Synthesis of a new asymmetric semi permeable membrane and based alloy of two polymers PVC and PSU. Application in the treatment of a colored solution.

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Abstract

Dyes are an important in synthetic organic compounds. Are used in large quantities in the textile industries, plastic, cosmetic and tanning, etc. Use of indigoid dyes in textile finishing processes experienced in recent years a strong increase, causing a large volume of wastewater loaded with these dyes. Their release into aquatic systems without any prior treatment causes damage to the environment due to their toxicity, which requires treatment with suitable techniques that respect the environment. However, the complexity of these pollutants and their color greatly affect the effectiveness of treatments applied conventionally. Discoloration tests wastewater of textile industry and some colored solutions were carried out by the ultrafiltration membrane method. During this work, we synthesized a microporous asymmetric membrane alloy polysulfone and polyvinyl chloride. The objective of this work is to show the feasibility of the purification of industrial wastewater charged with indigoid dyes by ultrafiltration technique, using a new organic asymmetric membrane based on a mixture of two thermoplastic polymers, which are polysulfone (PSU) and polyvinyl chloride (PVC). From the results obtained in this work, it is found that the fading rate of the order of **89%** corresponds to a membrane pressure of **20 cm Hg**, in a basic medium at a pH of **11.80**. According to this study, it appears that the operation of this asymmetric membrane based mixture (PSU and PVC) is very effective for the discoloration of a water solution of indigo dyes loaded with.

Keywords: *Wastewater; Indigo dye; Asymmetric membrane; Polysulfone; Polyvinyl chloride; Discoloration.*

1. Introduction

During recent years, the methods of separation and/or concentration by membranes have had a remarkable development in various application fields, namely; biotechnology, food industry, pharmaceutical, textile, water treatment and industrial effluents, etc. **[1]**. Textile finishing industries are described by a high consumption of water, colorants, additives and various chemicals as a result of different methods that result in very large amounts of wastewater and stained which are very harmful to health human and ecosystem **[2]**. This type of wastewater always attracts the attention of researchers and scientists, by inventing new side

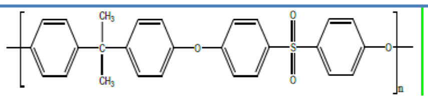
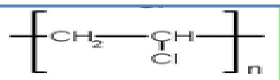
processing techniques conventional ones [3]. To treat this wastewater, several methods are used, outlining the techniques of physic-chemical treatment [4], adsorption [5], biodegradation, chemical oxidation, photo-degradation, solvent extraction [6, 7], coagulation/flocculation [8], microfiltration (MF) [9], ultrafiltration (UF) [10], nanofiltration (NF) [11-13], reverse osmosis (RO) [14], etc. In recent techniques are based on the use of permeable membranes [15], because of their high efficiency of purification and simple operating conditions [16]. These membranes are often based organic polymers for example cellulose acetate, polystyrene, polyurethane, polysulfone, polyvinyl chloride [17]…, and are sometimes used an alloy of macromolecular compound. During this work, we synthesized, at first, a new permeable membrane based on a combination of different percentages of polysulfone and polyvinyl chloride in a solvent which is N, N dimethylformamide (DMF), to treat wastewater from the textile finishing industry [18, 19]. And in a second step, we characterized the membrane obtained according to the hydrodynamic conditions of the ultrafiltration (UF) on the one hand, and by polarizing microscopy, on the other hand.

2. Materials and methods

2.1. Polymers used

The polymers used to synthesize the asymmetric membrane are polysulfone and polyvinyl chloride whose physical and chemical properties are summarized in Table 1. The polysulfone exists as grains and polyvinyl chloride (PVC) as a white powder.

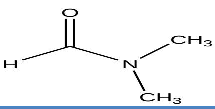
Table 1: Physical/mechanical, thermal and chemical properties of PSU and PVC [20-22].

Properties	PSU	PVC
Structure		
Physical/mechanical	- High stiffness and mechanical strength. - Thermal stability. - Amorphous polymer having a glass transition temperature. - Good electrical and dielectric properties. - Dimensional stability. - His yellow and transparent color.	- Polymer therefore essentially amorphous atactic. - The density is 1.38 g/cm^3. - Transparent and relatively permeable to water vapor. - Provides excellent rigidity to the vicinity of its glass transition temperature. - Excellent resistance to abrasion. - Fragile to shocks at low temperatures.
Thermal	- Thermally stable. - Available on their degradation products. - Some authors studied the polysulfone from decomposition of bisphenol A at 380 °C, where degradation is not yet very important.	- To a glass transition temperature between 75 and 80 °C. - At room temperature, it is rigid and that above 90 °C PVC decomposes in a flame by releasing gaseous hydrochloric acid but it is self-extinguishing.
Chemical	- Good resistance to acids and alkalis, oils and grease and surfactants. - They are attacked by ketenes, esters and certain solvents. - The solubility of polysulfone in these products allows the manufacture of paints and varnishes.	- Resistant (up to 60 °C) to acids and bases as well as oils, alcohols and aliphatic hydrocarbons. - Sensitive to aromatic and chlorinated hydrocarbons, esters and ketenes which cause swelling. - Flexible and sensitive to atmospheric agents and sunlight.

2.2. Synthesis of asymmetric membrane

During this stage, we have a mixture, a 1g mass (10%) composed of PSU and PVC as a polymer and 9g (90%) of the solvent N, N-dimethylformamide (DMF) (Table 2) as a solvent. The resulting mixture was stirred using a magnetic stirrer until complete dissolution of the mixture at room temperature. Colluding prepared is spread on a glass plate using a glass rod with a well defined thickness. This plate is then immersed in a water bath (non-solvent) producing a plasticizing film according to the mechanism of phase inversion **[23]**.

Table 2: Physical and chemical properties of DMF.

Solvant	Chemical formula	Density	Molar mass	Melting point	Boiling point
N, N-dimethylformamide	C_3H_7NO 	0,9445 (g/ml)	73,09 (g/mol)	- 61 °C	153

2.3. Usual water loaded with indigo dye

Samples of colored water used in this study were made by adding 1.25g of blue indigoid ($C_{16}H_{10}N_2O_2$) in a 500 ml capacity beaker containing distilled water. To the resulting mixture, we added successively using a micropipette and a small volume of some chemical additives namely hydroxide sodium hydroxide, acetic acid and the wetting agent. The mixture was stirred to prepare using a magnetic stirrer until complete dissolution of indigo dye. Note that at the end of this step, patterns colored water samples obtained were characterized by measuring their pH and λ_{max}.

2.4. An ultrafiltration membrane

Compound of an Amicon ultrafiltration cell 36 cm^3 of capacity equipped with a nitrogen cylinder R and a graduated pressure system.

2.5. Characterization of the membrane

✓ To assess the hydrodynamic characteristics of the synthesized membrane, we measured successively the membrane thickness, the degree of swelling, permeability and selectivity.

✓ To control the microscopic features of our diaphragm, we analyzed the sample of this membrane by infrared spectroscopy (IR) and the morphological structure determined using a polarizing microscope.

3. Results and Discussions

3.1. Measuring the thickness of the membrane

The membrane thickness has an influence on the flux and selectivity; it can be changed by changing the characteristics of the rule used in their preparation. This size is determined by two L_1 and L_2 measurements.
L_1= the thickness of the substrate alone = 2200µm
L_2= the thickness of the substrate and the membrane = 2400µm
From these measurements we can determine the thickness of the membrane by a simple calculation using the following equation: $E = L_2 – L_1$, so: the thickness E is 200µm.

3.2. Measurement of swelling ratio

We studied the swelling state of the membrane synthesized from a mixture of two PSU polymers and PVC, which we conducted experiments from distilled water. The swelling rate is calculated from the following relationship:

$$Tg = \frac{m_h - m_e}{m_h} * 100$$

T_g: swelling rate expressed by percentage weight ; m_h: membrane wet mass and m_e: membrane dry mass
The results of the swelling ratio of the membrane as a function of time of immersion in distilled water are summarized in Table 3.

Table 3: Values of the rate of swelling the membrane as a function of the time of immersion.

Time of immersion (min)	m_e (g)	m_h (g)	T_g (%)
30	0.0135	0.0161	16
60	0.0137	0.0173	20
90	0.0135	0.0173	22
120	0.0150	0.0206	27
150	0.0166	0.0242	31
180	0.0155	0.0254	38
210	0.0158	0.0289	45

The membrane is left in contact with distilled water for 24 hours was dried with absorbent paper sheets and weighed. m_e = 0.0412 g; m_h = 0.1369g, So: Tg = 70%
These results show that when the time of immersing the membrane in distilled water is increased, the swelling rate increases to 70%.

3.3. Microscopic morphology of the membrane

Morphology of the membrane by the polarizing microscope "Leintz Laborlux 11 pols".

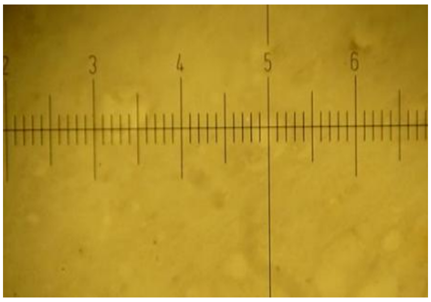


Figure 1: Morphological characterization of the membrane by the microscope Polarizing (G*10).

The picture of Figure 1 shows that the membrane having a homogeneous surface has reliefs and aggregates, which are due to the effect of spreading, that is to say because of the impurity and the dust which accumulates on the glass plate. The trappings ports are on the order of a micrometer that was specified by the MEB.

3.4. Hydrodynamic characterization of the membrane

3.4.1. Permeability of the membrane with distilled water

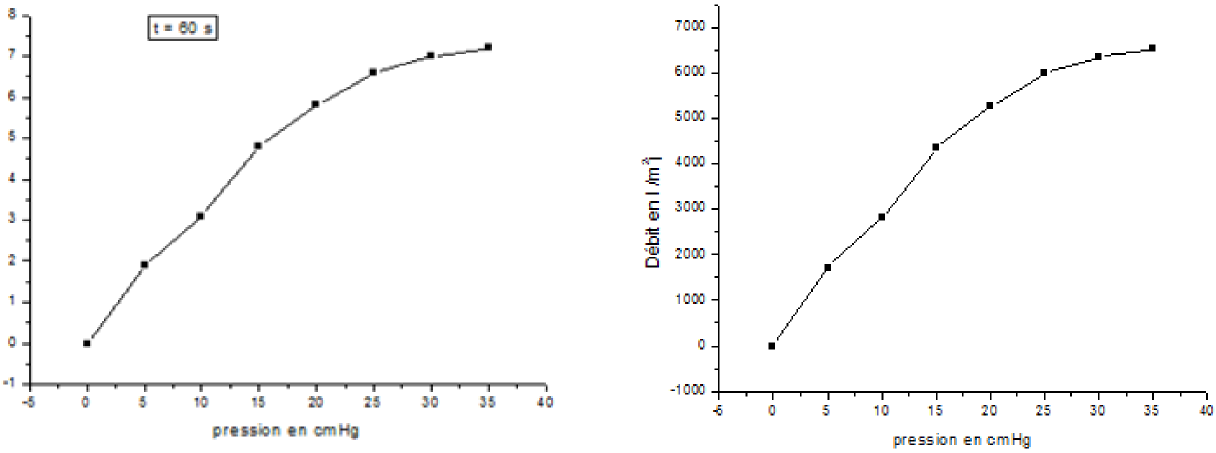
Experience 1:

The protocol consists of the filtration of a sample of water distilled according to the pressure and volume to be filtered by a fixed filter time of 60s.

The results of the ultrafiltration membrane, distilled water are summarized in Table 4 and presented by Figures 2 (a), (b) below:

Table 4: Permeability of the membrane with distilled water at t = 60s.

Pressure (cm Hg)	0	5	10	15	20	25	30	35
Volume (ml)	0	1.9	3.1	4.8	5.8	6.6	7	7.2
Flux (l/m^2.j)	0	1721	2809	4350	5256	5981	6343	6524



(a) (b)

Figure 2: Permeability of the membrane with distilled water (a), evolution flow depending on pressure (b).

According to Figures 2 (a) and (b).

We notice that the volume of ultrafiltrat increases under the effect of pressure, confirming that the membrane is permeable for these optimum conditions.

Experiment 2:

A time variable between 0 to 240 s and the maximum pressure p=20 cmHg at room temperature.

Table 5: Permeability of the membrane with distilled water at P = constant.

Time (s)	0	30	60	90	120	150	180	210	240
Volume (ml)	0	3.6	6.7	10.4	13.8	17	20.1	23.3	26.6

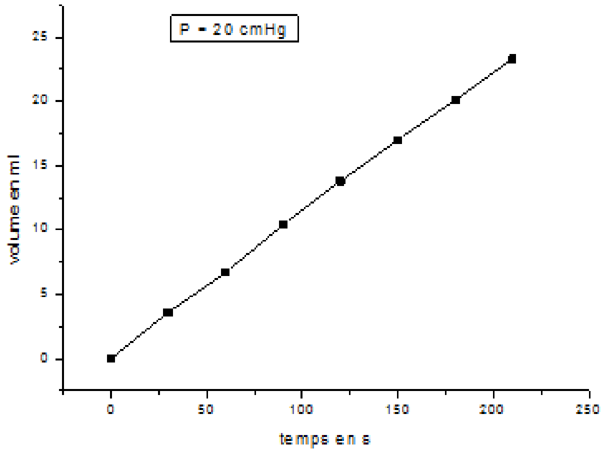


Figure 3: Permeability of the membrane with distilled water.

The results obtained show that the volume change with time is a well-defined line of slope V = a.t, which concluded that the membrane is asymmetrical and semipermeable.

3.4.2. Model solution discoloration rate processed (indigo)

To calculate the fading rate of the prepared sample, we made a simple ultrafiltration membrane applied to the synthesized using the Amicon cell with a volume of 50 cm^3.

The bleaching rate is given by the following relationship:

$$\%TD = \frac{A_i - A_f}{A_f} * 100$$

With: A_i: Absorbance of the initial dye and A_f: Final absorbance dye.

The results about the fading rates are summarized in the Table 6:

Table 6: Rate of discoloration after ultrafiltration on the synthesized membrane.

Solution model	0	λ_{max}	pH_i	A_i	pH_f	A_f	%TD
Indigo	vat dye	675	11.8	2.5	9.5	0.27	89.2

3.5. Characterization spectroscopy

3.5.1. Infrared spectroscopy (FTIR)

The results obtained by the Fourier Transform Infrared spectroscopy in attenuated total reflectance (FTIR-ATR) of the synthesized membranes (M**psu**, M**pvc** and M**s**) are shown in Figures 4, 5 and 6. **Table** 7 contains the frequencies of the functional groups exemplified by their characteristic bands.

According to figures 4, 5 and 6, we find that the two characteristic peaks of polymers used, such as sulfone group is attributed to vibrations pulled to 1317cm^{-1} and 727cm^{-1} and the vinyl chloride is attributed to the stretching vibration at 617 cm^{-1}. For the solvent used should be visible by two characteristic bands are: at 1671cm^{-1} and 698 cm^{-1}. From the Figure 5 and according to the comparative analysis of 3 and 4 specters we admit he has not had any reaction between the two polymers, the membrane is derived from amorphous polymer alloy as physical copolymers.

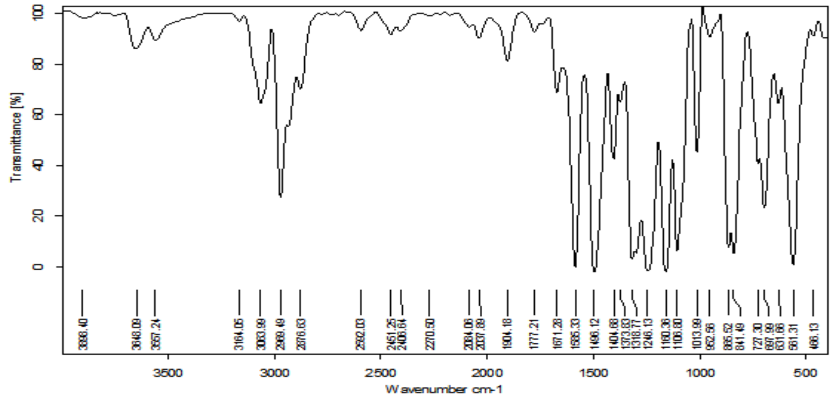


Figure 4: Infrared spectrum of the membrane based on PSU.

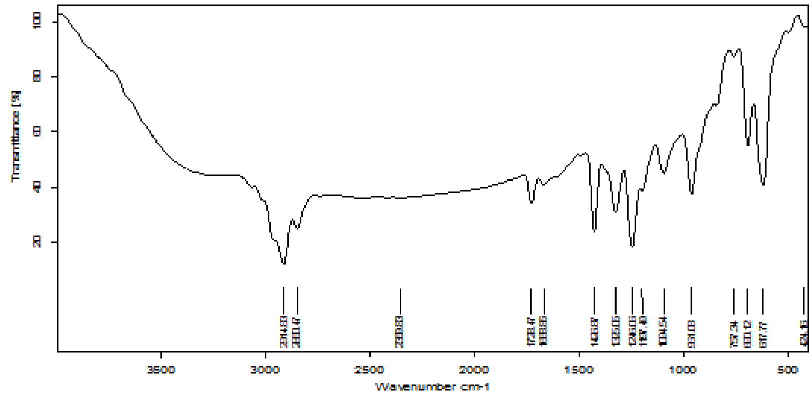


Figure 5: Infrared spectrum of the PVC-based membrane.

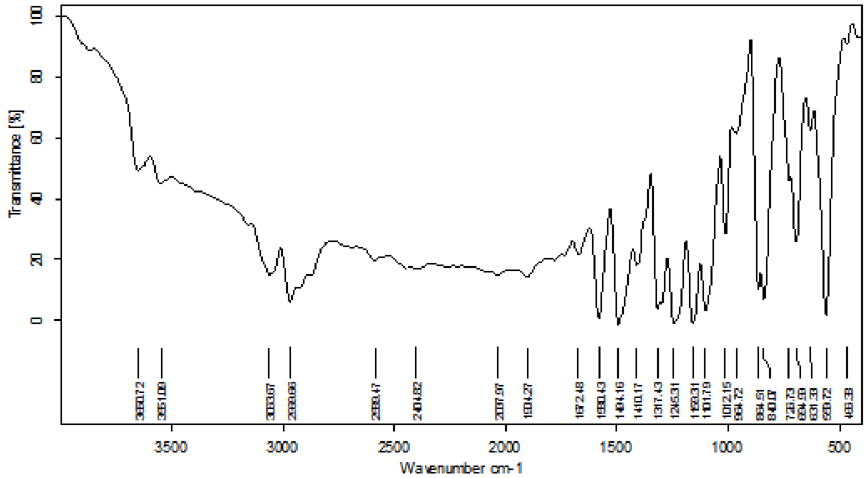
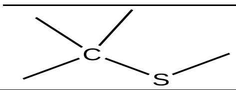
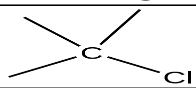
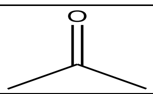
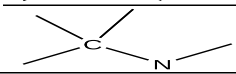


Figure 6: IR spectrum of the membrane based on PSU and PVC (MS).

Table 7: Allocation of different peaks obtained by infrared analysis by FTIR mode.

Composed	Functional grouping	Characteristic vibration frequency in cm^{-1}
Polysulfone	O=S=O	1300-1380
		700-740
Polyvinylchloride		610-1175
Solvent (DMF)		1630-1680
		690-720

4. Conclusion

In this work, we have been able to synthesize an asymmetric microporous membrane by the phase inversion process. The latter was optimized by ultrafiltration of a solution based colored indigo dye often employed in the textile industry, its hydrodynamic performance and mechanical on the one hand and the discoloration rates of up to 89% of a solution formulated in the presence of indigo one hand, allow the use in prospects in test treatment wastewater directly from an industrial unit of textile.

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