Results and discussion

3.1. The influence of time and pressure on the permeability of the membrane

The permeability of the synthesized membrane depends on several parameters, among which we find pressure, time, the nature of the membrane, the nature of the contaminant to be removed, and the membrane pores size.

Figure 2 (a) and 2 (b) respectively shows the influence of pressure and time on the permeability of the membrane.



(a) (b)

Figure 2: The impact of time (a) and pressure (b) on the permeability of the membrane

From this figure, we see that the rate of ultra-filtration of the three membranes' mass loaded with different percentage of TiO_2 increases progressively as the pressure and time increase. This rate of increase is fairly proportional to the operated pressure, which respects the law of Darcy. Furthermore, we notice the rate is much better for the membrane charged with 0.05g TiO_2.

3.2. Measurement of Thickness of the membrane

From the equation $E = L_2 - L_1$, we calculated and recorded in Table 1 the thickness of the membrane with the micrometer.

Table 1: The thickness of the synthesized membrane.

	L_1	L_2	$E = L_2 - L_1$
Membrane 1 (0.98g PSU/0.02 TiO_2) (M_1)	2240	2479.96	239.96
Membrane 2 (0.96g PSU/0.04 TiO_2) (M_2)	2240	2479.98	239.98
Membrane 3 (0.95g PSU/0.05 TiO_2) (M_3)	2240	2479.97	239.97

From Table 1, we observed that the values of the thickness remain the same for the three membranes. It is concluded that the percentage % of the charge does not affect the thickness of the membrane.

3.3. The Structural characterization of the membrane

3.3.1. Analysis by Fourier Transform Infrared (FTIR)

The Fourier transform infrared spectrum (FTIR) allowed us to give the presence of the functional groups which exist in the chemical structure of the membrane. Figure 3 shows the peaks of the FTIR in which the analyzed samples were prepared by the dimethylsulfoxide (DMSO) [24].

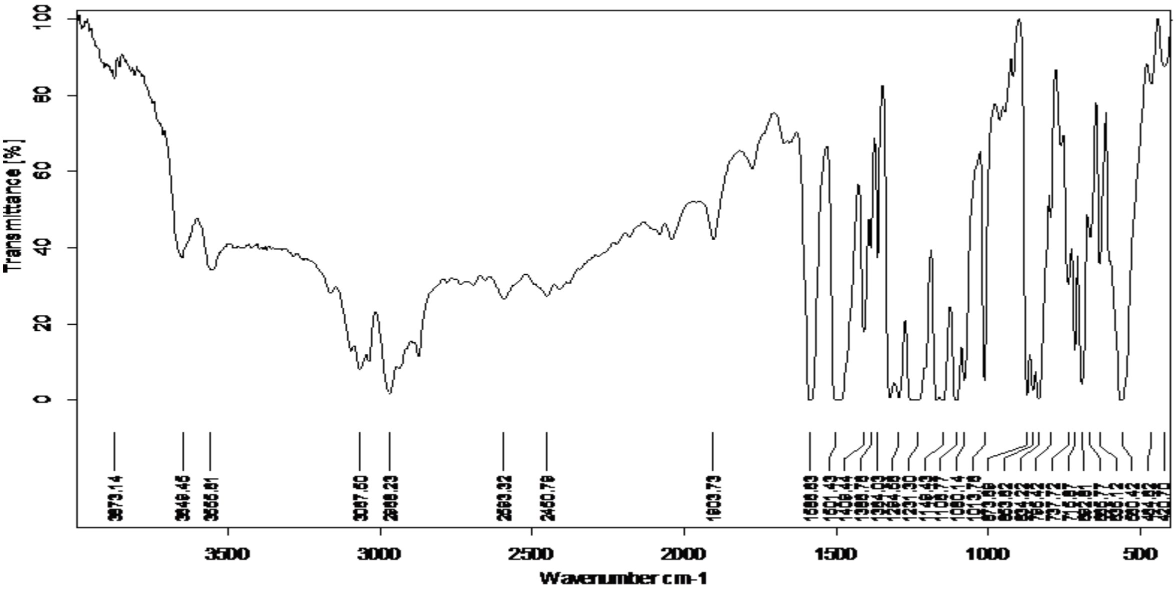


Figure 3: The specter of the FTIR

3094-3069 υC-H ; 1579 and 1485 υC=C aromatic ; 1324 and 1299 υO=S=O ; 1245 υC-O-C ; 1162 υO=S=O ; 1152 υC-O-C saturated aliphatic; 701 and 837 disubstituted benzine; 628 υC-H ; 561 υO=S=O.

3.3.2. The NMR Analysis :

Figure 4 shows the spectra of ^1H-NMR. In this study, we used the dimethylsulfoxide (DMSO) to solubilize the analyzed samples.

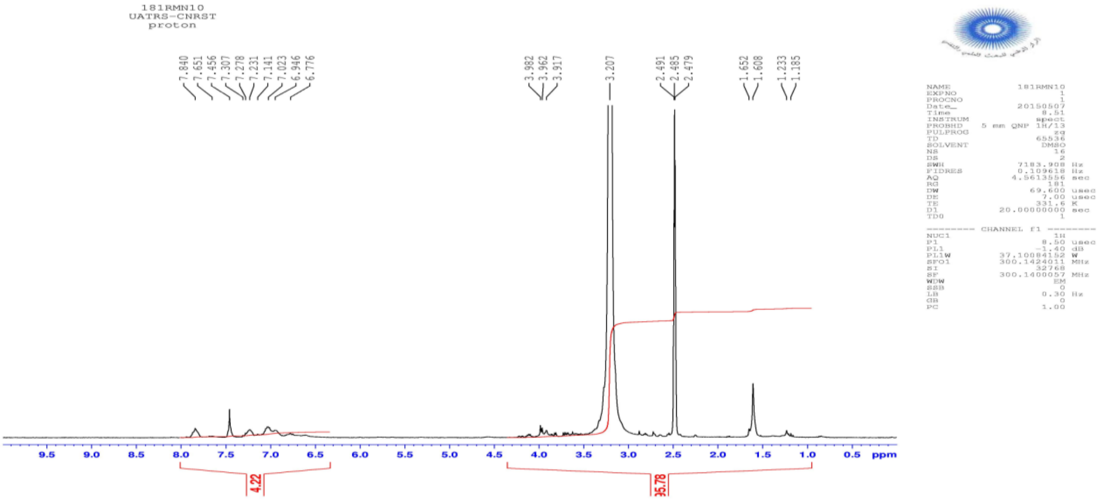
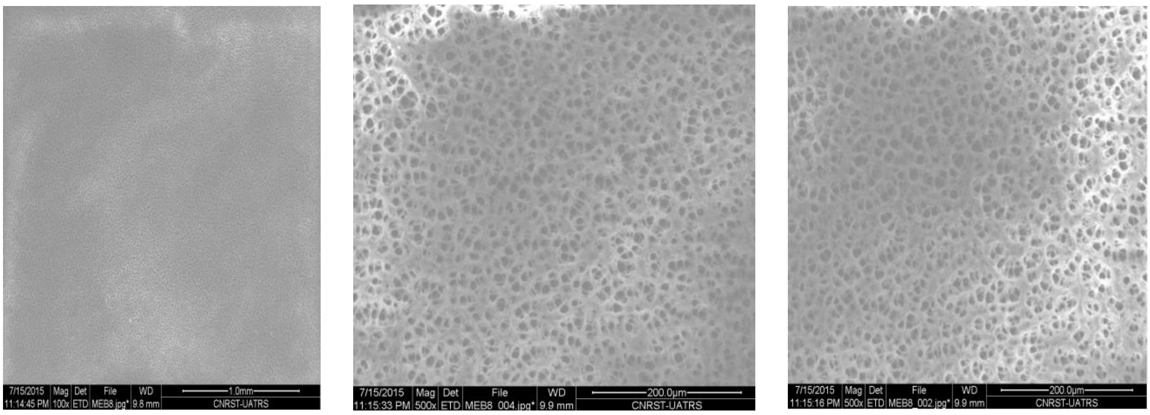


Figure 4 : The ^1H NMR spectrum

NMR ^1H: 1.7 (s, 6H, CH_3), 6.84 – 7.08 (s, 4H, aromatic linked with oxygen), 7.09 – 7.86 (s, 4H, aromatic linked with carbon), 7.8 – 7.9 (s, 4H, aromatic linked with sulfur).

3.4. Scanning electron microscopy:

The scanning electron microscopy (SEM) is a technique of electron microscope capable of producing high resolution images of a sample surface using the principle of electron-matter interactions.



M_1 M_2 M_3

Figure 5: SEM photographs at various percentages % of TiO_2

- M_1 (0.98g PSU/0.02 TiO_2)
- M_2 (0.96g PSU/0.04 TiO_2)
- M_3 (0.95g PSU/0.05 TiO_2)

According to this figure, we notice that the membrane structure is well modified under the effect of different percentages of titanium dioxide. Indeed, the structure of the active surface of the optimized membrane M_3 (PSU 0.98 / 0.05 TiO_2 / DMF), which is seen by the SEM, shows a homogenization and an increase of pores' density with respect to the membranes M_1 and M_2. That explains well the hydrodynamic property of the optimized membrane M_3.

3.5. Discoloration rate of indigo

In Figure 6, we have shown the fading rate of the dye of the vessel (indigo) by the method of ultra-filtration. According to this figure, we observe that the indigo discoloration rate, which is obtained by the ultra-filtration process, is 76%, 80% and 86% respectively for the membranes M_1, M_2 and M_3. This selectivity of the optimized membrane M_3 on the coloring retention rate due to indigo has confirmed the asymmetric membrane structure.

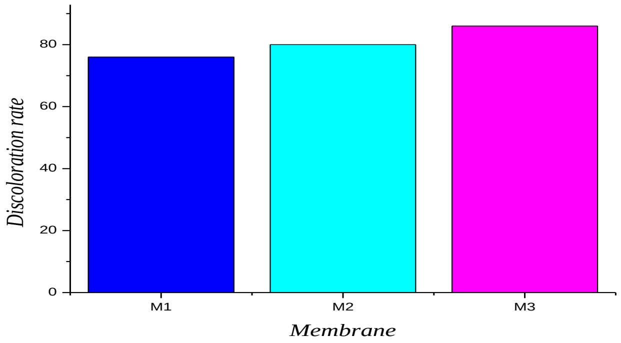


Figure 6: Discoloration rate of indigo

Conclusion

This work aimed to study the influence of the mass of titanium dioxide on the permeability on the one hand, and the selectivity and mechanical property of the membrane optimized on the other hand, which led us to optimize the massic components of the membrane based on PSU, TiO_2 and DMF.

Furthermore, the hydrodynamic properties, which are represented by the flow rate and the retention rate (selectivity), were evaluated in comparison with the synthetic membranes. Indeed, the optimized membrane, which has a flow rate of 4 ml and a dye retention rate of 86% being M_3 of formulation in massic percentages polymer/load/solvent, is of (0.95 / 0.05 / 90).

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