Benkhaya et al.

Synthesis of a New Asymmetric Composite Membrane with Bi-Component Collodion: Application in the Ultra filtration of Baths of Reagent Dyes of Fabric Rinsing/Padding

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Abstract

A new microporous hydrophilic bi-component membrane used in ultrafiltration was prepared through a technological symmetric porous support of polyester coated with a thin active layer physical copolymer (Polysulfone/Polyetherimide) noted (PSU/PEI) in their solvent. The microporous layer of the surface of the membrane was characterized using the scanning electron microscope (SEM). The ultrafiltration method was used to treat the synthetic reactive dyes (black sunzolsuncion and orange) through aqueous solutions as well as for textile raw effluent supplied through rinsing and padding baths of the textile industry. The influence of the molecular weight of the reactive dye and the effect of the used membranes have been studied with regard to their impact on the permeate flux at different transmembrane pressures, the color retention scale, the chemical oxygen demand (COD) and conductivity were determined in order to quantify the separation efficiency of the membrane. The conductivity rate (> 75%), the high COD and color retention (> 90%) were obtained by the optimized composite membrane for both the studied dyes in an alkaline medium.

Keywords: Bi-component membrane, Polysulfone (PSU), Polyetherimide (PEI), Ultrafiltration, Rinsing and padding baths, technical porous symmetric support in polyester.

1. Introduction

Ultrafiltration (UF) is a well developed technology of membrane separation which has been applied in food processing, juice, pharmaceutics, biotechnology, purification and industrial water treatment [1,2]. Textile industries use large amounts of water and chemicals for the wet treatment of textile in which the used chemical reagents are very diverse in chemical composition from inorganic compounds to polymers to organic products [3, 4]. The presence of very low concentrations of dye in the effluent is visible and undesirable. [2] Due to their chemical structure, dyes are resistant to discoloration by the exposure of water to light and many other chemicals [2, 5]. A multitude of dyes are difficult to bleach because of their complex and synthetic structure. There are many varieties of the structure such asazo, diazo, anthraquinone, triphenylmethane dyes, phthalocyanine, and metal complex dyes. The discoloration of the textile dye effluent does not occur during aerobic treatment by the municipal sewage system [6]. The conventional method of treating textile wastewater consists either of chemical coagulation using iron, lime, alumina sulfate and/or coagulation/flocculation [7] poly electrolytes, biological treatment (activated sludge) or of adsorption (activated carbon). The conventional coagulation process generates a huge volume of dangerous sludge and a problem of sludge disposal. To meet the

legal requirements for the discharge of textile wastewater, researchers are trying a combination of two or more treatment methods for a complete and successful removal. The combination of electrochemical treatment and the chemical coagulation [8], the electrochemical oxidation and the activated sludge process [9], the chemical coagulation and ion exchange [10], the combined chemical coagulation and the combination of electrochemical method have been reported for the treatment of textile effluents and comply with legal requirements or reuse standards. Each processing method has its own advantages and disadvantages and the choice of method depends primarily on the processing target to achieve.

However, emissions regulations are stricter and there is a growing trend and interest in the advanced methods of treatment such as ozonation, catalytic photo, and membrane processes. The latter is better suited for the treatment of textile wastewater [11] and particularly for the color removal [12, 13].

The recovery and reuse of textile wastewater have been extensively studied by membrane researchers [14, 17]. Membrane techniques are promising in this area because they have the potential to eliminate the dye stuffs or to allow re-auxiliary chemicals used for dyeing or concentrate dyes and adjuvants and produce purified water.

Indeed, the membrane processes can be used for the purification of these waste streams [18-20], on using microfiltration [21, 22], ultrafiltration [23-25, 21], nanofiltration [25-27], or reverse osmosis [28, 29, 21]. Many applications of ultrafiltration (UF) have been reported for the separation of certain dyes, such as the direct, disperse and reactive indigo [30, 31].

The aim of this work is to study the performance of a new asymmetric composite membrane bi-component matrix in the field of ultrafiltration of aqueous synthetic reactive dyes (using the black and orange).

Currently, there are conventional ultrafiltration membranes which are essentially prepared by the dipping method phase. The latter generates an asymmetric porous structure with two major limitations, one relatively low in porosity while the other's size of distribution is quite wide [32-34]. In consequence, these membranes have two obstacles:

A low rate of flow because of poor porosity (limited permeability).

A high rate of fouling due to low distribution of asymmetric pores on the surface [35].

The flow rate and the selectivity during the filtration are directly related to the thickness of the active film layer or to the hydrophilic coating [36]. The active coating layer is expected to inhibit the adsorption of solutes on the surface without any obstacle of the water permeability. The asymmetric porous structure of the Technological Support of the Polyester's fabric should be responsible for the required mechanical stability.

2. **Materials and methods**

Experimental studies were performed in three steps:

The synthesis of a new asymmetric composite membrane bi-component collodion with a thin active layer based on physical copolymer (Polysulfone / Polyetherimide);
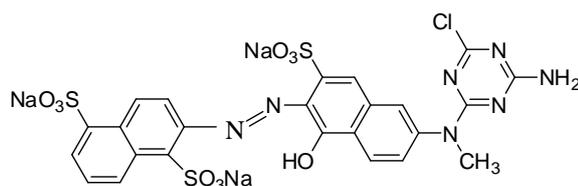
The hydrodynamic and microscopic characterization of the optimized composite membrane;

The ultrafiltration of solutions of rinsing/padding textile.

The structures and molecular weights of the two azoic reactive dyes used are shown in Figure 1.
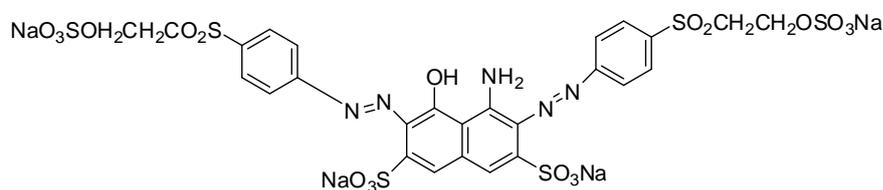
Chemical structures of black Sunzol (M_{black} = 991.82g.mol^{-1})

Chemical structures of orange Suncion (M_{orange} = 762.04g.mol^{-1})

Figure 1: Chemical structures and molecular weights of the two azoic reactive dyes used.

2.1. Membrane preparation

All round pieces of technological support of polyester fabric (diameter 2.5 cm) were washed successively with acetone to remove the initial color of the substrate and surface contaminants. The latter were then dried in an oven at 50 ° C for 10 min. The membranes were prepared by a dip coating process as follows:

An amount of weight of the copolymer (PSU/PEI) was dissolved together in the solvent and sonicated for 15 minutes in an ultrasonic bath (figure 2). The obtained preparation was then poured into a Petri dish. The upper face of the support is then immersed in the collodion and prepared for one minute. The membrane is then placed in an oven hang 30 minutes at 50 ° C.

Figure 2: Ultrasonic bath.

2.2. Wastewater characteristics of textile

Table 1 shows the characteristics of wastewater provided by the textile industry rinsing baths which contain a variety of components of different concentrations [37].

Table 1: Characteristics of textile wastewater. [38]

Parametre	Unit	Value
pH		7.11
Conductivity	(μS cm^{-1})	3840
Turbidity	(NTU)	4.02
COD	(mg l^{-1})	708
Particle size distribution	(μm)	0.768
TDS	(mg l^{-1})	3137
Colour		0.12
Cl^{-}	(mg l^{-1})	>125
SO$_4^{-2}$	(mg l^{-1})	28
Ca^{2+}	(mg l^{-1})	42
Mg^{2+}	(mg l^{-1})	18.6
Na^{+}	(mg l^{-1})	1008

2.3 .Preparation of solutions of synthetic models

The experiments were performed using two reactive azoic dyes (Black Sunzol and Orange Suncion) known to contain anionic sulfonate groups.

Two solutions of baths of rinsing/padding of textile were prepared using reactive azoic dyes and sodium chloride. These synthetic solutions were prepared by dissolving 0.17 g of dye powder in a 250 ml flask containing distilled water. This mixture was heated for 30 min at a temperature of 80 ° C to ensure the complete dissolution of the dye. After cooling, the flask contents were poured into a 250 ml flask. Then an amount of 0.10 g of NaCl was added and supplemented with distilled water to the mark.

The actual wastewater of textile is strongly alkaline (pH 10.0 to 12.5) and is characterized by a strong color and a high pH. Indeed, in the dyeing and finishing phase of the textile material in textile units, we used some substances such as NaCl or Na_2CO_3 which are needed to improve the aggregation of the dye on the modified fibers to fix the dyes. Immediately after the pH was adjusted to 10 with a 5 M of solution of sodium hydroxide and the solutions prepared were homogenized by magnetic stirring. The concentration of dye and the NaCl concentration are equal to 6, 8.10^{-4} mol / l and 4, 2.10^{-2} mol / l.

The major parameters characterizing the baths of rinsing / padding of these solutions are registered in Table 2.

Table 2: Characteristics of solutions of baths of rinsing/padding of textile.

Parametre	Unit	Black Sunzol	Orange Suncion
Molecular weight	$(g\ mol^{-1})$	991	762
pH		9.89	10.46
Conductivity	$(\mu S\ cm^{-1})$	5690	7320
[dye]	$(mol\ l^{-1})$	$6,8.10^{-4}$	$6,8.10^{-4}$
COD	$(mol\ l^{-1})$	540	431
[NaCl]	$(mg\ l^{-1})$	$4,2.10^{-2}$	$4,2.10^{-2}$

2.4. Analytical methods
The pH and conductivity were determined respectively by means of the pH-meter and conductivity meter.
The color retention, COD and salt were calculated by the following equation:

$$R = 100 * (1 - \frac{C_f}{C_i})$$

C_f: is the final concentration of the ultra-filtered solution;
C_i: is the initial concentration of the solution.

2.5. Experimental facility
All experiments were performed by a dead-end filtration using a cylindrical ultrafiltration cell equipped with a flat module whose active surface is 4.9 cm^2 and which included a magnetic stirrer to homogenize the feeding solution (figures 3 and 4). The membrane was placed on a porous aluminum holder as shown in figure 4.
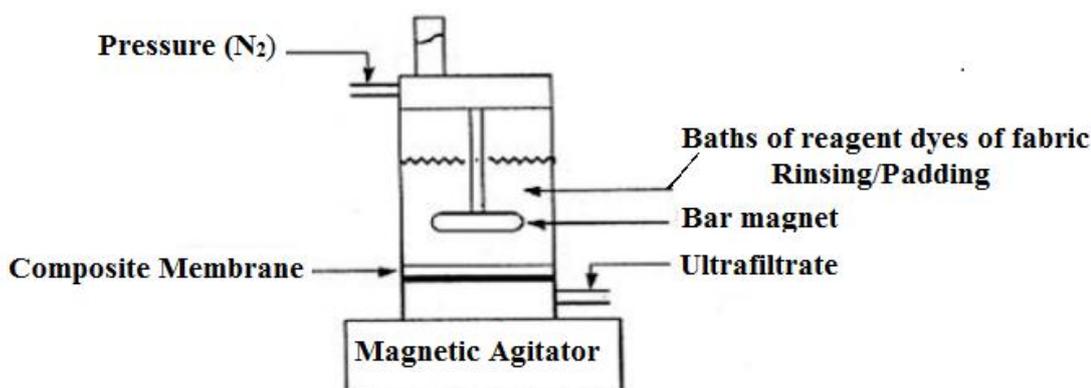

Figure 3: Experimental setup.

Figure 4: Photo the experimental setup.

The flow rate of the permeate was calculated by continuously measuring the volume of ultra filtration view of time and pressure applied successively during the filtration. The plant was cleaned with chemicals and distilled water after each experiment. The permeability of the membrane was reassessed.

The concentrations are determined either by UV-visible spectrophotometry for the dyeing solution at the maximum absorption wavelength or by conductivity for the NaCl solution.

2.6. Chemical cleaning

The first step of chemical cleaning is to circulate the distilled water in the system for 40 min, then to apply the basic cleaning by using a sodium hydroxide solution (5 mol.l^{-1}) at pH = 11 for 20 min. The second step in the process is to rinse the installation again in the distilled water for 40 min and then applying an acid cleaning with a hydrochloric acid solution at pH=3 for 20 min.

Finally, a step of rinsing with distilled water was applied for 40 minutes. The steps of the membrane cleaning process were followed without applying pressure in order to remove organic and inorganic substances which might initiate the clogging of the membrane. Therefore, the permeability of the membrane was re-evaluated in order to check the status of membranes' fouling.

2.7. Mechanical properties: the sample is attached to the two jaws

The used apparatus is called tensile machine (Figure 5). This apparatus comprises a force sensor which translates the force applied to a sample during deformation into an electric potential. The sample is attached to the two jaws one of which is fixed and the other is left mobile (Figure 6). The movable jaw is attached to a crosspiece, through the force sensor. The crosshead moves on two screws at a predetermined speed through a gear system. During stretching, the force sensor transmits a signal which is proportional to the force imposed on the sample. The force sensors are sensitive in a limited range of forces but they are easily interchangeable.

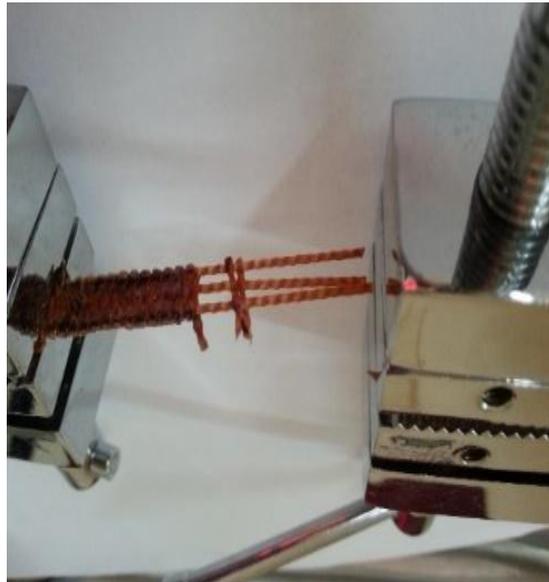**Figure 5:** Tensile testing machine.

Figure 6: The two jaws.

3. Results and discussion

The obtained composite membranes in this work are asymmetrical with a hydrophilic layer which is characterized by NMR and Fourier Transform Infrared (FTIR).

3.1. NMR Studies {^1H} and {^{13}C} of the membrane

The characterization by nuclear magnetic resonance spectroscopy (NMR) of the synthesized membrane is given by Figures 7 and 8.
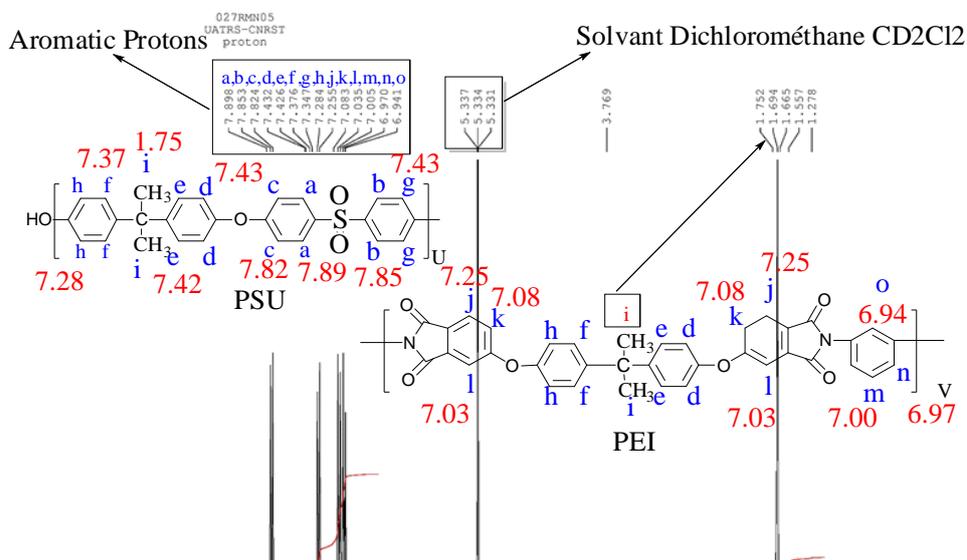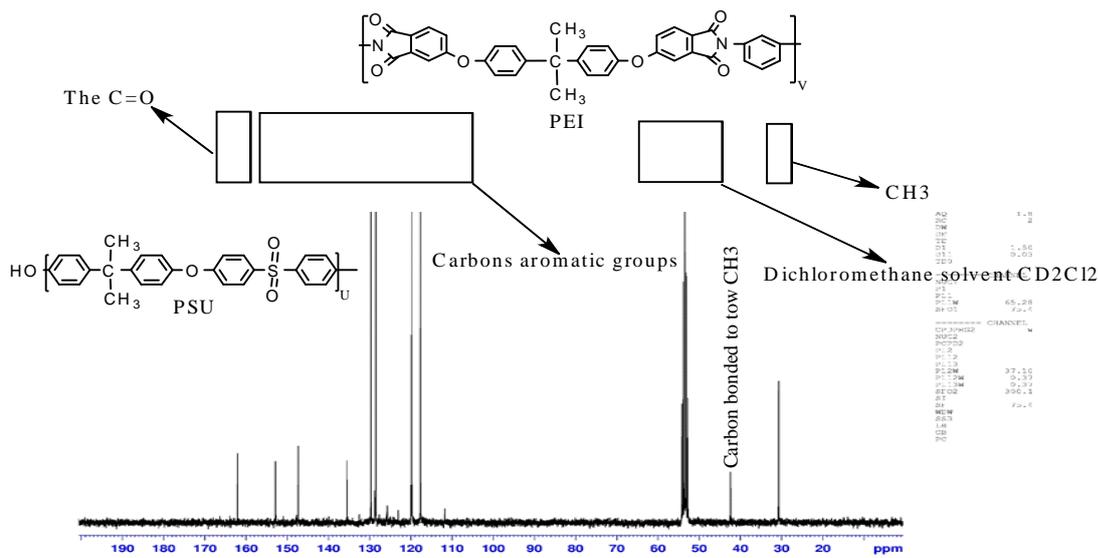

Figure 7: NMR spectrum {^1H}.

Figure 8: NMR spectrum {^{13}C}.

This spectrum shows that there are indeed two structures (PSU/PEI) in the form of physical copolymer.

3.2. Microscopic Characterization of the membrane
3.2.1. FTIR Study of the membrane
The spectrum of the Fourier Transform Infra Red (FTIR) of the macromolecular matrices used in the preparation of the active layer of the optimized membrane is shown in Figure 9.
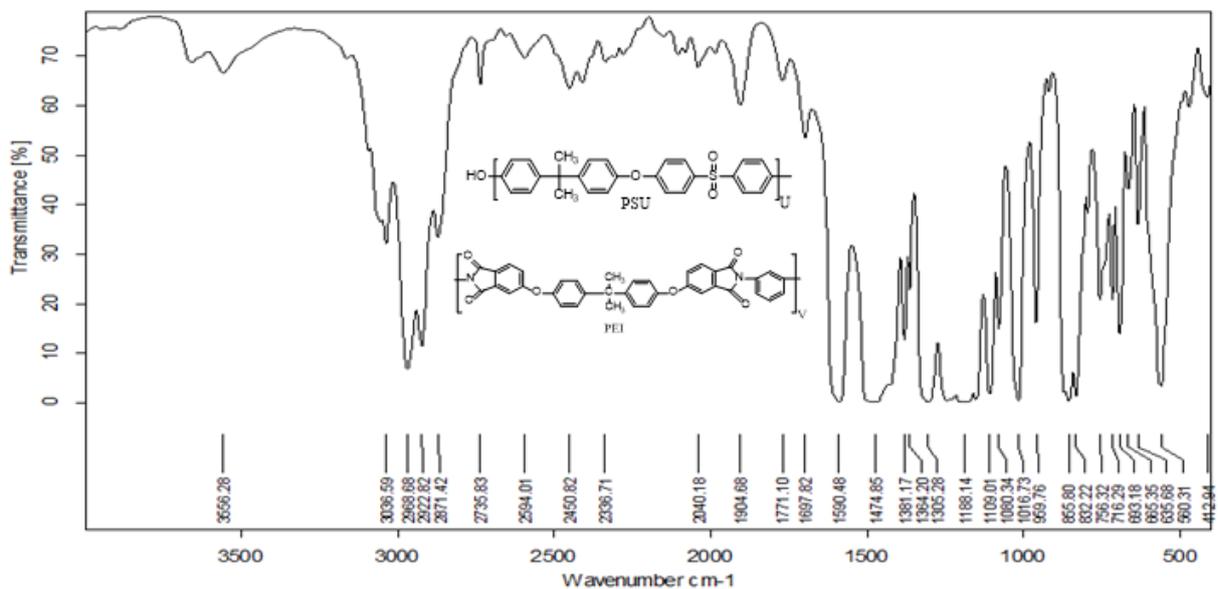

Figure 9: IR spectrum of the optimum membrane.

We found, on the one hand, the characteristic peaks of the two copolymers used for the synthesis of the active layer of the membrane and, on the other hand, we observed that the peak is attributed to the used solvent (Table 3). This could explain the starting part of the solvent during the solidification of the synthesized membrane.

3.2.2. Hydrodynamic Characterization of the composite membrane
Figures 10 and 11 below show the flow depending on the pressure and volume, on the one hand, and according to the mass content of PSU and PEI on the other.

Table 3: Different bands of infrared absorption IR of PSU, PEI.

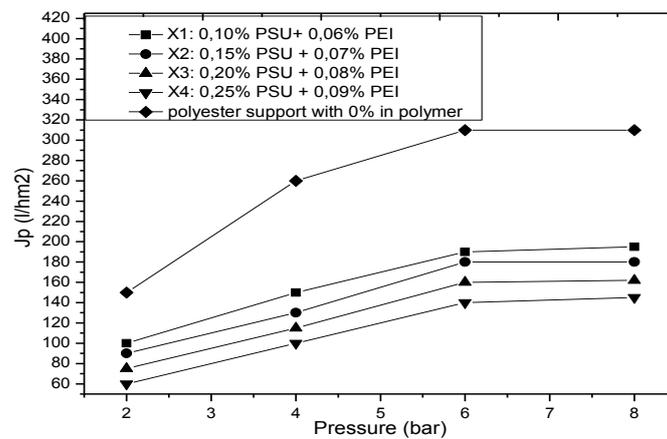| Band υ cm^{-1}	Functional grouping
1170-1300	
2850-3000	
1020-1220	
650-1175	
1630-1710	
3074-1708	
1293-585	

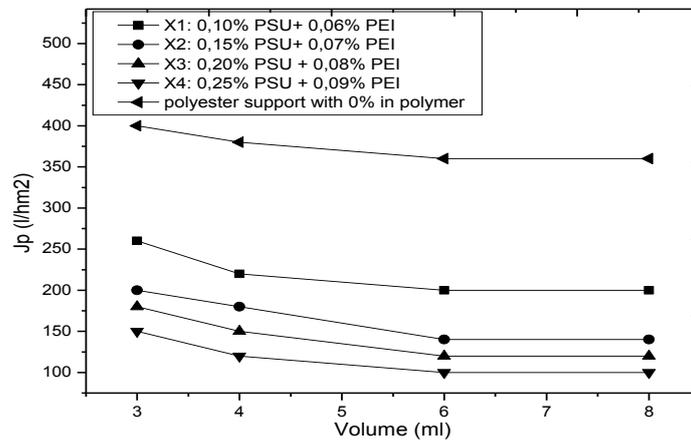**Figure 10:** Flow rate in view of pressure.

Figure 11: Flow rate in view of volume.

In figure 10, we observed two phases: a heating phase and a stationary phase. While in Figure 11 we observed a decreasing stage and a stationary phase. This is probably due to saturation of the pores of the membrane.
In parallel, we noticed in the case of membrane resulting from massic collodion PSU (0.10) / PEI (0.06) the best hydrodynamic properties.

3.2.3. The selectivity of the membrane
Figure 12 below shows the selectivity of the composite membrane in view of the different molar masses of dextran.
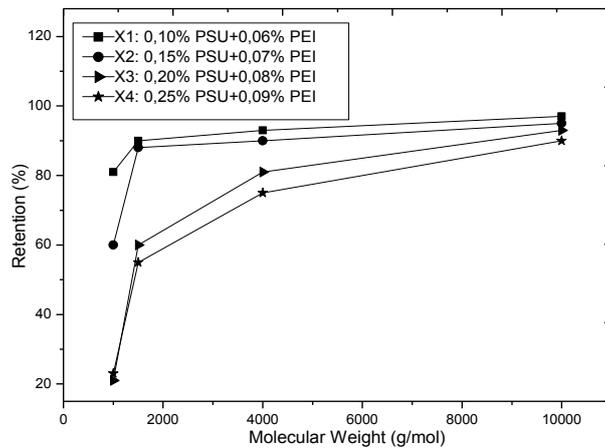
Figure 12: The retention curves of composite membranes obtained from mixtures of different masses of PSU and PEI.

We notice that two phases are distinguished. An increasing phase which corresponds to the molecular mass between 1000 and 4000 g / mol and a stationary phase which corresponds to the higher molecular weight of 4000 g / mol. In parallel, we observed a better retention in the case of membrane resulting from massic collodion PSU (0.10) / PEI (0.06).

3.2.4. The morphology of the membrane

Figure 13 shows the morphology of the porous virgin technological support before and after being coated with the thin active layer of different mass percentage. This layer has been studied by using scanning electron microscope (SEM).
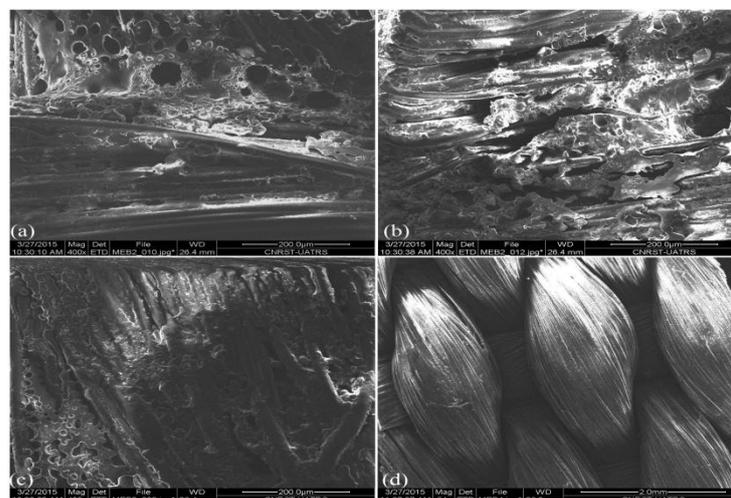

Figure 13: The morphology of the following membranes: 0.10% PSU + 0.06% PEI (a); 0.15% PSU + 0.07% PEI (b); 0.20% PSU + 0.08% PEI (c) and the porous technological support with 0% of polymer (d).

3.2.5. Tensile testing of the optimum membrane

In most cases, macromolecular materials are used in the solid state. It is therefore necessary to define the techniques in order to characterize the mechanical properties such as flexibility, rigidity, elasticity and impact strength. In general, we distinguish between three types of power solid macromolecular materials:

- Elastomers;
- Thermoplastic;
- Thermosetting.

Tensile tests help to explain the mechanical behavior of the studied materials (Figure14).
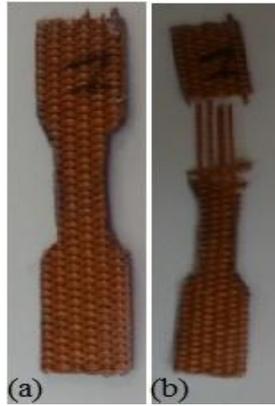
Figure 14: Samples before (a) and after (b) the tensile test.

Figure 15 shows the tensile test performed on the porous technological support before (curve a) and after (curve b) coating.
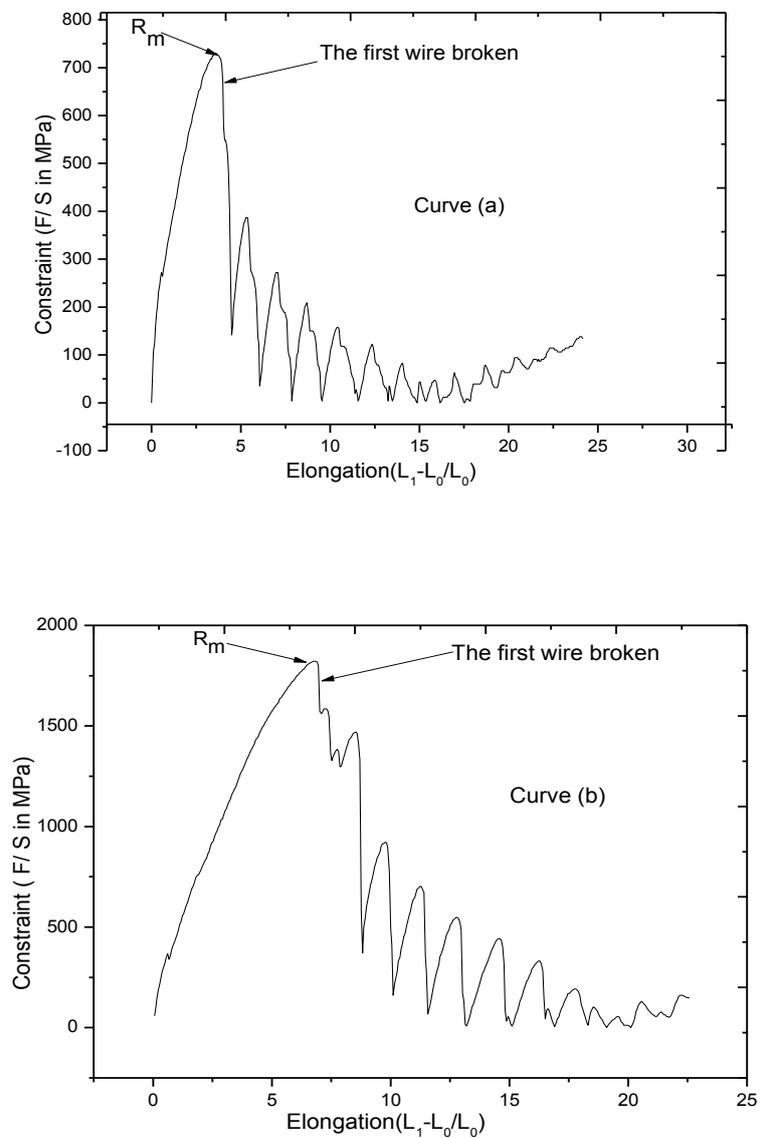

Figure 15: The conventional traction curves before (a) and after (b) coating.

The Curves (a) and (b) represent the behavior of the most thermoplastic polymers, particularly amorphous polymers, at room temperature. These are ductile materials. From the curves above, an elastic area there is observed with a maximum tensile strength R_m = 740 MPa (a) and R_m = 1850 MPa for (b), then the appearance of a decrease, called necking.

Necking is represented by a drop of the curve to a low yield point. This is called a draw hook. Therefore the sample is deformed at, almost constant stress until breakage. The stress at high yield stress and strain at break are the main features of this essay.

3.2.6. Ultrafiltration state in the treatment of rinsing / padding bath of textile

Figures 16 and 17 illustrate the rate of COD, conductivity and color of the two colored solutions after the ultrafiltration process. Over 90% of the color was retained by the membrane at a transmembrane pressure above 6 bars. The good retention of COD was also obtained (>80%).

The transmembrane pressure varied from 2 to 7 bars during the filtration. The equations for the linear portions of the obtained traces are shown in the corresponding figures (16 and 17). It is obvious that the membrane flux was lower for the corresponding pure water. This is a phenomenon that can be due to the presence of organic and inorganic solutes retained on the surface of the membrane which also cause the polarization of concentration [39].

The dissolved organic and inorganic compounds are the main causes of membrane fouling. This can reduce the permeate flux and consequently influence the retention of organic compounds [40]. The factors influencing membrane fouling can be classified into three categories: the membrane properties, the operating parameters and the rinsing waste water [41]. Membrane fouling is a complex phenomenon with multiple origins and still poorly understood.

This fouling results from the interaction between the fouling material and the membrane but also between the materials themselves. It was recognized that the electrostatic interaction is a hydrophobic / hydrophilic interaction between the membrane and the fouling materials. This interaction has a significant impact on membrane fouling. This is particularly true for the more difficult or related clogging problems caused by the adsorption of natural organic materials and polymers of the membrane.

The balance of electrostatic repulsion forces and the hydrophobic adhesion determines the results of the membrane as well as the efficiency of chemical cleaning.
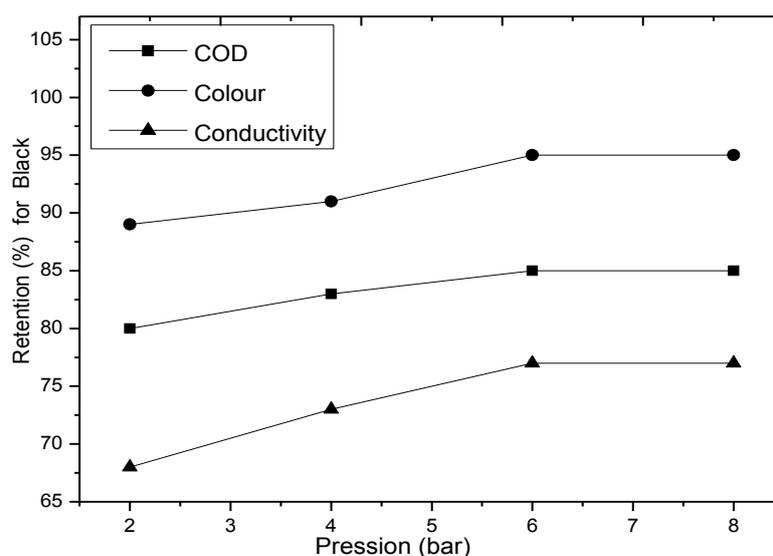

Figure 16: The retention rates in view of transmembrane pressure by the membrane of massic collodion PSU (0.10) / PEI (0.06).
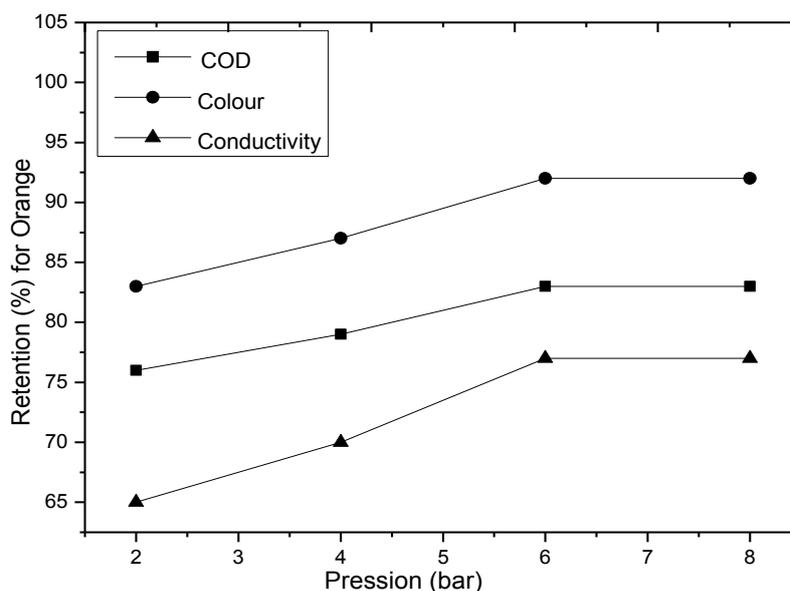
Figure 17: The retention rates in view of transmembrane pressure by the membrane of massic collodion PSU (0.10) / PEI (0.06).

Dye molecules can be adsorbed onto the surface of the membrane which affect the permeate flux due to physicochemical interactions namely the hydrophobic interactions (dispersion forces), the polar interactions (dipole forces) and the transfer of load (hydrogen bonding).

The organic adsorption is due to the ability to reduce the repulsive interaction between the soil (organic, inorganic and colloidal) and the membrane as well as between the dirt themselves. After the adsorption has taken place, the dye aggregates would build a multiple underlayer and finally most of the dye concentration would increase and be compacted after the preparation of the undercoat.

During the penetration of the dye solution, the adsorption of the dye molecules in the membrane surface and inside the pores contributes to the reduction of the pore size of the membrane and therefore participates in the modification of the coefficient of pure water permeability and retention of the dye. The dye molecules include amino, hydroxyl and sulfonic groups as substituents bonded to the aromatic nuclei. These functional groups may interact with the membrane which also has functional groups as carboxyl, amide and amino.

The nature of the membrane material, type of solute, the solute concentration, flow rate and pH are the most important parameters which can determine the adsorption of the dye [39] and the mixtures of NaCl. In each instance, there are different electrostatic interactions between dye, NaCl and the membrane. Salt retention and the conductivity rate increase with the transmembrane pressure that acts particularly on the salt retention.

When the membrane is placed in contact with an ionic solution (colored solution or a textile effluent), the association and dissociation of the functional group on the surface of the membrane leads to the formation expenses. Thus, the generated load can be related to ionization of the functional group existing on the surface of the membrane which greatly depends on the pH and which leads to the dissociation of the acid and the base. At pH = 10, if the generated charge is negative, a repulsive force with negative ions appears and leads to a decrease of the conductivity value.

Another interpretation may also be taken into consideration:

Na^+ has a high affinity for sulfonic groups to complex with anionic dye molecules and their partially neutralized negative charge. Due to the oppositely charged solutes (cationic salt particles and anionic dye), electrostatic interactions prevent the formation of complex with high molecular weight between the dye molecules and the salt particles. This can affect the conductivity of the solution.

In fact, the chemical structure (shape, number of active groups, stability of a negative charge) of the dye could give the difference in affinity of these reactive dyes vis-a-vis the surface of the membrane.

On the one hand, the negatively charged membranes increases the electrostatic repulsion of anionic compounds and secondly the studied dyes are characterized by having sulfonic groups (anionic), which interact strongly with the negative charge of the membrane. This phenomenon warrants high color retention and improves the retention of the salt which affects the conductivity retention ratio.

These results are convincing (most critical) in terms of environment, economics and industrial management for the treatment of textile dyes by the ultrafiltration process. Our study is a preliminary work that predicts the performance of ultrafiltration in the treatment of industrial effluents from textile using similar experimental conditions.

Conclusions

In this study, we have developed in a first step, a composite semi-permeable membrane based on a thermoplastic polymer mixture at various weight percentages cast on a technological permeable support based on polyester.

The study of membrane separation efficiency was evaluated according to three parameters determining retention (color, COD and conductivity) for the treatment of solutions of baths of rinsing/ padding of textile.

The addition of chemicals such as the sequestering and others have not been required to improve the permeate quality.

The following conclusions are based on experiences from:

- Retention rates (> 90%), COD high (> 80%) were obtained for solutions of baths of rinsing / padding of textile;
- Better conductivity rates (> 75%) and strong color retention;
- Good mechanical properties of 740 MPa to 1850 MPa after the coating;
- UF process was chosen as an appropriate and an effective method to reduce the conductivity, the COD and color retention in textile effluents.

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