Removal of Direct Blue Dye from Aqueous Solution Using New Polyurethane - Cellulose Acetate Blend Micro-filtration Membrane

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From the ecological point of view, the waste waters that come from the industries which are using dyes represent a problem because these dyes have carcinogen, teratogen and mutagen effects. In this paper we studied the removal of Direct Blue dye (DB) from water using a membrane separation process, more exactly frontal micro-filtration. The solutions of DB (which is an anionic, disazo dye) had concentrations between 2.7·10⁻⁴M and 2.21·10⁻⁵M. The cationic surfactant cetylpyridinium chloride (CPC) was used at submicellar concentration of 10⁻⁴M. The optimum ratio of DB/CPC concentrations for the formation of micellar aggregates dye – surfactant was conductometrically and spectrophotometrically determined. The blend was then microfiltrated using a cellulose acetate – polyurethane blend membrane with a pore dimension of 0.86μm. The separation performance of the blend membrane related to the dye solution was determined by calculating the retention degree of the dye based on the initial concentration and respectively on the filtrate solution concentration. Thereby, retention degree values between 25.6% and 95% were obtained for the microfiltrated DB solutions. Adding CPC to the DB solutions created an interaction between CPC monomers and dye aggregates which formed mixed micelles. Thus, the retention degree increased to values between 64-100%.

Keywords: microfiltration, direct blue dye, cetylpyridinium chloride, blend membrane

Worldwide there are over 100 000 dyes commercially used and annually there are produced more than 7·10⁵ tones of dyes. From the ecological point of view, the waste waters that come from the industries which are using dyes are a major problem for the textile industry. For this purpose, biological and physico-chemical methods are being used. The physico-chemical processes include electro-flotation, flocculation, electro-kinetic coagulation, precipitation, ion exchange, irradiation, electrochemical destruction, ozonation and membrane filtration. Biological methods include aerobic and anaerobic digestions use microorganisms [2, 4-6].

One of the most effective and economical methods used in removal of toxic metal ions and dissolved organic compounds, is micellar-enhanced ultrafiltration (MEUF). This method was introduced in 1980 for the removal of copper ions from wastewaters [10]. Micellar-enhanced ultrafiltration (MEUF) is a surfactant based separation process. In the MEUF process, the surfactant is added to the polluted aqueous solution containing metal ions and/or organic solutes [1, 3, 11-16]. When the surfactants are added to the contaminated solution, at levels near critical micellar concentration (CMCs), surfactant monomers will assemble to form micelles. The micellar solution can then be filtered using membranes to remove the aggregates containing the pollutant.

For many organic substances, surfactants induce changes in the absorption and fluorescence spectra, protonation constants, and other physico-chemical properties, like surface tension, conductivity and viscosity. The changes can be observed below and above critical micellar concentration (CMCs) [17 - 19]. The utilization of a single ionic surfactant is possible to remove organic and inorganic compounds simultaneously. Cetylpyridinium chloride (CPC) is a cationic surfactant which can be used to remove dissolved organic compound from waste waters [20, 21].

Direct dyes have been used to dye cellulose. Most direct dyes have disazo and trisazo structures and they are the largest class of dyes with the greatest variety of colors. These very water soluble azo dyes, at low concentrations (10 – 50 mg/mL), can cause highly colored waste streams [8]. Direct Blue (DB) dye is an anionic, disazo dye.

In this paper we studied the removal of Direct Blue dye from synthetic aqueous solutions using a membrane separation process, more exactly frontal micro-filtration. We studied the use of polyurethane – cellulose acetate blend micro-filtration membrane for the micro-filtration of surfactant – dye solutions, according with MEUF procedure.

Experimental part

Materials and methods

The anionic, disazo direct blue 1 (DB) dye (MW 1008.859) was purchased from Sigma – Aldrich (scheme 1). The cationic surfactant, cetylpyridinium chloride monohydrate (CPC) was purchased from Sigma – Aldrich (MW 358.01) (scheme 2).
The synthetic aqueous solutions of Direct blue dye had the concentrations between $2.7 \times 10^{-6}$ M and $2.21 \times 10^{-5}$ M; they were prepared daily by dilution from bulk solutions. The cationic surfactant was used at sub-micellar concentration, at $10^{-4}$M. The formation of micellar aggregate surfactant – dye takes place, was studied by conductometric method, using an Inolab conductometer 730 and respectively by spectrophotometric method, using an UV-VIS 2450 Shimadzu spectrophotometer.

The mix (DB – CPC solutions) was then microfiltered using new polyurethane – cellulose acetate blend membrane [22] that has the characteristics presented in table 1.

Investigations for determining the purification rate of dye solutions were performed using a synthetic solution of different concentrations with the aim of a micro-filtration laboratory installation with frontal feeding, presented elsewhere [22, 23].

The separation performance of the membrane related to direct blue dye solutions was determined by calculating the purification rate of the dye solution based on the initial concentration and filtrate solution concentration respectively according to the relationship:

$$G\% = \frac{C_1 - C_2}{C_1} \times 100$$

where:
- $C_1$ – initial solution concentration;
- $C_2$ – filtered solution concentration.

The measures were carried out at $\lambda = 574$ nm using a METERTECH SP 870 PLUS spectrophotometer. The reference curve is mathematically described by the equations (2), with a correlation coefficient $R^2 = 0.9996$:

$$A = 12281 \times C$$

where:
- $A$ – absorbance;
- $C$ – direct blue dye concentration (mol/L)

**Results and discussions**

In aqueous solutions the formation of micelles is detected by some changes in physical properties like conductivity. For the direct blue dye solutions, it can be observed (fig. 1) first an increase of specific conductivity due to adding of cetylpyridinium chloride, and then it follows a decrease of the specific conductivity.

The dyes can be, themselves, considered amphiphilic molecules, because their nonionic part has grafted functional ionic groups. But, because they do not have long-chain alkyl groups they present a weak surface activity and do not form micelles in water [18]. The increase of the concentration of a dye can lead to the formation of aggregate (dimers, trimers), depending on their hydrophobic/hydrophilic balance.

The adding of CPC at a sub-micellar concentration to the DB dye, with a $2.5 \times 10^{-5}$M concentration, leads to an interaction between the CPC monomers and dye aggregates, and also, the formation of mixed micelles. The decrease of the specific conductivity (fig. 1) is due to the formation of the mixed micelles dye – surfactant.

The changes in absorption spectra, presented in figures 2 and 3, are due to the interactions between the dye and the surfactant.

From the figures 2 and 3, it can be observed a significant increase of the absorbance in visible domain, because of the interaction between the cetylpyridinium chloride and the azo groups of the dye molecules. As the concentration of CPC is growing, more and more dye molecules create an interaction with the surfactant, and in this way the $\pi-\pi$ conjugation is blocked.

The decrease of the absorption in the spectra for the solution 1:1, DB ($2.5 \times 10^{-5}$M) – CPC ($1 \times 10^{-4}$M) concurs with the decrease of specific conductivity, proving the formation of mixed micelles.

The purification rate obtained at the microfiltration of the DB dye solutions is presented in figure 4, and has values between 25.6 and 95 %. The adding of CPC, at a sub-micellar concentration, to the DB dye solutions leads to an increase of the purification rate. For the molar ratio of 1:4, DB – CPC the purification rate is between 69 % and 100 % (fig.5). The best purification rate was obtained at the micro-

![Scheme 1. Direct Blue 1 dye](https://example.com/scheme1.png)

![Scheme 2. Cetylpyridinium chloride monohydrate](https://example.com/scheme2.png)

**Table 1**

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Inflation rate, G.u., (B_{water}/B_{membrane})</th>
<th>Porosity, ϵ, %</th>
<th>Water permeability, (P, \text{m}^3/(\text{m}^2\cdot\text{h}\cdot\text{atm}))</th>
<th>Average pore diameter, (d_m, \mu\text{m})</th>
<th>Thickness, (t, \mu\text{m})</th>
</tr>
</thead>
<tbody>
<tr>
<td>COMP</td>
<td>2.803</td>
<td>73.71</td>
<td>0.16</td>
<td>0.86</td>
<td>175</td>
</tr>
</tbody>
</table>

**Fig. 1. Specific conductivity of Direct blue dye in the presence of CPC**
filtration of DB dye – CPC solutions, molar ratio 1:8 (fig. 6). As it can be observed in figure 6, the purification rate was 100% for the solution with the $2.77 \times 10^{-6}$ M concentration and for the solution with $5.54 \times 10^{-6}$ M concentration. The CCP monomers and the dye aggregate interact and lead to the formation of the DB dye – CPC micellar aggregate. The formation of these micellar aggregate determines the obtaining of some purification rates between 64 and 100 % at the micro-filtration of the DB dye - CPC solutions.

In order to remove efficiently reactive dyes from a textile effluent it is necessary to have a correlation between the dimensions of dye molecules and the pore diameter of micro-filtration membrane in order to satisfy the compromise between the retention of pollutant and fouling.
of membrane. In opposite way with the aspects presented in this paper concerning the increasing volume of the dye molecules (micellar aggregates dye – surfactant), if the diameter of membrane pores is smaller, as in the case of ultrafiltration membranes, the dye molecules should be broken. In this case is recommended to be used a combination of two advanced processes: ultrasonication (when the dye molecules are partially destroyed), followed by ultrafiltration (when the remaining molecules are retained, avoiding the membrane fouling with initial dye molecules) [24].

Conclusions

The interaction between the dye and the surfactant was studied by two investigation methods, conductometry and respectively spectrophotometry. It was determined the concentration at which the formation of mixed micelles takes place. The purification rate of the dye solutions, for the microfiltration of the DB dye - CPC solutions is bigger than in the case of DB dye solution micro-filtration. It was obtained a purification rate of 100% for the micro-filtration of both molar ratio of 1:4 and 1:8 of DB dye - CPC solutions. The pretreatment of anionic dye with a cationic surfactant leads to the formation of big size micellar aggregates that can be retained on the membrane used in the microfiltration process. New micro-filtration polyurethane – cellulose acetate membrane was used successfully for the filtration of dye – surfactant solutions, avoiding the expensive ultrafiltration membrane and the special operating parameters required such as: high pressure of processing wastewater, using an ultrasonication device for pretreatment, etc.

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References


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