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EFFECT OF DYE CONTENT IN A TREATED SOLUTION ON PERFORMANCE OF THE UF CERAMIC MEMBRANE

Low-pressure membrane processes have been studied in order to treat aqueous solutions of dyes. The influence of dye concentration (10, 20, 100 g/m^3) on separation efficiencies of organic dyes (Methyl Orange, Titan Yellow and Direct Black) was analyzed. CéRAM INSIDE® (Tami Industries) membranes with various cut-off values (1, 15 kDa) were examined. The ultrafiltration process was carried out at the transmembrane pressures of: 0.03, 0.06, and 0.09 MPa. It was found that the process efficacy was affected not only by the kind of dye, but also by the dye concentration, applied pressure and membrane cut-off. With increasing dye content in the treated solution the rejection coefficient improved.

1. INTRODUCTION

Lack of water is a worldwide problem that will be exacerbated by water pollution. The textile industry consumes large volumes of water in numerous wet processes. Therefore it produces enormous amounts of textile wastewater heavily charged with unconsumed dyes and other chemicals [1]. Dyeing wastewater contains large amounts of dyestuff together with significant amounts of suspended solids, dispersing agents, salts and trace metals. This dyeing wastewater can cause serious environmental problems due to its high colour, large amount of suspended solids and high chemical oxygen demand [2]. Even small quantities of dyes can determine colour of large water bodies [3, 4]. Coloured dye effluents are generally considered highly toxic to the aquatic biota, affecting the symbiotic process by disturbing the natural equilibrium through reduced photosynthetic activity due to the colouration of water in streams. Some dyes are reported to cause allergy, dermatitis, skin irritation, and cancer in humans. Thus, the removal of dyes from effluents before they are mixed up with unpolluted natural water bodies is important [5, 6].

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The treatment of wastewater containing dyes and its decolourization involves serious problems. A wide range of pH, high salt concentrations and complex chemical structures hinder even more their treatment [4]. The conventional treatments of wastewater containing dyestuff include biological oxidation, chemical coagulation and adsorption. The traditional processes for treatment of dye-house effluents prove to be insufficient to purify the important quantity of wastewater after the different operations of dyeing and washing [7]. Furthermore, the composition of wastewater from the dyeing and textile processes varies greatly from day to day and hour to hour, depending on the dyestuff type, the fabric type and the concentration of fixing compounds which are added [2].

Membrane separation processes could be a promising alternative for the removal of a variety of dyestuffs. Membrane pressure-driven processes, especially nanofiltration and reverse osmosis, are being increasingly used in the treatment of textile wastewater [8–13]. However, these techniques are characterized by high energy consumption. Therefore low-pressure membrane processes (microfiltration and ultrafiltration) could be economically more favourable in the dye effluent treatment.

A membrane installation should be characterized by a process stability, high availability, and simple preliminary treatment. Membranes applied should have high chemical, thermal and biological resistances. Ceramic membranes are able to mach these demands due to their high chemical and physical stability, and long lifespan. Other advantages of ceramic membranes include the ability to use steam sterilization and back flushing, high abrasion resistance, high fluxes, bacteria resistance, possibility of regeneration and dry storage after cleaning [14]. The supports for the inorganic membrane elements are made from aluminum oxides, zirconium oxides, titanium oxides or silicon carbides [15, 16]. These materials can fulfil high requirements relating to mechanical stability. The supports can be designed for a single-channel or multichannels modules. The membrane layer is only few μm thick and is placed on the inner side of the channel.

The aim of the present paper was to investigate the membrane process efficiency for aqueous solutions containing three organic dyes at various concentrations in aqueous solutions. The effect of the dye concentration, as well as the molecular weight of the dye and the membrane cut-off on the process efficiency was reported.

2. MATERIALS AND METHODS

Commercially available CéRAM INSIDE® (Tami Industries) ceramic membranes, with the cut-off values of 1 kDa and 15 kDa, were used in the experiments. The membranes were 0.25 m long and had one channel with the diameter of 6 mm. The external diameter of the membrane was equal to 10 mm. The membrane surface area amounted to 0.0042 m^2 (per module).

Transport and separation properties of the membranes were tested with respect to three anionic dyes (Methyl Orange – MO, Titan Yellow – TY, Direct Black – DB). The characteristic of the dyes is given in Table 1. The molecular weights of tested dyes ranged from 327 to 1060 Da. The permeation measurements were carried out with distilled water and aqueous solutions of dyes. Dye concentrations in model solutions were equal to 10, 20 and 100 g/m^3. The dye concentrations in permeate and concentrate were determined spectrophotometrically by measuring of the absorbance at the wavelength of maximum absorbance of the sample.

Table 1

Characteristics of the dyes under investigation

Dye	Molecular weight [Da]	Type	pH[a]	Dye	λ_{max}^{b} [nm]	Structural formula
Methyl orange C.I.[c]13025	327	acid dye	5.7	MO	465	$C_{14}H_{14}N_9O_9SNa$
Titan yellow C.I. 19540	696	direct dye	5.5	TY	399	$C_{28}H_{19}N_5Na_2O_6S_4$
Direct black C.I. 35435	1060	direct dye	7.6	DB	585	$C_{44}H_{32}N_{13}O_{11}S_3Na_3$

[a]Determined for the dye solutions of concentration equal to 100 g/m^3.
[b]Wavelength corresponding to the maximum absorbance of the dye solution.
[c]Colour index number.

The ProFlux M12 (Millipore) installation (Fig. 1) was used in the experiments. To provide constant concentration of examined solutions, permeate was recirculated to the feeding tank. The ultrafiltration process involved the pressure range from 0.03 to 0.09 MPa.

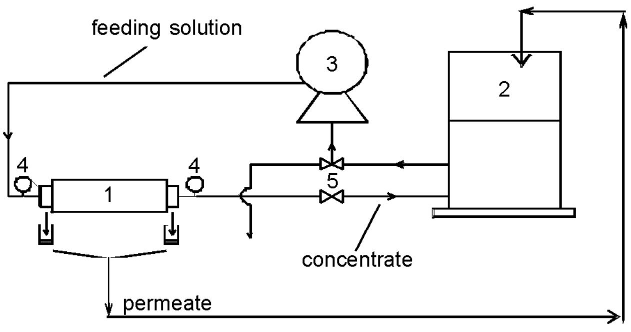

Fig. 1. Laboratory UF installation ProFlux M12: 1 – ceramic membrane module, 2 – feeding tank, 3 – pressure pump, 4 – pressure sensor, 5 – valve

3. RESULTS AND DISCUSSION

Figure 2 shows the distilled water flux at three transmembrane pressures for two membranes (1 kDa and 15 kDa). As it was expected there was an evident relationship

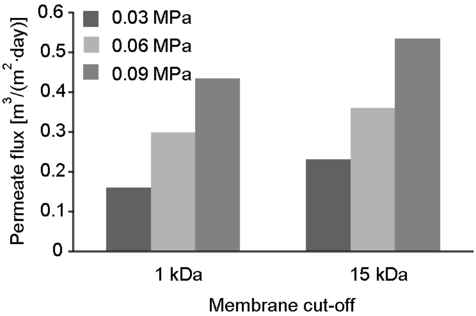

Fig. 2. Water volumetric flux vs. transmembrane pressure and membrane cut-off

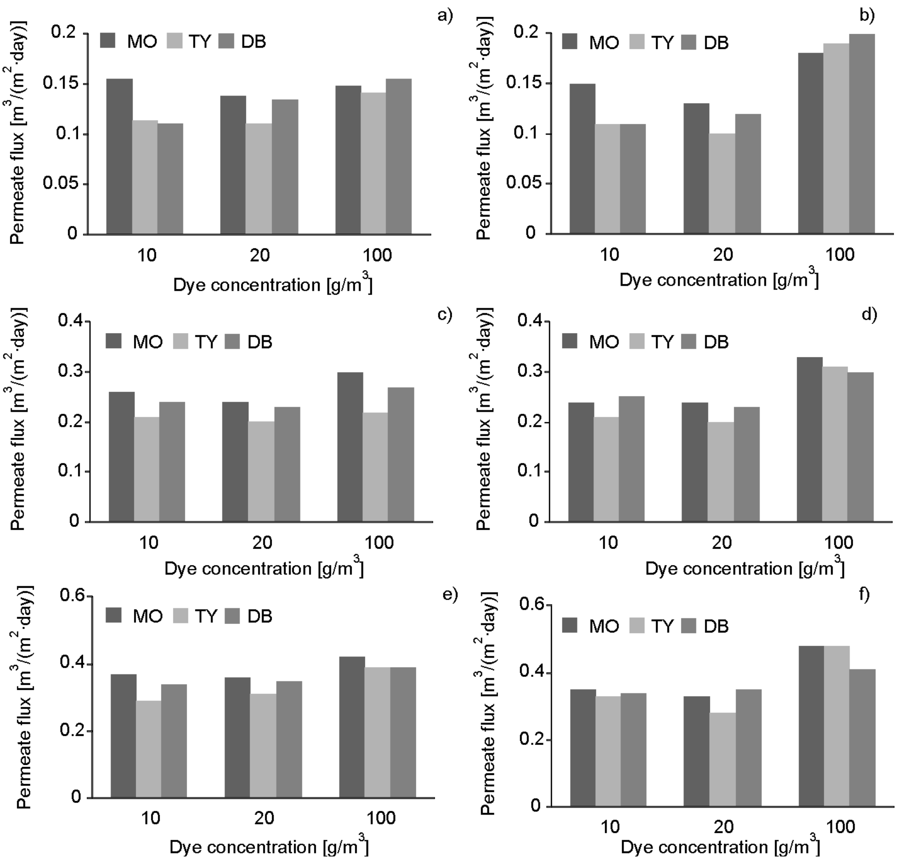

Fig. 3. Permeate volumetric flux of solutions containing MO, TY, DB for 1 (a, c, e) and 15 (b, d, f) kDa membranes vs. dye concentration under 0.03 (a, b), 0.06 (c, d), and 0.09 (e, f) MPa

between water permeability and applied pressure. It was also found that permeability of the membrane with the higher cut-off value was higher than the permeability of 1 kDa membrane. The water flux ranged from 0.16 $m^3/(m^2 \cdot day)$ to 0.44 $m^3/(m^2 \cdot day)$ for 1 kDa membrane and from 0.21 $m^3/(m^2 \cdot day)$ to 0.54 $m^3/(m^2 \cdot day)$ for the 15 kDa membrane.

The ceramic membrane permeabilities in the course of ultrafiltration of organic dyes solutions are shown in Fig. 3. It was found that the membrane permeability was dependent on the initial concentration of dye, the applied pressure and the membrane cut-off value. It is interesting to note that the membrane type was of less importance, although the distilled water fluxes varied with membrane cut-off (Fig. 2).

The lowest permeate flux (approximately 0.10 $m^3/(m^2 \cdot day)$) was obtained under the pressure of 0.03 MPa (Figs. 3a, b). Increasing pressure caused the increase in the permeate flux (to approximately 0.48 $m^3/(m^2 \cdot day)$) (Fig. 3f). The highest permeate flux was observed when the 15 kDa membrane was used under the highest pressure. Under the lowest pressure, the highest permeate flux was obtained for solutions with the highest initial concentration.

The presence of dye molecules in treated solutions caused decrease in the membrane permeabilities. This demonstrates that the membranes were blocked by rejected particles. As a measure of the pore blocking degree, the relative membrane permeability was taken into account (Table 2). It was determined as the ratio of the volumetric flux of a dye solution to water volumetric flux.

Table 2

The relative permeability of ceramic membranes

Dye	1 kDa membrane			15 kDa membrane		
	Dye concentration [g/m^3]					
	10	20	100	10	20	100
0.03 MPa						
MO	0.98	0.87	0.93	0.64	0.57	0.76
TY	0.72	0.70	0.89	0.46	0.45	0.81
DB	0.70	0.85	0.98	0.49	0.51	0.84
0.06 MPa						
MO	0.84	0.78	0.99	0.65	0.65	0.90
TY	0.69	0.67	0.74	0.58	0.54	0.85
DB	0.79	0.76	0.89	0.68	0.64	0.82
0.09 MPa						
MO	0.84	0.82	0.97	0.65	0.62	0.89
TY	0.67	0.71	0.90	0.62	0.52	0.90
DB	0.77	0.80	0.90	0.64	0.66	0.76

At higher initial concentrations of dyes, membrane blocking was less effective. This can be explained in terms of aggregation of dye particles in the treated solutions.

At low dye concentrations, the degree of aggregation is lower. Thus, non-aggregated dye particles can freely enter the membrane pores and block them. Aggregated dye particles, due to their bigger diameters, will be rejected by the membranes.

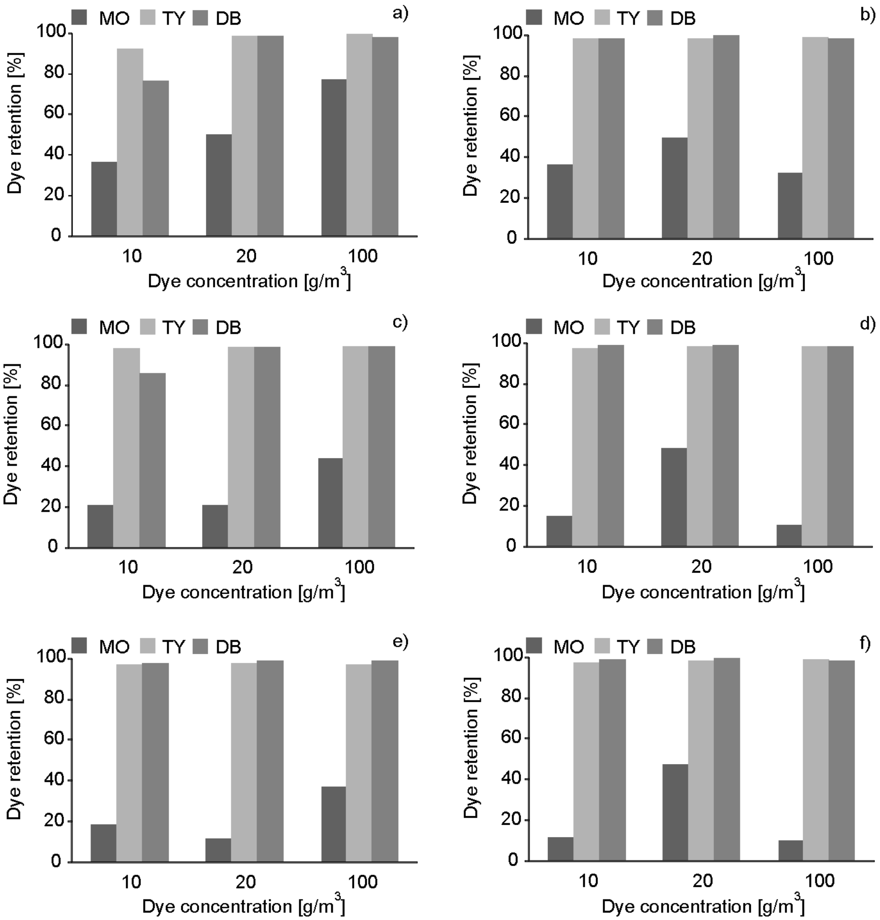

Fig. 4. Dye retention for solutions containing MO, TY, DB for 1 (a, c, e) and 15 (b, d, f) kDa membranes vs. dye concentration under 0.03 (a, b), 0.06 (c, d), and 0.09 (e, f) MPa

The transport properties of ceramic membranes influenced directly the separation properties. The experimental results are shown in Fig. 4. The molecular weight of a dye has a significant influence on the process efficiency. The dyes of higher molecular weight (Titan Yellow, Direct Black) were removed with much higher efficacy than the low molecular weight dye (Methyl Orange) irrespective of the membrane cut-off. The applied pressure had an insignificant influence on the removal efficiency of high-molecular weight dyes. Dye rejection coefficients for Titan Yellow and Direct Black were very high and varied from 85 to 99.3%, depending on the initial dye concentration. The worst removal efficiency was noticed when the initial dye concentration was lowest, but when the dye concentration was increasing, the results of ultrafiltration process were improved. When the initial concentration was equal to 10 g/m^3 the aggregation degree of dye particles was rather low, thus more single dye particles were available in the treated solution. As a consequence, the separation efficiency became worse.

The retention coefficient of Methyl Orange depended on the initial concentration of dye in a higher extent, but there was no visible trend between the initial concentration of dye and the removal efficiency. Generally, the separation of Methyl Orange was rather low – the retention coefficients varied from 11% to 77%, depending on the membrane cut-off and the applied pressure. The best results were obtained for 1 kDa membrane and the lowest pressure (Fig. 4a). The poor rejection of Methyl Orange could be attributed to small size of the dye particles. The worsening of separation of low molecular weight dye upon increasing pressure was observed. Higher pressure caused more intensive passing of dye particles through the membrane. When the concentration of Methyl Orange was the lowest and the applied pressure was the highest, there was the dye rejection was worst (Fig. 4e, f). Probably, under the low concentration, dye aggregation was hindered and a greater number of non-aggregated dye particles penetrated through the ceramic membrane.

4. CONCLUSIONS

The experimental results demonstrated that the commercially available ceramic membranes can be successfully applied to treat organic dye solutions, particularly when the solutions contain high-molecular-weight dyes (> 700 Da). The effectiveness of organic dye removal depends on its initial concentration in the treated solution, applied pressure and the membrane cut-off. For low molecular weight dyes the increase in the membrane cut-off and transmembrane pressure causes worsening of dye rejection. For high molecular weight dyes the rejection degree is almost complete (97–99%) unless the dye content in the separated solution is rather high (100 g/m^3). The decrease of dye concentration brings about deterioration of the separation efficiency.

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