APPLICATION OF PVDF ULTRAFILTRATION MEMBRANES TO TREAT AND REUSE TEXTILE WASTEWATER

V. Buscio, M. Crespi, C. Gutiérrez-Bouzán*

Institut d’Investigació Tèxtil i Cooperació Industrial de Terrassa (INTEXTER),
Universitat Politècnica de Catalunya-BarcelonaTech (UPC).
C/ Colom 15, 08222, Terrassa-Spain.

Corresponding author: Tel.: +34 93 739 80 08; fax: +34 93 739 82 72.
E-mail addresses: gutierrez@intexter.upc.edu

Abstract

In this work, the feasibility of polyvinylidene difluoride (PVDF) ultrafiltration membranes to treat textile wastewater was studied. The C.I. Disperse Orange 30 and C.I. Disperse Rubine 73 were selected as pollutant for the membrane filtration study. The results showed about 90% and 96% of COD decrease and dye removal, respectively. In addition, very low fouling was observed which demonstrated the feasibility of applying this type of membranes to treat textile wastewater. Finally, after the membrane treatment, 100% of the obtained permeate was reused. Fabrics dyed with the reused water were evaluated respect to references carried out with softened tap water. No significant colour differences were observed between reference fabrics and the fabrics dyed with the permeate.

Keyword: Textile wastewater; Disperse dyes; Water reuse; Colour removal; Membrane treatment
1- Introduction

Dyes are widely used in different industries such as textile, leather, paper, plastics, and food [1,2]. There are more than 100,000 different synthetic dyes and their annual production is about $7 \cdot 10^5$ tonnes [3]. Particularly, the textile industry consumes $10^7$ kg of dye per year [4] and 15% of dyes consumed are discharged into the textile wastewater [5] causing serious problems upon aquatic flora and fauna [6]. Dyes are classified according to their chemical structure and how they are applied in the dyeing process [7]. The most common dyes are reactive, acid, direct, vat and disperse [8,9]. Disperse dyes are non-ionic aromatic compounds with low solubility in water [10]. They are widely used in the dyeing of polyester fibre. This fibre represents about the 50% of the total world textile fibre consumption [11].

In general, dyes are difficult to remove because they are stable to light and oxidizing agents, and with low biodegradability [12,13]. The most used technologies to treat wastewater containing dyes are based on biological [14,15] or/and physical-chemical processes [16–18]. Although these treatments are able to meet legislative requirements, they do not allow water reuse in textile processes [19,20]. The reuse of textile wastewater is an important challenge since between 60 and 100 L of water are needed to produce a kilogram of textile product [21]. Other treatments such as photo-fenton [22], photocatalytic [23] and electrochemical [24] have been studied. These methods provided high colour removal but the generation of by-products and the high cost are their main limitations [25].

Membrane technology has shown great potential to treat textile wastewater as it can be applied to remove different kind of dyes. In addition, it allows both the reuse of auxiliary chemicals and some concentrate dyes [26] and produces a permeate with high quality, which can be reused in new textile processes [27]. In general, reverse osmosis (RO) [28,29] and nanofiltration (NF) membranes [30,31] are the most studied in the treatment of effluents containing dyes. The main limitation of membrane processes such as NF and RO is the decline of permeate flux caused by the accumulation of
particles on the membrane surface [32]. This phenomenon is especially observed in RO membrane resulting in an increase of the treatment cost [33,34]. Ultrafiltration membranes (UF) exhibit low fouling and high efficiency to separate chemicals with high molecular weight or insoluble dyes like disperse.

On the basis of these considerations, the aim of this work is study the feasibility of PVDF ultrafiltration membranes to treat textile wastewater containing disperse dyes. Two different disperse dyes, C.I. Disperse Orange 30 (DO30) and C.I. Disperse Rubine 73 (DR73) were selected for the membrane filtration study. Subsequently, the permeate was reused in new polyester dyeings. Finally, fabrics dyed with the reused effluent were evaluated respect to references carried out with softened tap water.

2- Experimental

2.1- Reagents

Two disperse dyes provided by Archroma-Spain were selected for the study of permeate reuse: C.I. Disperse Orange 30 and C.I. Disperse Red 73. Figure 1 shows their chemical structures.

![Figure 1- Chemical structure of C.I. Disperse Orange 30 and C.I. Disperse Red 73](image)

To determine the dye concentration in the permeate, N,N-dimethylformamide (purity 99.5%, Scharlau) and softened tap water were used as solvents. The pH of synthetic effluents dye baths was adjusted with NaOH and HCl. Sodium hypochlorite solution (6-14% active chlorine) acquired from Sigma-Aldrich was used for the membrane cleaning.
2.2- Synthetic effluents preparation

To simulate the effluents discharged after the dyeing process, four solutions of either DO30 or DR73 were prepared in softened tap water. The pH of the effluents was adjusted at 6.0-6.5. The main characteristics of the effluents used in this study are shown in Table 1.

<table>
<thead>
<tr>
<th>Dye</th>
<th>pH</th>
<th>Conductivity (µS·cm⁻¹)</th>
<th>COD (mg·L⁻¹)</th>
<th>Dye concentration (mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO30</td>
<td>6.4</td>
<td>1321</td>
<td>120.6</td>
<td>77.4</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>1359</td>
<td>102.5</td>
<td>76.1</td>
</tr>
<tr>
<td>DR73</td>
<td>6.4</td>
<td>1557</td>
<td>106</td>
<td>77.2</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>1438</td>
<td>109</td>
<td>77.8</td>
</tr>
</tbody>
</table>

2.3- Membrane Treatment

In this work, a PVDF hollow fibre membrane module ZeeWeed-1 (ZW-1) (GE Power & Water, Canada) was used. Its main specifications and operation characteristics are shown in Table 2.

<table>
<thead>
<tr>
<th>Table 2- ZW-1 Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
</tr>
<tr>
<td>Configuration</td>
</tr>
<tr>
<td>Membrane Surface</td>
</tr>
<tr>
<td>Pore size</td>
</tr>
<tr>
<td>Maximum Transmembrane Pressure (TMP)</td>
</tr>
<tr>
<td>Typical Operating TMP</td>
</tr>
<tr>
<td>Maximum TMP Back Wash</td>
</tr>
<tr>
<td>Operating pH range</td>
</tr>
</tbody>
</table>

A laboratory scale reactor was built to position the membrane module, according to its geometry and specific requirements (Figure 2). The membrane reactor was a 20 L cylindrical vessel. It was fed from a 20 L tank by a centrifugal pump. A peristaltic pump
was used for the permeate effluent. The membrane module had an air inlet with the purpose to decrease the fouling. The laboratory scale reactor operated in cycles of 15 minutes of filtration and 30 seconds of backwashing with permeate.

![Figure 2- Laboratory scale reactor: a) Membrane reactor, b) Feed tank, c) Permeate tank](image)

The membrane treatment was carried out at constant TMP (0.2 bar) and at room temperature. A concentration factor of 10 was selected for this study. Finally, after each filtration process, the membranes were cleaned with a sodium hypochlorite solution (5 mg·L⁻¹).

### 2.4- Permeate reuse

The reuse dyeing tests were performed in a laboratory Ti-Color dyeing machine (Integrated Color Line) under the following conditions: 10 g of polyester fabric, dye concentration 3% o.w.f (over weight of fibre) and liquor ratio 1:20 (1 g fibre/20 mL dye bath). The dyeing method conditions are shown in Figure 3.
2.5- Analytical methods and Measurements

The permeate flux was determined to evaluate the membrane fouling. It was determined by measuring the permeate volume collected in a certain period of time (Eq. 1)

\[ J = \frac{V}{A \cdot \Delta t} \]  

Where \( J \) is the permeate flux (L·m\(^{-2}\)·h\(^{-1}\)), \( A \) is the effective area of the membrane (m\(^2\)) and \( V \) is the collected volume in a time interval \( \Delta t \) (L·h\(^{-1}\)).

The dye removal (\%\( R_{dye} \)) was calculated from concentrations of feed and permeate using the Eq. 2:

\[ \%R_{dye} = \left( \frac{C_f - C_p}{C_f} \right) \cdot 100 \]  

where \( C_f \) and \( C_p \) are the concentrations of dye in feed and permeate, respectively. The dye was dissolved in an aqueous solution, which contained N,N-dimethylformamide 1:1, and determined with UV-Vis spectrophotometer UV-2401 (Shimadzu Corporation) at the maximum wavelength of the visible spectrum (430nm for DO30 and 528nm for RD73). For each dye, the calibration curve was:

DO30: \( \text{Abs} = 0.0235 \cdot \text{conc} - 0.0046 \) and \( R^2 = 0.9997 \)

DR73: \( \text{Abs} = 0.0483 \cdot \text{conc} - 0.0087 \) and \( R^2 = 0.9996 \)
COD was determined according to the methods recommended by American Public Health Association [33]. The COD reduction (%RCOD) was calculated using the Eq. 3:

\[ %R_{COD} = \left( \frac{(COD_f - COD_p)}{COD_f} \right) \cdot 100 \]  \hspace{1cm} (3)

where COD\(_f\) and COD\(_p\) are the COD values in feed and permeate respectively.

The conductivity was measured following the method 2510 B [35] with a conductivity meter GLP 31 (CRISON). The pH was determined according to the method 4500 H+B [35] using a pH meter GLP 21 (CRISON).

The quality of dyed fabrics was studied from colour differences (DE\(_{CMC(l:c)}\)) using a Macbeth Colour Eye 7000A spectrophotometer. The difference in colour was determined in conformity with the Standard UNE-EN ISO 105-J03 [36].

The equation for DE\(_{CMC(l:c)}\) describes an ellipsoidal volume with axes in the direction of lightness (L), chroma (C), and hue (H) centered about a standard. Colour difference is composed of three components:

- **Lightness component** (DL\(_{CMC}\)) that is weighted by the lightness tolerance (DL*/lSL). If DL\(_{CMC}\) is positive, the reused dyeing is lighter than the standard. If DL\(_{CMC}\) is negative, the reused dyeing is darker than the standard.

- **Chroma component** (DC\(_{CMC}\)) that is weighted by the chroma tolerance (DC*\(_{ab}/cSc\)). If DC\(_{CMC}\) is positive, the reused dyeing is more chromatic than the standard. If DC\(_{CMC}\) is negative the reused dyeing is less chromatic than the standard.

- **Hue component** (DH\(_{CMC}\)) that is weighted by the hue tolerance (DH*\(_{ab}/S_S\)). It describes the difference between the hue angle of the standard and the hue angle of the reused dyeing in a polar coordinate.

Colour difference is calculated from the Eq. 4:

\[ DE_{CMC(l:c)} = \sqrt{\left( \frac{DL^*}{lSL} \right)^2 + \left( \frac{DC^*}{cSc} \right)^2 + \left( \frac{DH^*}{S_S} \right)^2} \]  \hspace{1cm} (4)

The lengths of the semi axes of the ellipsoid are calculated from the values L*\(_f\), C*\(_{ab,R}\) and h*\(_{ab,R}\) that correspond to the reference as follows:
\[ S_L = 0.040975 \frac{L^*_R}{(1+0.01765 L^*_R)} \text{ if } L^*_R \geq 16 \text{ or } S_L = 0.511 \text{ if } L^*_R < 16 \quad (5) \]
\[ S_C = [0.0638 \frac{C^*_{ab,R}}{(1+0.0131 C^*_{ab,R})}] + 0.638 \quad (6) \]
\[ S_H = (FT+1-F)S_C \quad (7) \]
where
\[ F = ((C^*_{ab,R})^4/(C^*_{ab,R})^4+1900))^{1/2} \quad (8) \]
\[ T = 0.36 + 0.4 \cos(35+h_{ab,R}) \text{ if } h_{ab,R} \geq 345^\circ \text{ or } h_{ab,R} \leq 164^\circ \quad (9) \]
\[ \text{or } T = 0.56 + 0.2 \cos(168+h_{ab,R}) \text{ if } 164^\circ < h_{ab,R} < 345^\circ \quad (10) \]

In summary, a dyeing is considered acceptable when the DE\textsubscript{CMC}(l:c) value is lower than 1, measured with Macbeth Colour Eye 7000A spectrophotometer with respect to a reference sample.

3- Results and Discussion

3.1- Membrane treatment

The synthetic dye baths were treated by means of an ultrafiltration membrane laboratory scale reactor. The trans-membrane pressure was set at 0.2 bar. Along the filtration process, the permeate flux remained constant at 20.9 L·m\textsuperscript{-2}·h\textsuperscript{-1} and 21.7 L·m\textsuperscript{-2}·h\textsuperscript{-1} for DO30 and DR73 respectively. The low fouling observed in this laboratory scale reactor showed the feasibility of applying this type of membranes to treat textile effluents.

The efficiency of the membrane process in the treatment of textile effluents containing disperse dyes was determined by means of permeate characterization. Permeate samples were taken and analysed daily.

Both effluents showed similar behaviour producing high quality permeate. The pH and conductivity values did not change with respect to the initial effluent due to the low retention of inorganic ions by ultrafiltration membranes.

The treatment of DR73 exhibited 92% COD reduction and 97% dye removal (8.5 mg·L\textsuperscript{-1} and 2.8 mg·L\textsuperscript{-1} respectively). Similar results were also achieved for the DO30 effluent: 90% of COD decrease (10.5 mg·L\textsuperscript{-1}) and 95% of dye removal (3.8 mg·L\textsuperscript{-1}).
3.2- Selection of reference fabric

Replicates of same dyeing can exhibit slight differences in their colour coordinates. For this reason, before the permeate reuse study, it is important to select properly for each dye the reference fabric. With this purpose, colour differences were measured and compared between replicates. All experiments were run in triplicate.

Table 3 shows the values of $\text{DE}_{\text{CMC}(2:1)}$, DL, DC and DH for fabrics dyed with DO30 and softened tap water. As it was expected, low values of $\text{DE}_{\text{CMC}(2:1)}$ were found between replicates (<0.4). According to the results, the lowest $\text{DE}_{\text{CMC}(2:1)}$ were found when replicates 1 and 3 were compared with the replicate 2. For this reason, the replicate 2 was selected as the reference fabric for DO30 dye and it was used with this purpose in the permeate reuse study.

<table>
<thead>
<tr>
<th>$\text{DE}_{\text{CMC}(2:1)}$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>DL</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>*</td>
<td>0.18</td>
<td>0.38</td>
<td>1</td>
<td>*</td>
<td>-0.03</td>
<td>-0.13</td>
</tr>
<tr>
<td>2</td>
<td>0.13</td>
<td>*</td>
<td>0.21</td>
<td>2</td>
<td>0.03</td>
<td>*</td>
<td>-0.10</td>
</tr>
<tr>
<td>3</td>
<td>0.28</td>
<td>0.22</td>
<td>*</td>
<td>3</td>
<td>0.13</td>
<td>0.14</td>
<td>*</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DC</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>DH</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>*</td>
<td>-0.06</td>
<td>-0.13</td>
<td>1</td>
<td>*</td>
<td>-0.17</td>
<td>-0.34</td>
</tr>
<tr>
<td>2</td>
<td>-0.10</td>
<td>*</td>
<td>-0.07</td>
<td>2</td>
<td>0.08</td>
<td>*</td>
<td>-0.17</td>
</tr>
<tr>
<td>3</td>
<td>-0.03</td>
<td>-0.11</td>
<td>*</td>
<td>3</td>
<td>0.24</td>
<td>0.12</td>
<td>*</td>
</tr>
</tbody>
</table>

The same procedure was carried out with DR73 dye (Table 4). In this case, $\text{DE}_{\text{CMC}(2:1)}$ were higher than $\text{DE}_{\text{CMC}(2:1)}$ with DO30 which means that the reproducibility of fabrics dyed with DR73 was lower. This fact was taken into account to evaluate the feasibility of permeate reuse. The replicate 1 was selected as the reference for DR73 dye.
Table 4- Colour differences obtained in reference fabrics dyed with DR73

<table>
<thead>
<tr>
<th>DE_{CMC(2:1)}</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>DL</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>*</td>
<td>0.63</td>
<td>0.19</td>
<td></td>
<td>1</td>
<td>*</td>
<td>-0.41</td>
</tr>
<tr>
<td>2</td>
<td>0.55</td>
<td>*</td>
<td>0.59</td>
<td>2</td>
<td>0.34</td>
<td>*</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>0.28</td>
<td>0.65</td>
<td>*</td>
<td></td>
<td>3</td>
<td>0.00</td>
<td>-0.29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DC</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>DH</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>*</td>
<td>-0.38</td>
<td>0.08</td>
<td></td>
<td>1</td>
<td>*</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>0.28</td>
<td>*</td>
<td>0.47</td>
<td>2</td>
<td>-0.33</td>
<td>*</td>
<td>-0.14</td>
</tr>
<tr>
<td>3</td>
<td>-0.19</td>
<td>-0.58</td>
<td>*</td>
<td></td>
<td>3</td>
<td>-0.20</td>
<td>-0.10</td>
</tr>
</tbody>
</table>

3.3- Permeate reuse

The treated effluents were used in order to study the feasibility of the permeate reuse. The dyeings were carried out with 100% of permeate. Dyeings obtained were evaluated with respect to a reference dyeing (selected in section 3.2).

Table 5 exhibits the values measured in the permeate reuse study. Fabrics referenced as 1-3 were dyed with the permeate obtained in the treatment of synthetic effluents containing DO30 dye. Fabrics referenced as 4-6 used permeate from synthetic effluents containing DR73 dye.

Table 5- Colour differences values in the permeate reuse study

<table>
<thead>
<tr>
<th>DO30 dye</th>
<th>DR73 dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE_{CMC(2:1)}</td>
<td>DL</td>
</tr>
<tr>
<td>1</td>
<td>0.54</td>
</tr>
<tr>
<td>2</td>
<td>0.55</td>
</tr>
<tr>
<td>3</td>
<td>0.64</td>
</tr>
<tr>
<td>4</td>
<td>0.84</td>
</tr>
<tr>
<td>5</td>
<td>0.87</td>
</tr>
<tr>
<td>6</td>
<td>0.82</td>
</tr>
</tbody>
</table>

From Table 5, it can be observed that dyeings showed DE_{CMC(2:1)} lower than 1, which is the maximum value accepted at industrial scale. For dyeings 1-3, DE_{CMC(2:1)} values
were mainly due to the influence of DC. The negative values of DC and DL mean that dyeings were less chromatic and darker than the replicates.

Regarding dyeings 4-6, fabrics dyed with permeate from synthetic effluents containing DR73 dye, exhibited \( \text{DE}_{\text{CMC}(2:1)} \) higher than dyeings 1-3. This fact could be attributed to the reproducibility of the dyeings with this dye, which it was discussed in section 3.2. In this case, the three components (DL, DC and DH) have influenced in the value of \( \text{DE}_{\text{CMC}(2:1)} \). The positive values of DC and DL mean that dyeings were more chromatic and lighter than the replicates.

4- Conclusion

Synthetic textile effluents containing disperse dyes were treated by means of PVDF ultrafiltration membrane.

The membrane treatment provided up to 90% and 96% of COD decrease and dye removal, respectively. In addition, no fouling was observed during the experiments. According to the results in the permeate reuse study, the dyeing performed with 100% of permeate exhibited similar characteristics than dyeing with softened tap water. The colour differences values were lower than 1 and therefore they met the established acceptance range. Due to the huge amounts of water consumed in the textile industry, the feasibility of UF membranes to treat and reuse textile effluents is a promising result.

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References


