Ultrafiltration of Aqueous Solutions of Food Dye in the Presence of Surfactants

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The objective of the study is the low-pressure membrane process for treating aqueous solutions containing food dyes and surfactants. The influence of surfactants (SDS – sodium dedecil sulphate, SO – sodium octanoate) in the separation of synthetic food dyes (E104 – quinoline yellow) was analyzed. Polysulfone and polysulfone-polyaniline membranes were used. Dye and surfactant concentrations used were 10% (equivalent to 100g/m^3). The pressures used in the ultrafiltration process were 0.1, 0.2 and 0.3 MPa. When dye containing solutions were passed through the membranes, an increase in their flux was observed. The presence of surfactants in the solutions lead to a decline in flux when pressures of 0.1 and 0.2 MPa were used, but an improvement could be seen as the pressure increased to 0.3 MPa, for both dead-end and cross-flow filtration. Using only dead-end alternative, higher fluxes were achieved for both membranes, but it decreases with time due to accumulation on the membrane surface. The use of cross-flow filtration did not allow accumulation on the membrane surface so that the flux was constant in time.The use of anionic surfactants improved the food dye retention. The interactions between membranes and surfactants can be an important factor supporting the efficiency of the ultrafiltration.

Keywords: ultrafiltration, surfactants, dyes, membrabes, composite membranes

Nowadays, asymmetric membranes led to an extraordinary development of the separation processes such as microfiltration, ultrafiltration and reverse osmosis [1]. Dyes are commonly used in different process industries, such as food, beverages and tobacco industry [2]. Wastewater quality depends on the type of process they generate and is variable in time. Dye and surfactant interactions in aqueous solutions led to important development in the view of effluent treatment and water reuse [3-5]. Membrane processes such as ultrafiltration is considered an effective treatment for water regeration [6]. Micellar-enhanced ultrafiltration (MEUF) is one of the various membrane methods for removing traces of organic pollutants (including dyes) by using surfactant solutions [6-8]. The surfactants in aqueous solutions form micelles whose diameters are larger than the UF membrane pores. During the ultrafiltration process, micelles containing solubilised organic dyes are rejected by the membrane. Permeate stream is nearly free of impurities [6,7]. The advantages of micellar-enhanced ultrafiltration are relatively low energy requirement and low pressure driven [8]. The required pressure needed to drive micellar-enhanced ultrafiltration range from 97 to 587 kPa only. Anisotropic membranes ranging in nominal pore size from about 10 to 100 Å (1000 to 50,000 MWCO) can be used to reject surfactant aggregates called micelles. Anionic surfactants are widely use in production of detergent powders. The potential of anionic surfactant in removal of inorganic and organic materials from wastewater by micellar-enhanced ultrafiltration process has confirmed that higher percentage of solute removal was achieved [9-11].

This present work studies a low pressure membrane process for treating aqueous solutions containing both food dye and surfactant.

Experimental part

Materials and methods

Membranes

This study used our laboratory made membranes [12-15]. The ultafiltration membranes developed were polysulfone 12% prepared by phase inversion method, immersion-precipitation technique from a casting solution 12% polysulfone in dimethylformamide coagulated in water solution and a composite membrane polysulfone 12% -polyaniline obtained by polymerizing p-phenylene-diamine in the presence of hydroquinone. Polymer synthesis is proven by forming a black precipitate in solution [16-20].

Experimental solutiojns

This study used SDS – sodium dodecyl sulfate and SO – sodium octanoate, both anionic surfactants. The concentration of SDS amounted to 100g/m^3, below its crtical micelle concentration. The non-ionic surfactants normally constitute clusters of 1000 or more molecules, while ionic surfactants generally only manage to create clusters of 10–100 molecules, because their charges create electrostatic repulsions between head-groups which tend to break the particles apart [9, 10]. The CMC in pure water is 2.0 g/dm^3 at 20°C , and 2300 g/m^3 at 25°C and *p*H value of 7 [4]. The molecular formula of SDS is: $CH_3(CH_2)_{11}OSO_3Na$, and the molecular weight of SDS amounts to 288.38 g/mol. This anionic surfactant is commonly used in cosmetics and pharmaceuticals for its thickening effect and its ability to create a foam. SO - Sodium octanoate or sodium caprylate has the following molecular formula: $C_8H_{15}NaO_2$ and the molecular weight amounts to 166.19 g/mol. Sodium Caprylate is typically used in foods as abinder, emulsifier and also as a pesticide to fight fungal infectins.

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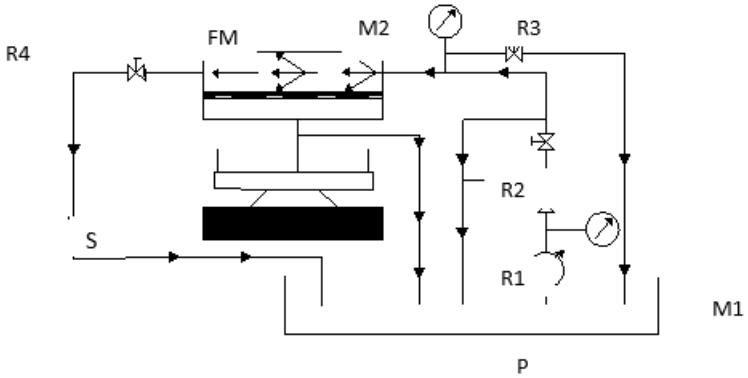

Fig. 1. Pilot set-up: P –centrifugal pump, FM – filtration module, S –digital scale, R – valve, M – manometer

It is also used in pharmaceutical industry and in bio industry. The dye used were food dye, chinoline yellow, also known as E104. The molecular formula of E 104 is: $C_{18}H_{13}NO_{5/8/11}S_{1/2/3}Na_{1/2/3}$ and the molecular weight amounts to 477.38g/mol. It is used as a synthetic colouring agent in food and drink products, as well as in cosmetics.

Ultrafiltration process

The ultrafiltation process in the presence of surfactants was investigated in a pilot laboratory set- up [21,22]. The membrane being tested had a diameter of 36 mm. The pressures used in the ultrafiltration process were 0.1, 0.2 and 0.3 MPa. Permeate volume fluxes and retention coefficients were determined on stady flow conditions. Permeate volume flow was calculated as shown bellow:

$$J = \frac{V}{t \cdot A}(m^3 / m^2 day), \quad (1)$$

where V is the permeate volume (m^3), t stands for the time (day), and A represents the effective membrane surface area (m^2).

Dye retention coefficient (R) was determined as:

$$R = \frac{C_k - C_p}{C_k} \cdot 100(\%) \quad (2)$$

where Ck and Cp denote the dye concentration (g/m^3) in retentate and permeate, respectively. [24-31]

To obtain a wider range of flow a centrifugal pump was used (Q= 40l/min), driven by a variable speed (n=287rpm) and additionally have ordered three valves, R1, R2, R3 used to divert part of the flow to the tank. Bypass sites R1 and R2 were used to divert part of the flow that had to reach the filtration module (FM). A third valve has been fitted in order to eliminate air from the system, but can also be used in the event of carrying out a new bypass. R4 valve ensured the functionality of the laboratory set-up in two ways, dead-end and cross-flow. Various flow rates are thus obtained at the same operating pressure.

The volume of filtrate was measured using a digital scale. The dye concentration in the feed and the permeate was determined using spectophotometric measurements of the absorbance at a wavelength of 575nm.

Results and discussions

The properties of the ultrafiltration membranes regarding transport and separation were determined on solutions containg dyes and solutions containing both dyes and tasks surfactants. Results shown in the figure 2 represent volume flux of polysulfone and polysulfone-polyaniline membranes for dye solution containing SDS and SO, at ΔP = 0.1MPa, 0.2MPa, 0.3MPa, for both dead-end and cross-flow operation process.

Dead-end filtration mode is the most common process for water treatment in the research laboratory. In this mode, the flow of water to be filtered is directed perpendicular to the membrane surface such that water is pushed through the membrane by the applied pressure. If the concentration of targeted species is high, the filtered materials can accumulate as a layer on the surface of the membrane. This layer formation results in a pressure drop across the membrane leading to increased resistance and reduced permeate flux [31-35]. Using only dead-end filtration, the volume flux of water varied from 0.28 to 0.59 m^3/m^2 day for composite membranes polysulfone – polyaniline. For membranes made of polysulfone, the flux varied from 0.62 to 0.98 m^3/m^2 day. A better flux is achived as the pressure increases to 0.3MPa. When dye is added, the flux increases therefore values achived for the polysulfone-polyaniline membrane rise from 0.31 to 0.87 m^3/m^2 day and for membranes made of polysulfone from 0.68 to 1.19 m^3/m^2 day. A better flux is also achived for the highest pressure used, 0.3 MPa. When solution containing both dye and surfactant were passed throught the polysulfone-polyaniline membrane a slight decrease could be observed at ΔP = 0.1MPa, 0.2MPa. Values decreased at 0.24 - 0.26 m^3/m^2 day. For ΔP = 0.3MPa an increase of permeability could be observed, so values achived 1.01 m^3/m^2 day. Similar results were observed for the polysulfone membrane, where for pressures of 0.1 and 0.2 MPa values decreased at 0.60 - 0.69 m^3/m^2 day, but for 0.3 MPa the value rises to 1.61 m^3/m^2 day. The decrease of membrane permeability could be attributed to fouling process. In the case of a cross-flow (or tangential flow) operation process, the feed stream is parallel to the membrane surface such that the feed water flow is perpendicular to the filtration flow. Continuous turbulent flow along the membrane surface creates a shear force that reduces the accumulation of species [31, 35-37]. Using only cross flow filtration, the volume flow of water varied from 0.27 to 0.91 m^3/m^2 day for composite membranes polysulfone – polyaniline. For membranes made of polysulfone, the flux varied from 0.58 to 1.07 m^3/m^2 day. A better flux is achived as the pressure increases to 0.3MPa. When dye is added, the flux increases therefore values achived for the polysulfone-polyaniline membrane rise from 0.29 to 0.96 m^3/m^2 day and for membranes made of polysulfone from 0.61 to 1.26 m^3/m^2 day.

A better flux is also achived for the highest pressure used, 0.3 MPa. When solution containing both dye and surfactant were passed throught the polysulfone-polyaniline membrane a slight decrease could be observed at ΔP = 0.1MPa, 0.2MPa. Values decreased at 0.18 - 0.29 m^3/m^2 day. For ΔP = 0.3MPa an increase of permeability could be observed, so values achived 1.14 m^3/m^2 day. Similar results were observed for the polysulfone membrane, where for pressures of 0.1 and 0.2 MPa values decreased at 0.48 - 0.62 m^3/m^2 day, but for 0.3 MPa the value rises to 1.71 m^3/m^2 day. Although the flux values are similar for dead-end and cross-flow operation process, the

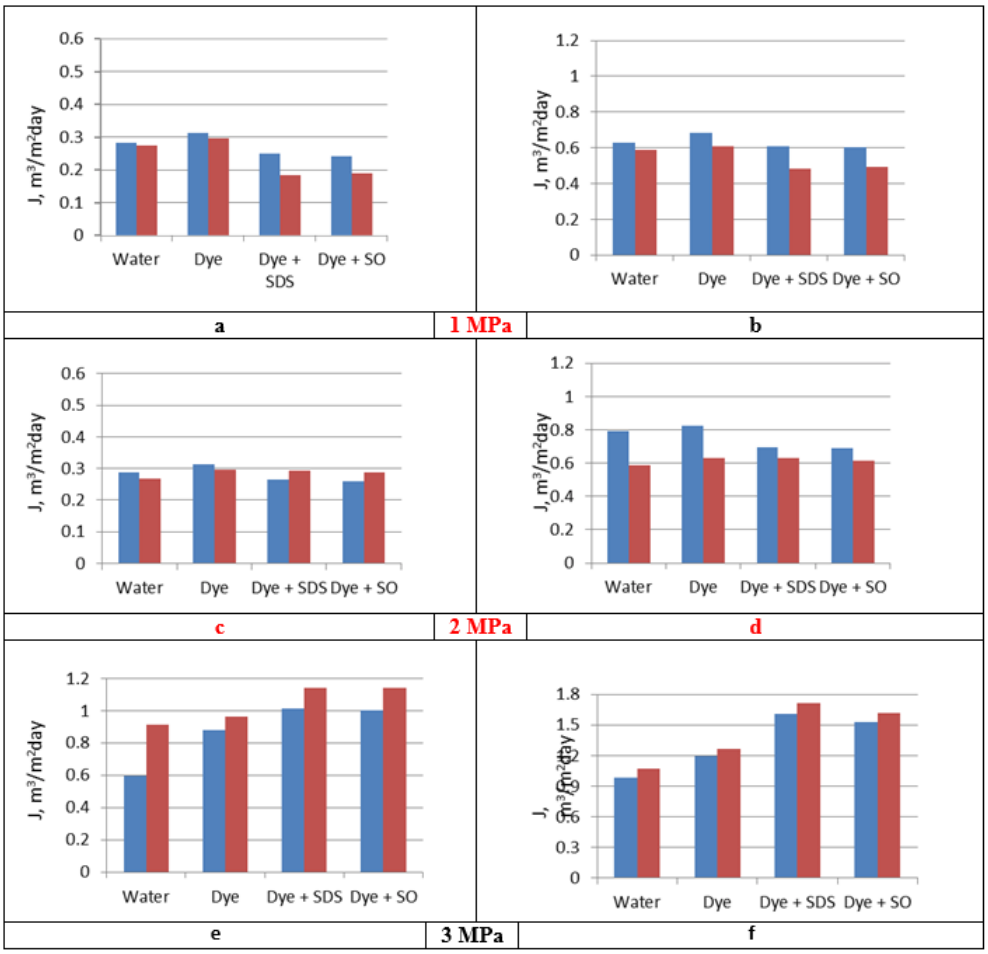

Fig. 2. Volum flux for polysulfone – polyaniline membranes (a,c,e) and polysulfone membranes (b,d,f). Dead-end (blue) and cross-fow (red) filtration fluxes were presented

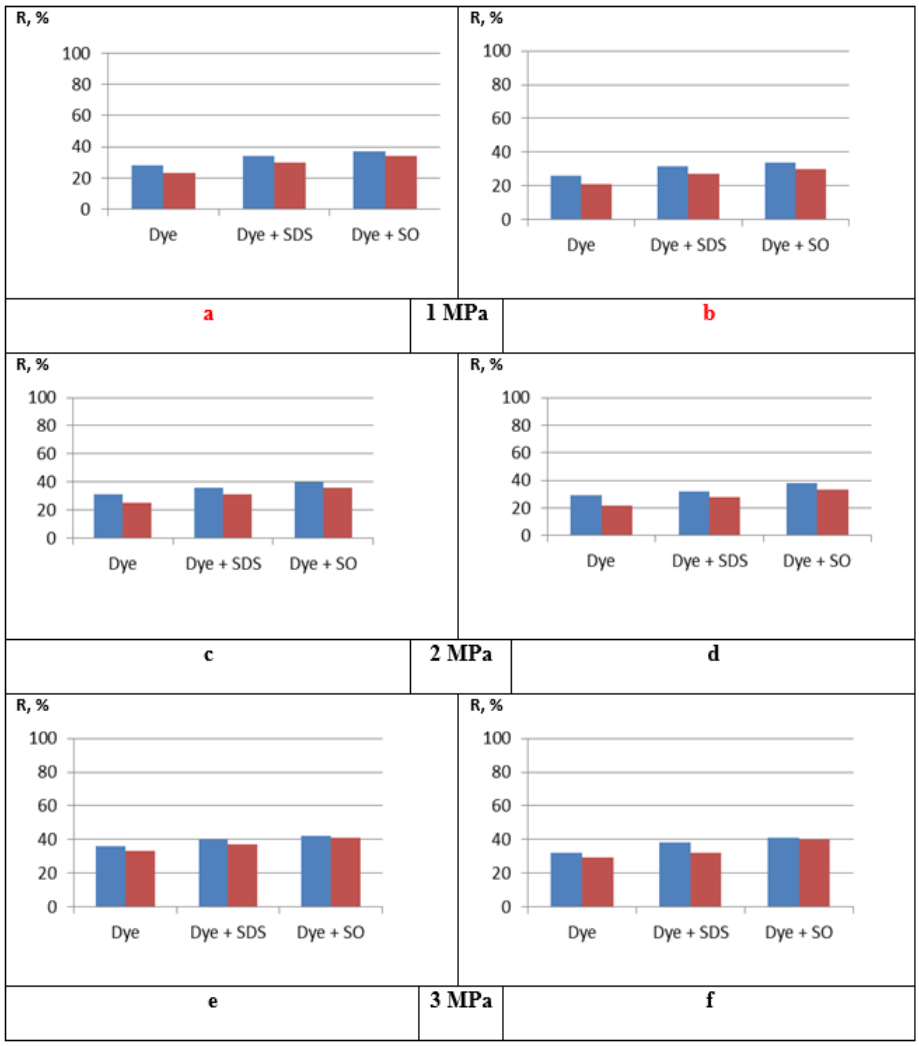

Fig. 3. Dye retention coefficient for polysulfone – polyaniline (a,c,e) and polysulfone (b,d,f) membranes. Dead-end (blue) and cross-fow (red) filtration retention were presented

use of cross-flow filtration did not allow accumulation on the membrane surface so that the flux was constant in time, unlike dead-end filtration where the flux decreases with time due to accumulation on the membrane surface. The efficiency of anionic surfactants separation for the polisulfone membranes is shown in the figure 3. The results obtained showed better dye retention. The coefficient for this type of membranes amounted from 28% at 1MPa to 42% at 3MPa. The pilot set-up was used for dead-end and cross-flow filtration. The retention coefficient for the solution containing dye varied from 26 to 32% for membranes made of polysulfone using dead-end filtration, and from 21 to 29% in cross-flow filtration. For membranes made of polysulfone-polyaniline, the retention varied from 28 to 36% in dead-end mode and from 23 to 33% in cross-flow operation process. When solutions containg both dye and surfactants were passed through the membranes, an increase could be observed for both membranes at ΔP = 0.1MPa, 0.2MPa, 0.3MPa and for both surfactants used. Solution containing SO showed a better retention than the ones containing SDS. The retention coefficient for the solution containing dye and SDS varied from 31.5 to 38% for membranes made of polysulfone using dead-end filtration, and from 27 to 32% in cross-flow filtration.

For membranes made of polysulfone-polyaniline, the retention varied from 34 to 40% in dead-end mode and from 30 to 37% in cross-flow operation process.

The retention coefficient for the solution containing dye and SO varied from 34 to 41% for membranes made of polysulfone using dead-end filtration, and from 30 to 40% in cross-flow filtration. For membranes made of polysulfone-polyaniline, the retention varied from 37 to 42% in dead-end mode and from 34 to 41% in cross-flow operation process. An increase in dye retention can be observed for both type of filtration. The separation of the solutions containing dye and surfactants can be considered as adsorption of surfactant monomers and dye particles in the membrane pores, thus reducing its size. The interactions between membranes and surfactants can be an important factor supporting the efficiency of the ultrafiltration.

Conclusions

The ultrafiltration efficiency of the solution containing both dye and surfactants is influenced by the type of membrane used, but also by the type of surfactant used. The transport propertyes of the polysulfone membranes are influenced by the content of the treated solutions Although in terms of flux the resulults are related, in terms of retention the SO showed better results, probably thanks to its structure.. The presence of the anionic surfactants led to an increase of dye retention.

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