Evaluation of different nanofiltration membranes for reuse of biologically treated denim textile mill wastewater

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ABSTRACT

The aim of this study was to investigate the reuse possibility with nanofiltration (NF) membranes of biologically treated textile wastewater (COD: 350 mg/L, color: 108.9 m^{-1} and conductivity: 2,843 µS/cm) of a local textile factory (denim washing and dyeing) in Tekirdag, Turkey. For this aim, the flux and permeate quality was evaluated within the context of COD, color and conductivity with different NF membranes (NP010 and NP030) under various pressures (4, 6, 8 and 10 bar). On the other hand mass transfer coefficients were calculated with Nernst–Planck equation based on experimental results. When compared with literature, NF permeate water was found to be alternative to freshwater in textile wet processing. According to the Nernst–Planck equation, the B_s (mass transfer coefficient) and R_s (removal coefficient) values are obtained. R_s and B_s values were determined as follows: 0.982 and 0.994 for COD, 0.995 and 0.959 for color, 0.295 and 0.3403 for conductivity and 6.79 and 3.38 for COD, 4.90 and 0.54 for color, 27.39 and 15.87 for conductivity, respectively. According to B_s and R_s , NP030 membrane was determined as the most convenient membrane for aerobically pre-treated wastewater.

Keywords: Reuse; Nanofiltration; Textile wastewater; Mass transfer coefficient

1. Introduction

Reuse of textile industry wastewater has become an important issue due to the water shortage which has increased in recent years [1]. Therefore, many advanced treatment methods such as adsorption, oxidation are used, especially membrane processes. However, pre-treatment process as biological treatment and coagulation/flocculation is necessary for advanced treatment. In some studies, nanofiltration (NF) membranes after pre-treatment for reuse of textile wastewater has been used [1–6]. Various researches were done to determine the mass transfer coefficients of NF membranes [7–13]. The mass transfer of NF membranes can be explained by thermodynamics of irreversible processes. The relationship between R(removal efficiency) and J_p (permeate flux) can be determined according to the Nernst–Planck equation. According to this model, *R* is determined by the following equation [7–9].

$$R = \frac{R_s \cdot J_v}{J_v + B_s} \tag{1}$$

In Eq. (1), R_s and B_s are constants as removal coefficient and mass transfer coefficients, respectively. These constant values are a function of membrane permeability. Eq. (2) is obtained with rearranging Eq. (1) [7–9].

$$\frac{1}{R} = \frac{1}{R_{\circ}} + \frac{B_{\circ}}{R_{\circ}} \cdot \frac{1}{I_{\circ}}$$
(2)

In this study, Eq. (2) is used to determine R_s and B_s values [7–9]. Koyuncu et al. [7] have studied the pilot-scale NF membrane for dye house effluents of textile industry. Permeate conductivity decreased with increasing pressure.

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To support this, with the mass transfer coefficient accounts, according to Eq. (2), mass transfer coefficient for conductivity was calculated. Kaykioglu et al. [8] have evaluated the Nernst–Planck equation for the permeate flux and removal rates (COD, color and conductivity) obtained from membrane applications (NF) to anaerobically and aerobically pre-treated textile wastewaters. Coskun et al. [9] have used reverse osmosis for the treatment of olive mill wastewater and have determined mass transfer coefficient for conductivity parameter. In all studies, permeate quality values have decreased with increasing pressure and calculated mass transfer coefficients have confirmed with these values. It is necessary to study more in order to find out the relationship between the removal efficiency and the operating pressure.

In this study, the reuse possibility of biologically treated textile wastewater of a local textile factory (denim washing and dyeing) was investigated in Tekirdag, Turkey. For this aim, the flux and permeate quality as COD, color and conductivity with different NF membranes (NP010 and NP030) was evaluated. On the other hand mass transfer coefficients were calculated with Nernst–Planck equation based on experimental results.

2. Materials and methods

2.1. Wastewater origin

In the study, aerobically treatment plant effluent, that is currently available in local textile factory (denim dye and washing) was studied, which has COD: 350 mg/L, color: 108.9 m⁻¹ and conductivity: 2,843 μ S/cm. In this plant, industrial and domestic wastewaters are treated by physical, biological (aerobic) and granule filtration. The capacity of wastewater treatment plant is 1,500 m³/d. Composite sample was taken for 24 h which was used as feed water in the membrane process.

2.2. Membrane equipment

The membrane system and membrane cell were supplied by Osmonics[®] Inc. and a GE SepaTM CF2, respectively. A cartridge filter (10 μ m pore size) was used as a pre-filter to remove coarse particulates from the wastewater. All membrane

Table 1

Characteristics of nanofiltration membranes

experiments were performed at 25°C. NF (NP010 and NP030) membranes were used to filter aerobically pre-treated textile wastewaters under pressures of 4, 6, 8 and 10 bar. A flat sheet type membrane was used in the experiments. NF membranes supplied by Macrodyn[®] Nadir. A new membrane sheet was used for each experiment. The characteristics of the membranes were given in Table 1. Membranes were pressurized by distilled water in order to get to the stable flux of the membranes used in experiments. Flowmeter is set at 300 L/h.

2.3. Analytical methods

COD, color and conductivity were analyzed for aerobically treated effluent and permeate water. They were performed according to ISO 6060 [14], ISO 7887 [15] and Standard Methods [16], respectively. pH and conductivity parameters were determined using WTW pH 315i/set and WTW Cond. 3210 Set 1 brand appliance, respectively. Color was analyzed by using ThermoSpectronic Aquamate brand spectrophotometer. Membrane performance was expressed as flux and removal efficiency. Permeate flux was determined gravimetrically. The time-dependent flow and pressure values measured in the experiment were calculated as follows:

Flux $(J_{v'} L/m^2 h)$ = permeate weight in terms of g and in 5 mi × density of the water/membrane area.

Removal efficiency was determined by the following Eq. (3):

$$R = \frac{C_{f} - C_{p}}{C_{f}} = 1 - \frac{C_{p}}{C_{f}}$$
(3)

where *R* is the removal rate, C_p and C_f represent the concentration of the feed solution and the permeate stream, respectively [1,17,18].

3. Results and discussion

3.1. Permeate flux and quality

Permeate fluxes were continuously monitored via digital balance connected to a computer. Permeate flux values obtained in different membrane pressure for 60 min are shown in Fig. 1.

Membrane type	Manufacturer	Meterial	Membrane property	M.O.P.ª (bar)	M.O.T. ^b (°C)	Solution	Molecular weight (Da)	Removal rate (%)
NP 010	Macrodyn® Nadir	Polyether sulfone	Hydrophilic	40	95	NaCl (0.5%) Na ₂ SO ₄ (0.5%)	58 142	5–15 25–55
						Laktoz (4%)	342	25–45
NP 030	Macrodyn®	Permanently	Hydrophilic	40	95	NaCl (0.5%)	58	25–35
	Nadir	Polyether sulfone				Na ₂ SO ₄ (0.5%)	142	80–95
						Laktoz (4%)	342	70–90

^aMaximum operation pressure.

^bMaximum operation temperature.



Fig. 1. The permeate flux values for NP010 and NP030.

It can be seen in Fig. 1 that permeate fluxes obtained with NP010 are higher than NP030 for all application pressures and increased with increasing pressure. The highest flux values were measured as 83.7 and 51.8 L/m² h with NP010 and NP030 membranes under 10 bar pressure, while the lowest flux values were determined as 50.3 and 22.5 L/m² h, respectively.

The quality of permeate water obtained (COD, color and conductivity) with NF membranes have been determined to assess of reuse of wastewater (Table 2). The permeate water quality has increased with increasing pressure for all experiments. The permeate waters obtained with NP010 and NP030 have 102-30 mg/L, 11.5-5.1 m⁻¹, 2,325-2,190 µs/cm and 80-20 mg/L, 6.7-4.1 m⁻¹, 2,284-2,062 µs/cm for COD, color and conductivity, respectively. Achieved removal efficiencies are shown in Fig. 2. It can be seen in Table 2 that permeate waters quality obtained with NP030 is negligibly better than NP010, especially in terms of conductivity parameter. According to literature, the industrial process water must have colorless, maximum 50 mg/L COD and maximum 2,200 µs/cm conductivity [19-21]. If permeate water quality are compared with the results process water quality mentioned in literature, it was proven that obtained permeate waters with NP010 and NP030 under 10 bar can be used in textile industry as a process water.

3.2. Mass transfer coefficiency

According to the Nernst–Planck equation (Eq. (2)), the B_s (mass transfer coefficient) and R_s (removal coefficient) values are calculated from relationship between $1/J_v$ and 1/R. The relationships between removal efficiencies (COD, color and conductivity) and permeate flux for aerobically pre-treated wastewaters are given in Fig. 3. B_s coefficient indicates passage of the materials through the membrane. Therefore, a lower B_s coefficient means higher performance of the membranes.

 R_s and B_s values were determined as follows for NP010 and NP030; 0.982 (R_s , NP010) and 0.994 (R_s , NP030) for COD, 0.995 (R_s , NP010) and 0.959 (R_s , NP030) for color, 0.295 (R_s , NP010) and 0.340 (R_s , NP030) for conductivity and 6.79 (B_s , NP010) and 3.38 (B_s , NP030) for COD, Table 2

Analysis results of permeate water samples and aerobically pre-treated wastewater

	COD, mg/L	Color, m ⁻¹	Conductivity, µs/cm					
Aerobically pre-treated wastewater (pH = 6.5)								
	350	108.9	2,843					
Membrane permeate water								
Pressure, bar	NP010							
4	102	11.5	2,325					
6	45	9.8	2,304					
8	32	7.6	2,205					
10	30	5.1	2,190					
Pressure, bar	NP030							
4	80	6.7	2,284					
6	40	6.3	2,190					
8	28	5.8	2,062					
10	20	4.1	2,162					



Fig. 2. COD, color and conductivity removal efficiencies.

4.90 (B, NP010) and 0.54 (B, NP030) for color, 27.39 (B, NP010) and 15.87 (B, NP030) for conductivity (Table 3). According to B and R, NP030 membrane was determined as the most convenient membrane for aerobically pre-treated wastewater due to the fact that B values in NP010 were significantly higher than NP030 applications. Kaykioglu et al. [8] have determined the mass transfer coefficients for NF (NP010 and NP030). Wastewater was supplied from textile factory where dyes 95% of cotton and aerobically pre-treated wastewater was used in membrane experiments. The B_c coefficiencies of our study were compared with study of Kaykioglu et al. [8] and the different results were obtained (Table 3). The B_{c} coefficients obtained in our study were compared with the B_{c} coefficients in the study of Kaykioglu et al. [8] and different results were obtained. According to Kaykioglu et al. [8], B_o value of conductivity in NP030 membrane was significantly lower than our study. This case can be related to the presence of different dissolved organic matter in the effluents due to the different wastewater and treatment mechanisms. The similar results were obtained for COD and color.



Fig. 3. The relationship between removal efficiency and permeate flux for (a) COD, (b) color and (c) conductivity.

4. Conclusions

This study focused on COD, color and conductivity removals from aerobically pre-treated textile wastewater with NF membranes for reuse. Also the performances of NF membranes with their mass transfer coefficients were investigated. The highest flux values were measured as 83.7 and 51.8 L/m² h with NP010 and NP030 membranes under 10 bar pressure, respectively. The permeate water quality

 B_s and R_s values for aerobically pre-treated wastewaters and B_s values of Kaykioglu et al. [8]

	This stu	dy	Kaykioglu et al. [8]		
COD	R^2	R_{s}	B_s/R_s	B _s	B _s
NP010	0.8997	0.982	6.9117	6.79	4.99
NP030	0.9074	0.994	3.4034	3.38	1.17
Color					
NP010	0.8073	0.995	4.9250	4.90	0.91
NP030	0.8841	0.959	0.5619	0.54	0.46
Conductivity					
NP010	0.7777	0.295	92.7510	27.39	39.35
NP030	0.7711	0.340	46.6610	15.87	3.06

has increased with increasing pressure for all experiments. According to literature, the permeate waters for NP010 and NP030 under 10 bar pressure can be used in textile industry as a process water. The B_s values in NP010 were significantly higher than NP030 applications. According to B_s coefficiency, NP030 membrane is the most suitable membrane. This case can be explained by difference of membrane materials. NP030 membrane is manufactured from permanently polyethersulfone while NP010 is polyethersulfone. More detailed analyses on the membrane surface are necessary to be able to determine the removal mechanisms.

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