Pilot scale nanofiltration membrane separation for waste management in textile industry

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Abstract This paper presents the pilot scale membrane separation studies on dyehouse effluents of textile industry. Nanofiltration (NF) membranes which have 2 m^2 of surface area were evaluated for membrane fouling on permeate flux and their suitability in separating COD, color and conductivity in relation to operating pressure and feed concentration from textile industry dyehouse effluents. Successive batch runs demonstrated that any serious membrane fouling was not experienced for NF membrane tested in treating this type of wastewater. The permeate flux was found to increase significantly with operating pressure. Flux decreased with increasing recovery rate. The overall removal efficiencies of COD, color and conductivity were found as greater than 97%. COD was lower than 10 mg/l at 12 bar pressures. Permeate COD was also increased with increasing recovery and COD was 30 mg/l with recovery of 80%. Almost complete color removal was achieved with nanofiltration membrane. Color value was also decreased from 500 Pt-Co to 10 Pt-Co unit. This significant reduction in color and COD makes possible the recycle of the permeate in the dyehouse. Permeate conductivity was decreasing with increasing pressure and retention of conductivity increases with increasing pressures. This phenomenon is expected from the analysis of conductivity mass transport model. Economical analysis have been done and the total estimated cost will be 0.81 \$/m^3 based on 1000 m^3/day of and this value is very economical for Istanbul City due to increasing industrial water supply tariffs.

Keywords Color removal; dyehouse effluents; mass transfer model; nanofiltration; pilot scale; reuse

Introduction

Textile industry wastewater is an important pollution source that contains high concentrations of inorganic and organic chemicals and is highly colored from the residual dyestuffs. The effluents thus generated contains a wide range of contaminants, such as salts, dyes, enzymes, yeasts, surfactants, scouring agents, oil and grease, oxidizing and reducing agents. In environmental terms, these contaminants mean suspended solids, COD, BOD, as well as high pH and strong color. Because color removal is not yet a concern for discharge to sanitary sewer in Turkey, COD and BOD removal becomes the major objective in wastewater treatment for the textile industry.

Biological treatment, chemical precipitation, membrane technology, activated carbon adsorption and evaporation is the common wastewater treatment techniques of textile industry effluents (Wenzel *et al*., 1996). Membrane technology can reduce the volume of wastewater generated, recover and recycle valuable components from the waste streams and/or recover the thermal energy in hot wastewaters. In addition, such process occupies only small portion of floor space. It is thus of special interest for the space-limited factories in Istanbul. To date, the majority of the applications investigated on reverse osmosis (RO) have been for the treatment of textile dyestuff effluents (Chen *et al*., 1997). The permeate is reused as wash-water and the concentrate can be either reused or discharged after post treatment such as wet oxidation and combustion. Nanofiltration membranes have also been used in textile dyestuff effluents. Full scale nanofiltration plant has been designed to treat reactive dye liquors from medium sized (200 m^3/month) cotton dyehouse (Buckley, 1992).

This paper contains the results of pilot scale experiments of textile industry effluents.

Nanofiltration (NF) membranes have been used during experimental runs for cost effective solutions instead of reverse osmosis(RO) membranes. Experimental studies have been carried out on dyehouse effluents of textile industry.

Mass transfer models

Many investigators have studied the mass transport model of NF membrane separation processes. The space charge (SC) model, assuming the pore as a straight capillary having charges on its surface, is often used to predict the rejection performance of NF membranes. The equation of the SC model are based on the Poisson–Boltzmann equation, the Nernst–Planck equation and the Navier–Stokes equation, respectively, for the radial distribution of electric potential and ion concentration for ion transport and for volumetric flow. The fixed charged model has been successfully tested in research, employing an ion-exchange membrane. (Chen *et al*., 1997, Garba *et al*., 1998, Timmer *et al*., 1994)

The model of Spiegler/Kedem from thermodynamics of irreversible processes gave the following equation,

$$R = 1 - \frac{1-\sigma}{1-\sigma.\exp\left(\frac{(\sigma-1)J_v}{P}\right)} \tag{1}$$

where R is real rejection, P is a solute permeability parameter ($=\omega RT$), σ is a reflection coefficient and J_v is a volume flux of solution (Schirg *et al*., 1992). Equation (1) leads to

$$R = \frac{J_v}{J_v + (P/\sigma)} \quad \text{and} \tag{2}$$

$$R = \frac{J_v}{J_v + B} \tag{3}$$

If the σ value is equal to 1, B is equal to P. On the other hand, if $J_v \to \infty$, R approaches σ. The σ value is obtained from intercept in a straight line relationship between R and $1/J_v$ (Nishimura *et al*., 1991).

The relationship between R and J_v can be described by another model based on the Nernst–Planck equation. According to this model, rejection (R) is given following formula (Timmer *et al*., 1997),

$$R_1 = \frac{R_{s_1,J_w}.J_w}{J_{w+} + B_{s_1,J_w}} \tag{4}$$

where R_{s1} and B_{s1} are the overall rejection and mass transfer parameters of component 1. R_{s1} and B_{s1} are functions of the membrane permeability, the charge of component and the reflection coefficient (Chen *et al*., 1997). This approach will be followed in data analysis in this study. Rearrangement of Equation (4) gives,

$$\frac{1}{R_1} = \frac{1}{R_{s1}} + \frac{B_{s1}}{R_{s1}}.\frac{1}{J_v} \tag{5}$$

Materials and methods

Textile industry characterization

Ever increasing water tariffs and scarcity of water sources in Istanbul forced many industries to adopt industrial wastewater reclamation and recycle. Among them is Altınyıldız textile industry with a total wastewater flow of about 3000 m^3/day. The project of wastewater reclamation and recycle of Altınyıldız textile industry was started in 1985 and the plants were constructed and taken into operation in April 1987 (Sarikaya *et al.*, 1998). The wastewater sources, flowrates and existing treatment methods are given in Table 1. Flow diagram of the plant is given in Figure 1. As shown in Figure 1, only less polluted fraction of wastewater from finishing process which amounts to about 1,200 m^3/day is passing through reclamation plant. Dyehouse effluents represent about 40% of total wastewater flow. This amount is also very large and textile industry is planning to reclaim the dyehouse effluents too. Thus, pilot scale experiments have been conducted with nanofiltration membrane to reclaim the dyehouse effluents. Acidic, disperse and metal complex dyes are being used in dyehouse. Wastewater characterization of dyehouse effluents is given in Table 2 (Kural, 2000).

Experimental system

Experiments have been performed with pilot scale Aquaset 9712 membrane filtration equipment. This system operates over the pressure range of 1–70 bar and contained a spiral wound module which housed membranes with 2 m^2 total membrane area. A heat exchanger permitted all filtration experiments to be controlled at 25–27°C. Nanofiltration membranes (TFC-S) manufactured by Fluid System were used for the dyehouse effluents. Pilot membrane system was operated in two modes. In semi-batch, unsteady-state mode of operation, retentate is recycled to the feed tank and permeate collected separately. In semi-batch, steady-state operation which is second mode, both retentate and permeate is recycled to the feed tank. For a series of experiments, wastewater was pumped from a 60 l for steady state mode and 150 l for unsteady state mode feed tanks into the spiral wound module. Flow diagram of pilot membrane system is given in Figure 2.

Analytical methods

Color was measured by a spectrophotometer (Hach) in Pt-Co units. COD was measured according to Standard Methods (APHA, 1989). pH was measured with an ion analyzer (Orion SA 720) . AGB-10001 Laboratory Data Logging type was used to measure temperature and conductivity. The process performance was evaluated by automatically measur-

Table 1 Wastewater sources, flowrates and treatment methods

Source	Flow Rate (m^3/d)	Treatment method
Wool Scouring	160	Physico-Chemical
Dyehouse	1,000	Chemical
Finishing	1,200–1,500	Chemical Filtration

Table 2 Wastewater characterization of dyehouse effluents

Parameter	Concentration (mg/l)	kg per ton of production
COD	500–800	161
BOD_5	400	43
SS	85	9
Color, Pt-Co	500	
Sulphide	2	0.2

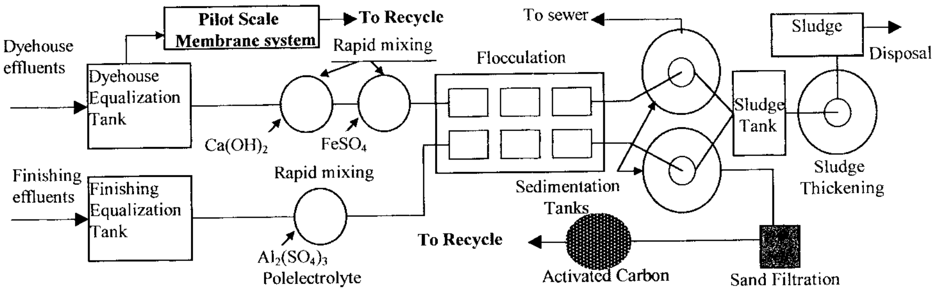

Figure 1 Flow diagram of existing wastewater treatment plant

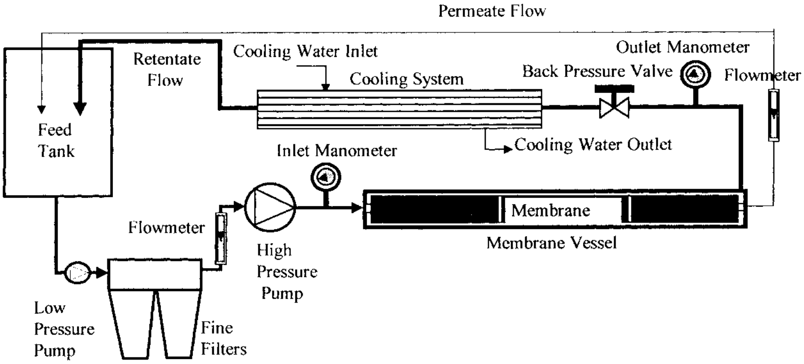

Figure 2 The flow diagram of the pilot membrane system

ing the permeate flow and the pressure at the inlet and outlet of the module during each experiment.

Results and discussions

Membrane fouling

Permeate flux is an important parameter in the design and economical feasibility analysis of membrane separation processes. Flux is affected by several factors such as feed pressure, operating temperature, feed velocity and/or composition (Chen *et al.*, 1997). Successive batch runs demonstrated that any serious membrane fouling was not experienced with dyehouse effluents. Figure 3 shows the relationship between permeate flux and transmembrane pressure at two different feed concentrations. At low pressures, the flux increased with increasing pressure. However, flux did not increase proportionally with the pressure at high pressures. Cheryan (1998) defined these two distinct as a pressure controlled region and mass transfer controlled region. In the mass transfer controlled region increasing the pressure only results in a build up of a solute layer.

A resistance model based on the Hagen–Poiseuille law and the resistance in series conceptually fits typical flux pressure data (Cheryan, 1998, Wu *et al.*, 1998):

$$J = \frac{P}{(R_m + R_f) + R_p} = \frac{P}{R_m' + \phi.P} \tag{6}$$

where J = permeate flux, P = transmembrane pressure, R_m = intrinsic membrane resistance, R_f = fouling resistance and R_p = pressure related resistance due to concentration polarization (therefore, $R_p = \phi.P$, where ϕ is an adjustable parameter). At low pressures, $R_m' > \phi.P$ and flux value will be approximately P/R_m'. Thus, at low pressures flux increases directly proportional to the pressure. At high pressures, $R_m' < \phi.P$ and flux will approach the limiting value $1/\phi$ (Wu *et al.*, 1998). A regression using Equation (6) was performed on the observed flux data (Figure 3) and the results are listed in Table 3.

As shown in Figure 4, flux decreased with increasing recovery rate. While recovery was increasing, feed stream concentration increased. If the membrane plant was operated at a recovery of 50%, the feed stream concentration was doubled. At high concentration factors,

Table 3 Regression results of resistance model

Feed Concentration (Conductivity, μS/cm)	R_m'	ϕ	R^2
700 (run 1)	0.4026	0.0065	0.988
520 (run 2)	0.3904	0.0035	0.998

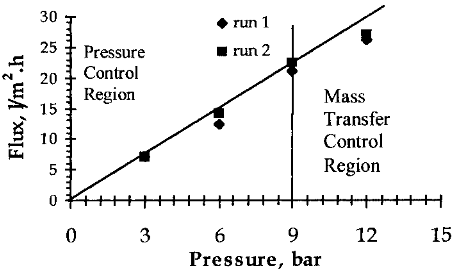

Figure 3 The relationship between the permeate flux and at two different feed concentration (Run 1: 700 μs/cm and Run 2: 520 μs/cm)

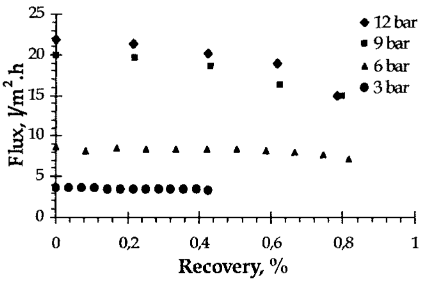

Figure 4 The relationship between the recovery rate and flux based on operating pressures

the negative effect of concentration polarization on membrane performance can be so serious that the flux is decreased. Deposition of solute on the surface of membranes can change the separation characteristics and the high concentration of solute at the membrane interface increases the risks of change in composition of the membrane material due to chemical attack (Taylor *et al.*, 1996).

Permeate quality

Nanofiltration membranes were evaluated for their suitability in separating COD, color and conductivity from textile industry dyehouse effluents. The overall removal efficiency of COD, color and conductivity were greater than 97%. Feed COD value was between the 550–720 mg/l and permeate COD decreased with increasing pressure (Figure 5.). COD was lower than 10 mg/l at 12 bar pressures. Permeate COD was also increased with increasing recovery and COD was 30 mg/l with 80% of recovery. Almost complete color removal was achieved with nanofiltration membrane. Color value was decreased from 500 Pt-Co to 10 Pt-Co unit. This significant reduction in color and COD makes possible the reuse of the permeate in the dyehouse.

Permeate conductivity decreased with increasing pressure (Figure 6). The retention of conductivity increases with increasing pressures (Figure 7). This phenomenon is expected from the analysis of conductivity mass transport model. As it has been shown that an increase in pressure would result in a decrease in $1/R$ or increase in R. According to Equation 5, the B_{s1} and R_{s1} values for different operating pressures are obtained from intercept in a straight line relationship between $1/R$ and $1/J_v$. The relationships between conductivity retention and permeate flux for NaCl solution (2000 mg/l) and dyehouse effluent are given in Figure 8 and 9. $B_{S(Cond.)}$ and $R_{S(Cond.)}$ values are given in Table 4 for NaCl solution and dyehouse effluent at different operating pressures. As shown in Table 4, mass

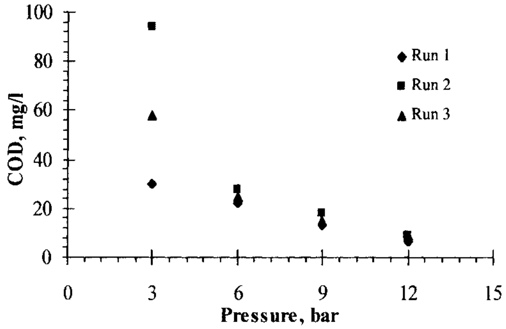

Figure 5 COD versus pressure

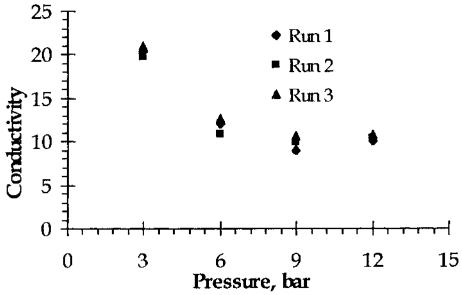

Figure 6 Permeate conductivity (μS/cm) versus pressure

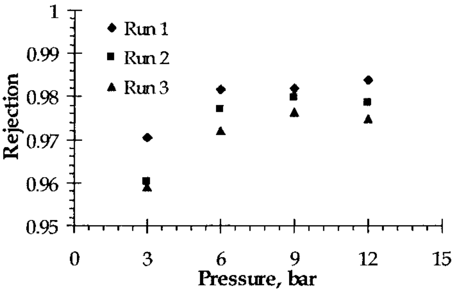

Figure 7 Retention of conductivity versus pressure

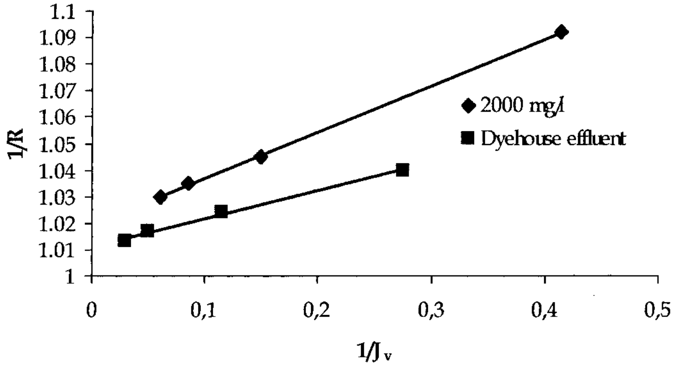

Figure 8 The relationship between conductivity retention and permeate flux for dyehouse effluents 2000 mg/l NaCl solution

Table 4 $B_{s(\mathrm{Cond.})}$ and $R_{s(\mathrm{Cond.})}$ values for NaCl solution and dyehouse effluent

Parameter	Dyehouse effluent	NaCl (2000 mg/l)
$R_{s(\mathrm{Cond.})}$	0.98922	0.98078
$B_{s(\mathrm{Cond.})}$	0.17232	0.17085

transfer parameter of conductivity increased with increasing pressure. The change in the rejection with increasing transmembrane pressure drop suggests that the contaminants of the dyehouse effluents do not interact strongly with the membrane element. Otherwise, the rejection would decrease with increasing pressure. An other expectation from this result is that fouling should not be a serious problem and may not occur inside the membrane (Wu *et al.*, 1998).

As recovery rate rises, the salt concentration in the feed stream increases, which causes an increase in the driving force for salt flow or salt passage. Higher salt concentration levels in the feed stream increase the osmotic pressure, which reduce the net pressure driving force and therefore permeate flow. As shown in Figure 9, conductivity rejection was decreased with increasing recovery rate and conductivity rejection decreased with decrease in pressure. Figure 10 illustrates the effect of recovery rate on feed conductivity.

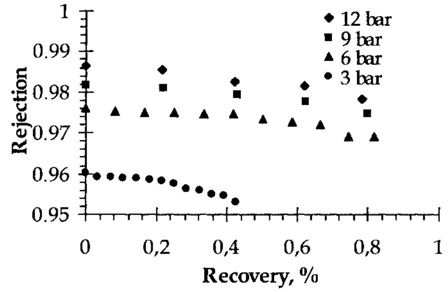

Figure 9 Conductivity rejection versus recovery rate

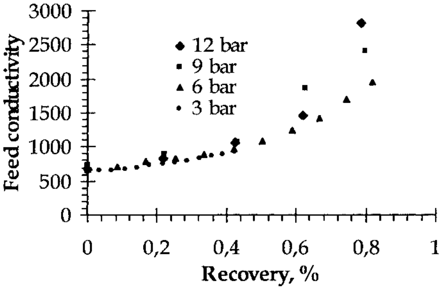

Figure 10 The effect of recovery on feed concentration

Economical evaluation

Economical analysis is reported in Table 5. The capital cost of the system will be approximately $300,000. The capital cost includes site development, utilities, equipment and land. As operating cost, energy, membrane replacement, labour, spare parts, chemicals, filter costs were included. The membrane life in this application was assumed to be 3 years and 1 kWh costs $0.062. Amortizing will be estimated for a period of 5 year and an interest rate of 10% for capital cost. Energy consumption versus pressure are given in Figure 11. Capital cost and operating cost were totalled to obtain the total production cost. Total production cost is affected by most of the operating parameters such as pressure, temperature, and plant capacity. Based on 1000 m^3/day of capacity, the total estimated cost will be 0.81 $/$m^3$. This value was represented as approximately 1$ /m^3 in the literature for reactive dyeing of cotton (Wenzel *et al.*, 1996). Industrial water supply tariffs of Istanbul City is 2–3 $/$m^3$. According to this value, recycling of their own wastewater for industries in Istanbul City will be very economical.

Conclusions

The resistance model described the effect of pressure on permeate flux. Although the values of limiting fluxes were not calculated, the limiting flux clearly increased with pressure. At low pressures, the flux increased with increasing pressure. However, flux did not increase proportionally with the pressure at high pressures. This was defined with two distinct regions as a pressure controlled region and mass transfer controlled region. Also, flux decreased with the increase in recovery. While recovery was increasing, feed stream concentration increased. In high recovery rates, flux was higher with high pressure and lower with low pressures. Fouling should not be a serious problem and may not occur inside the membrane.

Table 5 Summary of capital and operating costs (1,000 m^3/day of capacity)

	Costs ($/m3)
Capital cost	**0.22**
Operating Costs	
Energy	0.18
Membrane replacement	0.11
Labour	0.13
Spare parts	0.10
Chemicals	0.05
Filters	0.02
Total	**0.81**

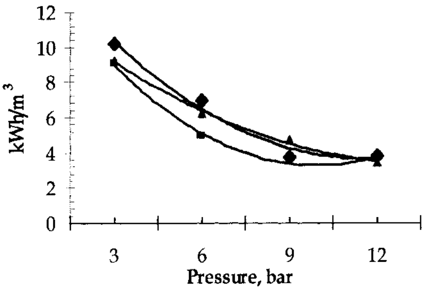

Figure 11 Energy consumption versus pressure

After nanofiltration of a textile dyehouse effluents to separate COD, color and conductivity, the overall removal efficiency of COD, color and conductivity were greater than 97%. Permeate COD decreased with increasing pressure. COD was lower than 10 mg/l at 12 bar pressures. Almost complete color removal was achieved with nanofiltration membrane. Color value was also decreased to 10 Pt-Co unit. This significant reduction in color and COD makes possible the reuse of the permeate in the dyehouse. Retention of parameters increases with increasing pressure. This phenomenon was explained from the analysis of conductivity transport model. $B_{s(Cond.)}$ and $R_{s(Cond.)}$ values for different operating pressures were obtained from intercept of the straight line relationship between $1/R$ and $1/J_{v.}$ Mass transfer parameter of conductivity($B_{S(Cond)}$). increased with increasing pressure. The total estimated cost will be 0.81 \$/m^3 for 1000 m^3/day of capacity and this value is very economical for Istanbul City due to higher industrial water tariffs.

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