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Treatment of a chemical industry effluent by nanofiltration and reverse osmosis

Ö. Aktaş[a,*], E. Sahinkaya[a], A. Yurtsever[b], S. Demir[c], M. Yüceyurt[d], A. Çakmak[d], Ç. Külekci[d], Ş. Tahmaz[d], M. Uludağ[d]

[a]*Bioengineering Department, Istanbul Medeniyet University, 34700 Istanbul, Turkey, Tel. +90.216.2803210; emails: aktasozg@gmail.com (Ö. Aktaş); erkansahinkaya@gmail.com (E. Sahinkaya)*
[b]*Department of Civil Engineering, Hasan Kalyoncu University, 27410 Gaziantep, Turkey, email: aayurtsever@gmail.com*
[c]*Environmental Engineering Department, Yildiz Technical University, 34220 Istanbul, Turkey, email: demirserkan@gmail.com*
[d]*ENTA Treatment Systems - Engineer. & Contract. LTD, Fazil Kaftanoglu Cad., No.: 7, Seyrantepe, 34485 Istanbul, Turkey, emails: mehmet@enta.com.tr (M. Yüceyurt), ali@enta.com.tr (A. Çakmak), caglar@enta.com.tr (Ç. Külekci), senay@enta.com.tr (Ş. Tahmaz), muzaffer@enta.com.tr (M. Uludağ)*

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ABSTRACT

Advanced filtration processes, namely nanofiltration (NF) and reverse osmosis (RO), can produce high-quality permeate from industrial effluents for a safe discharge or water reuse. In the present study, a biologically treated complex chemical industry wastewater was dead-end filtered through commercial NF and RO membranes. Dow Filmtec NF270, NF90, BW30 and SW30 membranes and Lewabrane RO B090 membrane were tested either separately or sequentially by NF followed by RO. Filtration through NF270 decreased chemical oxygen demand, color and conductivity from 202 mg/L, 222 Pt-Co and 10,150 μS/cm to 110 mg/L, 46 Pt-Co and 5,700 μS/cm, respectively. NF membrane mainly removed organic matter and divalent ions. RO membrane BW30 further removed these parameters as well as monovalent ions and thereby significantly decreased conductivity to 1,914 μS/cm. A secondary BW30 further decreased conductivity to 582 μS/cm for water reuse in industry. NF membranes served as pretreatment for RO membranes preventing fouling. Satisfactory membrane permeabilities were obtained as 2.2 LMH/bar for NF270 at 70% water recovery and 1.2 LMH/bar for the succeeding BW30 at 50% recovery at 15 bar filtration pressure. The study showed that sequential NF–RO process can successfully produce reusable permeates from a biologically pretreated chemical industry effluent.

Keywords: Chemical industry wastewater; Nanofiltration; Reverse osmosis; Membrane fouling; Water reuse

1. Introduction

Chemical industry produces a large variety of organic chemicals, which can be refractory in biological treatment. Some xenobiotic compounds may be discharged to the environment where they may lead to serious ecological hazards if they are not treated properly [1]. Besides, effluents of the industry may have high chemical oxygen demand (COD), color and conductivity. In terms of the reuse of industrial wastewaters, conductivity is the major problem since salts cannot be removed by conventional biological processes, microfiltration (MF) or adsorption [2], and nanofiltration (NF) and/or reverse osmosis (RO) processes are required for producing high-quality reusable permeates [3].

The main mechanisms for NF and RO filtration processes are sieving, charge rejection and solubility–diffusion [4]. NF mainly removes organic matter and multivalent ions efficiently, whereas RO can also efficiently remove monovalent ions. Depending on the type of ions dominant in a wastewater,

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* Corresponding author.

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NF, RO or a combination of them may be necessary in order to obtain reusable water. Sequential filtration processes, e.g., NF followed by NF or RO, can increase both filtration characteristics and pollutant removal efficiencies [5].

Particularly, RO filtration removes salts and thereby decreases conductivity much more efficiently compared with NF membranes. For example, in a comparative study of NF and RO membranes, it was shown that NF removed 79% of salts whereas RO removed 95% from a metal industry effluent [6]. NF may remove more than 80% of NaCl and 90% of Na_2SO_4 from a textile industry effluent [7]. On the other hand, conductivity removal reached up to 98% in the case of RO treatment of dairy wastewater [8]. Therefore, RO process is usually required when water recovery and reuse is particularly aimed [9].

Two major problems for NF and RO applications are membrane fouling and concentration polarization. Membrane fouling caused by pore clogging and cake formation are the main factors for flux decline [10]. Water recovery yield and permeate flux decrease significantly in RO compared with NF at the same filtration pressures [11]. Water recovery can reach up to 70%–85% in NF processes. On the other hand, in RO process, water recovery may reach up to 70%. Water recovery is very much dependent on the wastewater characteristics. For example, in the case of dairy wastewater, RO treatment could achieve very high recovery of about 90%–95% at fluxes of 11 LMH to achieve conductivity less than 50 µS/cm [12]. In another study with cooler condensates from a dairy factory, NF filtration achieved 87.5% water recovery with permeability of 4 LMH/bar to obtain 204 µS/cm conductivity [13].

Biological treatment of high-strength industrial effluents before dense membrane filtration is quite important in terms of decreasing membrane fouling, increasing water recovery and decreasing pollutant concentrations in the concentrate [14]. Also, retrofitting the existing biological treatment plants for water recovery with dense membrane treatment will be required more often in near future due to water shortage. Hence, more studies should be conducted on operational strategies of the dense membrane filtration of biologically treated industrial effluent to decrease operational and capital costs and to increase permeate quality.

The present study investigated the dead-end filtration of a biologically treated wastewater obtained from an industrial complex of five chemical plants by commercially available NF and RO membranes. It was aimed to determine the contaminant removal efficiencies and the achievable water recovery ratios of NF and RO membranes both separately and also sequentially by NF followed by RO. To the best of our knowledge, there is no previous study in the literature on the use of NF and RO membranes, either comparatively or sequentially, for the recovery of mixed chemical industry wastewaters.

2. Materials and methods

2.1. Wastewater characteristics

The wastewater was obtained from the wastewater treatment plant (WWTP) effluent of a mixed chemical industry of five different chemicals production plants, which produces and further bleaches acrylic tow and fiber, and various organic chemicals by using a wide range of chemicals including mainly acrylonitrile monomer, vinyl acetate monomer, dimethylacetamide, various dyes and pigments, optical whiteners, ammonia and organic chemicals including various amines, methyl alcohol, ethyl alcohol, various esters and various organic solvents. The wastewater characteristics are shown in Table 1. The wastewater involved particularly high total nitrogen concentration, high color, conductivity as well as high sulfate and chloride concentrations. After biological treatment of the wastewater in the real WWTP, COD and color were significantly reduced. However, conductivity did not change as expected.

2.2. Dead-end filtration tests

Effluent from the biological treatment of the full-scale chemical industry WWTP was regularly collected from the site before each test and used after filtration through a 0.45-µm MF filter in order to remove suspended solids, which may lead to fouling in the NF or RO membranes. Dead-end NF and RO filtration tests were performed using sequentially distilled water, then wastewater and finally distilled water again without changing the filter in order to obtain flux declines due to fouling and concentration polarization. The stabilized values of initial distilled water fluxes were used in the manuscript. The dead-end filtration mechanism used in the filtration tests are shown in Fig. 1. The dead-end mechanism involved Sterlitech HP4750 stainless-steel stirred cell, which can operate up to a maximum operating pressure of 1,000 psi (68.9 bar). Agitation was provided by a removable polytetrafluoroethylene stir bar. Working volume of the cell was 300 mL, and the filtration area was 14.51 cm^2.

NF (Dow Filmtec NF270 and NF90) and RO membranes (Lewabrane RO B090 and Dow Filmtec BW30 and SW30) were tested either separately or sequentially by NF followed

Table 1
Characteristics of the mixed chemical industry wastewater

Parameter	Average ($n^a = 30$)	Standard deviation	Maximum value	Minimum value
COD, mg O_2/L	1,571	375	2,967	1,053
Total N, mg N/L	232	62	464	172
Total P, mg P/L	1.41	1.66	6.08	0.36
Color, Pt-Co	703	234	1,400	353
Conductivity, µS/cm	9,243	1,053	10,900	7,520
pH	9.7	0.5	10.9	8.5
Oil and grease, mg/L	6	4.4	11.4	1.6
Sulfate, mg/L	2,008	285	2,670	1,500
Chloride, mg/L	1,500	727	3,090	161

[a] Number of samplings during 2 months.

by RO. The characteristics of the membranes are shown in Table 2. In the first set of experiments, NF270, NF90 and B090 were tested separately at 15 bar filtration pressure. In the following tests two-stage filtration sets were performed. The two-stage tests involved NF270–NF90 (at 7 bar pressure), NF270–BW30 (at 15 bar), BW30–BW30 (at 15 bar) and NF270–SW30 (at 20 bar for NF270 and 30 bar for SW30).

The flux difference in the distilled water filtration before and after wastewater filtration showed the flux decline caused by foulants present in the wastewater. Wastewater flux was continuously measured and recorded with respect to time and volume of permeate. The flux difference between initial distilled water and wastewater gives the total flux decline due to fouling and concentration polarization. Membrane flux is related to the targeted water recovery ratio (%R) or the corresponding volume reduction factor (VRF). Using the amount of permeate filtered, water recovery ratio (%R) and VRF were calculated during filtration tests according to the following equations:

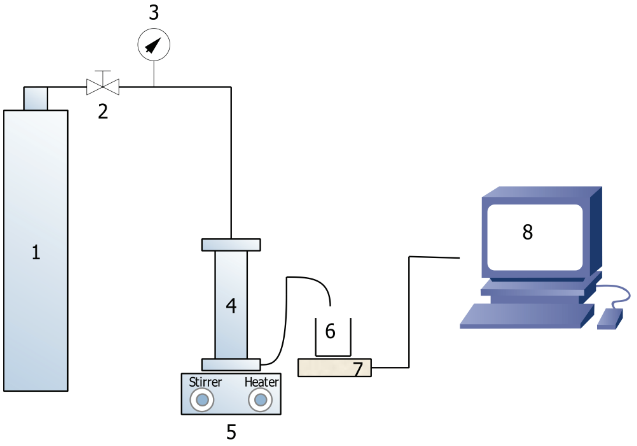

Fig. 1. Dead-end filtration mechanism: 1 – N_2 gas tube; 2 – N_2 gas valve; 3 – pressure gauge, 4 – dead-end mechanism; 5 – magnetic stirrer; 6 – filtrate collection beaker; 7 – digital weight and 8 – computer.

$$\mathrm{VRF} = V_i/V_r \tag{1}$$

where V_i and V_r refer to initial water volume (batch dead-end system) or feeding water flow rate (continuous cross-flow system) and the remaining volume of water (batch dead-end system) or concentrate flow rate (continuous cross-flow system), respectively.

$$\%R = V_p/V_i \times 100 \tag{2}$$

where V_p is the permeate volume (batch dead-end system) or flow rate (continuous cross-flow system). When these two equations are combined, the following equation is obtained:

$$\%R = (1 - 1/\mathrm{VRF}) \times 100 \tag{3}$$

These data were used for evaluating the filtration performances of each membrane. The batch-type dead-end filtration tests were used in our experiments to present the worst situation that could be encountered in the case of a continuous cross-flow filtration test. Treatment performances of each membrane were evaluated by measuring the removal of pollutants. COD, pH, color and conductivity analyses were performed in both the permeate and concentrate obtained after wastewater filtration as well as in the influent of the filtration tests. In addition, inorganic parameters involving monovalent and divalent ions were also measured in the two-stage filtration tests with NF270 and BW30 in order to show the removal of these parameters at each step and evaluate their impacts on membrane fouling. Water temperature was about 20°C during dead-end filtration tests.

2.3. Analyses

COD measurements were performed according to the standard methods [15]. The pH and conductivity of samples were analyzed electronically by probes. Color was measured by the Pt-Co method according to the standard methods [15]. Inorganic parameters such as Al, Cu, Fe, P, Ca, Mg, K, Si, Na, Cl and S were determined by inductively coupled plasma

Table 2
Characteristics of the NF and RO membranes used in the study[a]

	NF270	NF90	RO B090	RO BW30	RO SW30
Material	Polyamide	Polyamide	Polyamide	Polyamide	Polyamide
pH range	2–11	2–11	1–12	2–11	2–11
Maximum temperature, °C	45	45	45	45	45
Maximum pressure, bar	41	41	41	41	83
Water permeability, LMH/bar	10.85[b]	8.68[b]	3.01[c]	3.40[c]	0.58[d]
NaCl rejection, %	n.a.	n.a.	99.5[c]	99.5[c]	99.75[d]
$MgSO_4$ rejection, %	>97[b]	>97[b]	n.a.	n.a.	n.a.

[a] Source: Product data sheets.
[b] Permeate flow and salt rejection based on the following test conditions: 2,000 mg/L $MgSO_4$, 4.8 bar, 25°C, 15% recovery.
[c] Permeate flow and salt rejection based on the following test conditions: 2,000 mg/L NaCl, 15.5 bar, 25°C, 15% recovery.
[d] Permeate flow and salt rejection based on the following test conditions: 32,000 mg/L NaCl, 55 bar, 25°C, 8% recovery.
Note: n.a. – not available.

optical emission spectrometer (ICP-OES, Thermo ICAP600) analysis for water samples and by scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDS, Philips-XL30 SFEG) for the membrane cakes.

3. Results and discussion

3.1. Performances of single-stage NF and RO membranes

Separation performances of Dow Filmtec NF270 and NF90 NF membranes and Lewabrane B090 HF RO membrane at 15 bar pressure are shown in Fig. 2. For NF270, flux for distilled water stabilized at about 158 ± 5 LMH corresponding to permeability of about 10.5 LMH/bar (data not shown). This value is very close to the permeability reported by the producer (Table 2). Distilled water fluxes were also obtained after filtration of the wastewater in order to determine the effect of membrane fouling caused by the impurities found in wastewater. Distilled water flux following wastewater filtration decreased to 97 ± 3 LMH corresponding to permeability of about 6.5 LMH/bar showing a permeability decrease of 39% because of fouling. On the other hand, wastewater flux decreased from 100 to 33 LMH when VRF reached up to 3.3 corresponding to water recovery ratio (%R) of 70%. The reason for this drastic decline was due to both fouling and concentration polarization. Due to high water recovery rates, membrane fouling was caused by both precipitation of supersaturated inorganic salts and the adsorption of organic matter.

Other studies also showed permeate flux decline in dead-end filtration tests due to increase of salt concentration leading to osmotic pressure increase and concentration polarization [5,16,17]. The flux decline due to concentration polarization is completely reversible, whereas flux decline due to fouling can be either reversible or irreversible [5,17]. The flux difference between distilled water (J_{dwi}) and wastewater (J_{ww}) gives the total flux decline due to fouling and concentration polarization. The flux difference between initial distilled water and final distilled water (after wastewater filtration) (J_{dwf}) gives flux decline due to fouling. Consequently, the flux difference between final distilled water (J_{dwf}) and wastewater (J_{ww}) gives flux decline due to concentration polarization [17]. When 70% water recovery was reached, total flux decline ($(J_{\mathrm{dwi}} - J_{\mathrm{ww}})/J_{\mathrm{dwi}}$) was calculated as 79%, where 39% of it can be considered as flux decline due to fouling ($(J_{\mathrm{dwi}} - J_{\mathrm{dwf}})/J_{\mathrm{dwi}}$) as mentioned above and the remaining 40% due to concentration polarization. A previous study also showed that concentration polarization was a major factor for flux decline, particularly at neutral pH [17].

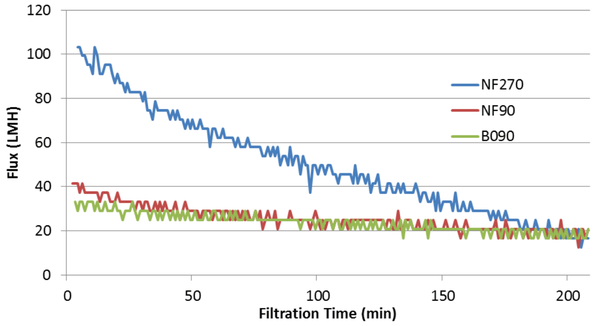

Fig. 2. Performances of NF270 and NF90 nanofiltration membranes and Lewabrane B090 HF reverse osmosis (RO) membrane for filtration of mixed chemical industry effluent at 15 bar pressure.

For NF90, flux for distilled water filtration stabilized at about 89 ± 5 LMH at 15 bar pressure corresponding to permeability of about 6 LMH/bar. This was much lower compared with NF270. After wastewater filtration, distilled water flux for NF90 declined and stabilized at around 50 ± 1.5 LMH, and permeability correspondingly decreased by 45% to 3.3 LMH/bar (data not shown). On the other hand, wastewater flux continuously decreased (Fig. 2). For a VRF value of 3.3 corresponding to 70% recovery, flux decreased from the initial value of 40 LMH to about 6 LMH (data not shown). Hence, total flux decline ($(J_{\mathrm{dwi}} - J_{\mathrm{ww}})/J_{\mathrm{dwi}}$) at %$R$ of 70% was 93%, 45% of which was due to fouling and the remaining 48% was due to concentration polarization. For the same water recovery (70%), flux was as high as 33 LMH in the case of NF270. Dense NF membranes, such as NF90 in our study, lead to low fluxes owing to the high osmotic pressure caused by efficient removal of salts [10]. Lower permeability (6.1 vs. 12.6 LMH/bar), higher flux decline (76% vs. 52%) and much higher conductivity removal (91% vs. 60%) were also reported in a previous study for NF90 compared with NF270 in the case of dye rinsing water with higher conductivity (11.2 mS/cm), COD (about 1,600 mg/L) and color (about 5,000 Pt-Co) compared with the chemical industry wastewater of our study [5]. However, flux decline due to membrane fouling was very low (2% for NF270 and 10% for NF90), and most of the flux decline was reversible and due to concentration polarization in that study. Another study on NF of pulp and paper mill effluent reported 33%–37% flux decline, of which only 10%–12% was due to fouling and the remaining 22%–25% was due to concentration polarization at transmembrane pressure between 12 and 36 bar [18]. Hence, it can be deduced that the mixed chemical industry in our study led to more membrane fouling due to its complex organic and inorganic content compared with the above mentioned studies.

In the case of RO membrane Lewabrane B090, distilled water flux was 60 ± 2 LMH at 15 bar pressure corresponding to permeability of about 4 LMH/bar. After wastewater filtration, distilled water flux declined by 30% to 42.2 LMH, and permeability decreased to 2.8 LMH/bar. Wastewater flux starting with about 30 LMH decreased in time. When VRF could be increased to a maximum value of 2.77 corresponding to about 64% water recovery, flux decreased to about 8 LMH. Flux was 15 LMH corresponding to permeability of 1 LMH/bar at 50% water recovery ratio (%R), which may be considered as the maximum acceptable recovery for an RO membrane. Total flux decline ($(J_{\mathrm{dwi}} - J_{\mathrm{ww}})/J_{\mathrm{dwi}}$) at %$R$ of 50% was 75%, 30% of which was due to fouling and the remaining 45% was due to concentration polarization. Flux and permeability were lower in the case of RO membrane B090 compared with NF membranes. This difference was much apparent particularly with NF270 and was much less compared with NF90. Hence, permeability and fouling characteristics of NF90 were much closer to the RO membrane B090 rather than the NF270. Therefore, it could be deduced that NF90 membrane acted very similar to an RO membrane.

Table 3 shows the rejection efficiencies of the three types of membranes for COD, color and conductivity parameters. The rejection efficiencies of NF270 for COD and color were as high as 70% and 90%, respectively. The effluent concentrations were satisfactory for discharge since the discharge standards were 250 mg/L for COD and 280 Pt-Co for color, and no discharge limit for conductivity. However, conductivity rejection remained at 27%, and permeate conductivity was far from being satisfactory for water reuse, since <600 μS/cm was required by the industry. The reason for this was that NF270 membrane could capture divalent ions, but not monovalent ions. The wastewater involved high chloride concentrations, which should be removed by an RO membrane if the wastewater is aimed to be reused. A literature cross-flow filtration test with NF270 for textile wastewater at pilot scale reported higher COD, color and conductivity rejection efficiencies of 98.4%, 98.6% and 66.4%, respectively, even at 6 bar pressure [19]. This difference can be attributed to difference in the type of organic matter and inorganic ion as well as the better filtration efficiency of cross-flow compared with dead-end filtration.

On the other hand, dense NF membrane NF90 and RO membrane B090 significantly decreased conductivity reaching up to 95% as well as COD and color. A previous study also showed comparable or even better conductivity removal (91% for NF90 vs. 71% and 92% for RO membranes) as well as COD and color removal efficiencies for NF90 compared with two RO membranes [5]. The difference between NF270 and NF90 was attributed to the highly negative charge of NF90, which led to higher rejection of chloride ions. Even though the molecular weight cut-off (MWCO) of NF90 (about 100 Da) is lower than that of NF270 (about 200–300 Da) [5], the MWCO may be still high for the rejection of monovalent ions. However, in the cases of NF90 and B090 membranes, flux decline increases significantly when water recovery ratio (%*R*) is higher than 50%. But NF270 membrane can serve as pretreatment for RO membranes to prevent fouling. Therefore, it is reasonable to use RO membrane, downstream of NF270 permeate.

Table 3 shows that both NF90 and B090 membranes achieved significantly low COD and color concentrations in the permeate. An important finding here was that conductivity was also low in NF90 as for the RO membrane B090. The reason for this may be that chloride ions were also rejected in NF90 because of Donnan effect owing to the negative charge of NF90 membrane surface. The decrease of pH in NF90 filtration may also be the result of negative charge of the membrane such that OH^- ions were rejected, but H^+ ions were allowed to pass.

3.2. Performances of sequential NF and RO membranes

In order to show the pretreatment efficiency of NF270 and filtration performances of succeeding NF or RO membranes, sequential NF–NF and NF–RO filtration tests were performed. In a sequential system, it is possible to operate under lower pressures. Therefore, pressure was decreased from 15 to 7 bar in the sequential filtration tests. Fig. 3 shows the membrane separation performances of NF90 and the preceding NF270 at 7 bar pressure.

Distilled water filtration flux for NF270 was on average 58 ± 4 LMH at 7 bar pressure corresponding to permeability of 8.3 LMH/bar (data not shown). After wastewater filtration, distilled water flux was as high as 63 ± 3 LMH showing that wastewater did not foul NF membrane at this pressure, and flux even increased rather than decrease. The reason for this may be that the membranes were probably not compacted well during the initial distilled water filtration tests. However, flux decline due to fouling was about 40% when NF270 was operated at 15 bar pressure. Hence, membrane fouling was less possible at a lower pressure. Wastewater flux, however, declined in time from 30 LMH to about 8 LMH because of accumulation of foulants on the membrane as expected. If 70% recovery and VRF value of 3.3 is aimed, corresponding flux will be 19 ± 2 LMH, and permeability will be 2.71 LMH/bar. Flux was lower, but permeability was higher than the permeability value of 2.2 LMH/bar in the case of previous tests at 15 bar pressure. This shows that at high pressure, it is normal to expect higher fluxes, but permeability may decrease resulting in a less energy efficient filtration. Total flux decline was 67% at %*R* of 70%.

On the other hand, succeeding NF90 membrane stabilized at distilled water flux of about 33 LMH corresponding to permeability of 4.71 LMH/bar. After wastewater filtration, distilled water flux declined by 15% to about 28 LMH

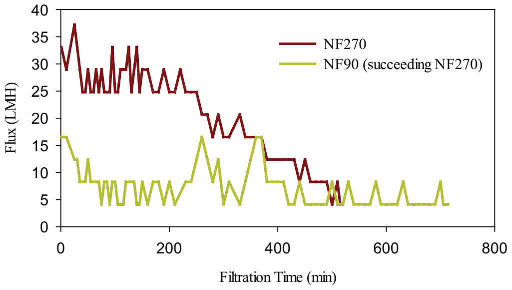

Fig. 3. Performances of membranes in a sequential system of NF270 and succeeding NF90 at 7 bar pressure.

Table 3
Treatment performances of NF270, NF90 and B090 membranes (at 15 bar pressure)

	NF270		NF90		B090	
	Influent	Permeate	Influent	Permeate	Influent	Permeate
COD, mg/L	206	65	193	26	189	7
Color, Pt-Co	225	24	440	0	434	7
pH	7.86	8.09	7.44	6.63	6.90	7.66
Conductivity, μS/cm	9,280	6,790	9,360	446	8,670	607

corresponding to permeability of 4 LMH/bar. Flux decline was lower, and permeability was higher after wastewater filtration compared with the previous filtration tests without NF270 pretreatment, where flux decline was 45% due to fouling. These findings showed that prefiltration with NF270 resulted in more efficient filtration in the succeeding RO membrane. When water recovery of 50% (VRF = 2) was reached for a highly extended filtration duration time over 700 min, flux declined to about 4.2 LMH corresponding to permeability of 0.6 LMH/bar. Total flux decline was 87% at %*R* of 50%.

Conductivity was decreased from 9,680 to 8,950 µS/cm by the initial NF270 showing only a slight decrease. In the succeeding NF90 permeate, conductivity decreased to 2,720 µS/cm. Conductivity was still high in the permeate of NF90, and this was even higher than the single-step NF90 treatment at 15 bar pressure, in which conductivity had decreased to 446 µS/cm. The reason for this was the higher pressure applied in previous tests as well as the changing characteristics of the influent wastewater, such that different type of ions may contribute to conductivity at samplings of different times. Particularly, higher pressure in dead-end filtration may lead to higher conductivity rejections as also shown in a previous two-step NF filtration study with pulp and paper mill wastewater [18]. In that study, conductivity removal efficiency of succeeding two NF membranes increased from 80% to 90% in total by increasing pressure from 12 to 36 bar at both steps.

In order to obtain better conductivity removal, it was decided to use RO membranes succeeding NF membrane NF270. Since chloride concentrations were high in the influent, Dow Filmtec BW30 membrane was further tested succeeding NF270, since NaCl rejection ratio was given as 99.5% by the producer. For NF270 membrane prefiltration, flux was obtained as 33 LMH and permeability as 2.2 LMH/bar at water recovery of 70% under 15 bar pressure (data not shown). The results were the same as in the case of previous single-step NF270 filtration test as expected. Fig. 4 shows the filtration performance of BW30 following NF270 prefiltration at filtration pressure of 15 bar. Flux starting from about 30 LMH decreased gradually but slowly to below 20 LMH during the filtration duration of 240 min. When water recovery reached 50% (VRF = 2), flux decreased to 18 LMH, and the corresponding permeability was equal to 1.2 LMH/bar for BW30. This flux was reasonable, and permeability was two times better than that of NF90, which had flux of only 4.2 LMH at 7 bar pressure resulting in permeability of only 0.6 LMH/bar following NF270 prefiltration. However, another study for textile effluent treatment for reuse, but in the case of single-stage filtration, showed that under the same operating pressure (10 bar), NF90 exhibited higher water permeability and more severe flux decline than BW30 because of its higher porosity and more serious concentration polarization and membrane fouling [20]. In the same study, conductivity removal was higher for BW30 (99.0%) compared with NF90 (87.9%) as in our study, and this finding was attributed to the relatively denser selective surface layer of BW30.

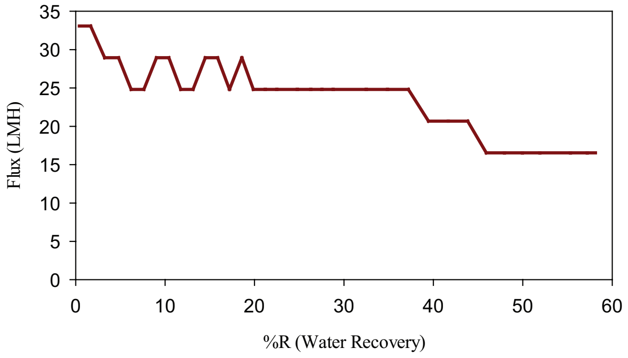

Fig. 4. Performance of BW30 RO membrane downstream of NF270 (sequential system – 15 bar pressure).

Table 4 shows the removal performances of the two membrane types at filtration pressure of 15 bar. NF270 removed COD, color and conductivity with efficiencies of about 45%, 80% and 44%, respectively. BW30 further removed these parameters with efficiencies of 90%, 74% and 66%, respectively. Although permeate conductivity of the sequential system of NF270 and BW30 was better than the sequential NF270 and NF90 system, conductivity was still high for water reuse in most industrial applications. The reason for this was oversaturation of salts on the concentrate side of the membrane, and thereby diffusion of salts through the membrane to permeate. In a study, single-stage BW30 achieved 97% conductivity removal from a metal effluent (from an initial value of 2.6 mS/cm) at a flux of 29.2 LMH and 14 bar pressure (permeability of 2.1 LMH/bar) in a cross-flow filtration system [6]. The lower conductivity rejection efficiencies and permeabilities in our study were because of dead-end filtration, which lead to higher concentration polarization and osmotic pressure. Hence, the effluent conductivities are expected to be lower and filtration permeabilities to be higher in a cross-flow system treating our chemical industry wastewater at pilot or full scale.

Table 4
Treatment performance of BW30 downstream of NF270 (sequential system – 15 bar pressure)

	COD, mg/L	Color, Pt-Co	Conductivity, µs/cm	pH	VRF
Influent	**202**	**222**	**10,150**	7.8	
NF270 permeate	**110**	**46**	**5,700**	8.01	7.96
NF270 concentrate	1,691	1,760	32,000	8.28	
NF270 + BW30 permeate	**11**	**12**	**1,914**	7.87	2.39
NF270 + BW30 concentrate	359	233	28,200	8.39	

Inorganic pollutants were also measured by ICP-OES in the influent as well as permeates and concentrates of the two membranes (Table 5). The influent, which is actually the effluent of the biological treatment of the full-scale WWTP, contained high sulfate (3,353 mg/L), which may lead to fouling of RO membranes related to precipitation of calcium and magnesium salts of sulfate. Besides, silicon over 10 mg/L may lead to membrane fouling. In the NF270 permeate, divalent ions such as sulfate, calcium and magnesium were significantly removed as expected. This prevented the fouling of the succeeding RO membrane. Hence, these results also showed the necessity of an NF membrane upstream of an RO membrane for the treatment of such an industrial wastewater with high conductivity. However, silicon and monovalent ions such as sodium were still high in the permeate of NF270, which explains the high conductivity values. BW30 further decreased the concentrations of divalent ions and significantly removed monovalent ions including sodium and chloride.

SEM-EDS analysis on the membrane cakes also supported the results. SED-EDS analysis gives the weight percentages of all elements on the membrane surface. SEM-EDS analyses were performed before and after wastewater filtration, such that the change in the amount of inorganic foulants can be determined. Weight percentages of Ca, Mg, Na and Cl increased on the NF270 membrane after wastewater filtration (Fig. S1). However, divalent ions did not change after wastewater filtration through the RO membrane following NF270 prefiltration, although Na weight percentage increased on BW30 from 0.10% to 0.58%, and Cl increased from 0.23% to 0.42% (Fig. S2).

However, although reuse requirements, as suggested by the industry, such as sulfate <20 mg/L could be obtained, other requirements for conductivity <600 μS/cm, chloride <50 mg/L and silicon <10 mg/L could not be met. Therefore, a secondary RO membrane may be required for obtaining reusable water, although effluent quality is expected to be better in a full-scale cross-flow filtration system.

For this purpose, two-stage BW30 filtration process was tested without an NF prefiltration. The treatment performance of the two-stage RO system can be seen in Table 6. Conductivity could be decreased significantly at the permeate of the second stage down to 582 μS/cm. However, flux was very low at the first stage (6 LMH), and permeability was only 0.4 LMH/bar at %*R* = 50% (VRF = 2) for the first-stage BW30 (Fig. 5). But duration of filtration test was supposed to be extended to 1,100 min to achieve VRF of 2. Such low flux and permeability will not be practically applicable. Therefore, pretreatment by NF is obligatory for this wastewater.

In the secondary BW30 filtration, about 85% water recovery (VRF = 6.6) was obtained within filtration duration of 360 min (Fig. 5). Flux decline was much slower compared with the first stage BW30, since most of the foulants were captured by the first RO membrane that was severely and

Table 5
Removal of inorganic parameters by sequential NF270 and BW30 RO membranes

Parameter	Influent	NF270 permeate	NF270 + BW30 permeate	NF270 + BW30 concentrate
Aluminum, mg/L	0.825	<0.003	<0.003	0.093
Magnesium, mg/L	9.25	2.53	0.44	16.93
Sodium, mg/L	2,088	1,708	477.6	9,503
Calcium, mg/L	53.94	12.39	1.6	29.17
Potassium, mg/L	56.1	31.29	13	259.6
Iron, mg/L	0.15	<0.00015	<0.00015	<0.00015
Phosphorus, mg/L	1.3	0.073	<0.003	0.82
Chloride, mg/L	2,619	–	55.5	1,296
Silicon, mg/L	25.92	17.48	12.9	93.4
Sulfate, mg/L	3,353	215	5.3	320

Table 6
Treatment performance of two-stage BW30 RO membrane (at 15 bar pressure)

	COD, mg/L	Color, Pt-Co	Conductivity, μs/cm	pH	VRF
Influent	221	214	9,570	7.85	–
BW30-1 permeate	58	37	3,400	7.63	1.99
BW30-1 concentrate	465	445	15,970	8.4	
BW30 + BW30 permeate	2	10	**582**	7.21	6.62
BW30 + BW30 concentrate	356	318	27,100	8.46	

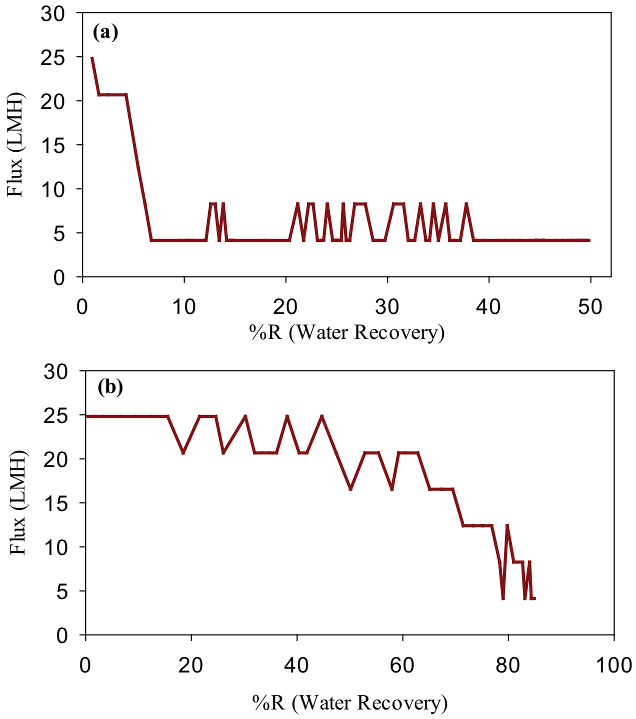

Fig. 5. Performance of (a) first-stage and (b) second-stage BW30 RO membrane (at 15 bar pressure).

rapidly fouled. In the second RO, flux declined from an initial value of 23 to 18 LMH for 50% recovery corresponding to permeability of 1.2 LMH/bar, which was exactly the same as in the case of sequential NF270–BW30 system. This showed that two-stage RO without NF filtration does not bring any further improvement in filterability through the secondary RO when compared with sequential NF–RO process. In a secondary BW30 filtration, 70% water recovery seems to be achievable such that permeability will be approximately 1 LMH/bar (Fig. 5). However, 85% water recovery is not applicable, because flux declines drastically down to about only 5 LMH at this recovery value. Therefore, a two-stage BW30 RO filtration following NF270 prefiltration seems to be a feasible option. It is important to note that both filtration and conductivity rejection efficiencies are expected to be higher in a continuous cross-flow filtration than the dead-end filtration of our study.

Considering the high salinity of wastewater, Dow Filmtec SW30 RO membrane, which is normally used for seawater treatment, was also tested after pretreatment with NF270. Filtration pressures were 20 bar for NF270 and 30 bar for SW30. NF270 decreased conductivity from 8,500 to 3,600 µS/cm. This conductivity removal was better than the previous NF270 filtration tests at lower pressures of 7 and 15 bar. Filtration pressure increased conductivity removal of NF membrane as expected. Succeeding SW30 could achieve conductivity of about 600 µS/cm in the permeate, which was not better than that of two-stage BW30. However, membrane permeability of SW30 was much worse compared with BW30 even after prefiltration through NF270. Flux remained very low at 6.3 LMH even at 30 bar pressure resulting in permeability as low as 0.21 LMH/bar (data not shown). On the other hand, BW30 following NF270 had previously achieved much higher permeability (1.2 LMH/bar) even at a much lower pressure of 15 bar.

4. Conclusions

Neither NF nor RO membranes were sufficient alone for an efficient filtration without membrane fouling. NF270 membrane served as a pretreatment step for RO membranes by removing calcium and sulfate salts as well as organic matter and thereby preventing their fouling of the RO membrane. RO memranes further removed these parameters as well as monovalent salts and thereby significantly decreased conductivity. Best RO performances were obtained by an RO membrane downstream of an NF membrane considering both permeability and filtration performances. Membrane permeabilites as high as 2.2 LMH/bar for NF270 for 70% recovery (VRF = 3.3) and 1.2 LMH/bar for BW30 after NF treatment for 50% recovery (VRF = 2) could be obtained at 15 bar filtration pressure. NF membrane (NF270) significantly rejected COD, color and conductivity with the efficiencies of about 45%, 80% and 44%, respectively, and thereby prevented the fouling of the following RO (BW30), which further removed these parameters with efficiencies of 90%, 74% and 66%, respectively. A secondary RO resulted in conductivity rejection efficiencies up to 94% in total. The results of the study showed that reusable chemical industry effluent can be obtained by applying a sequential NF–RO process with a proper choice of membranes and filtration pressure.

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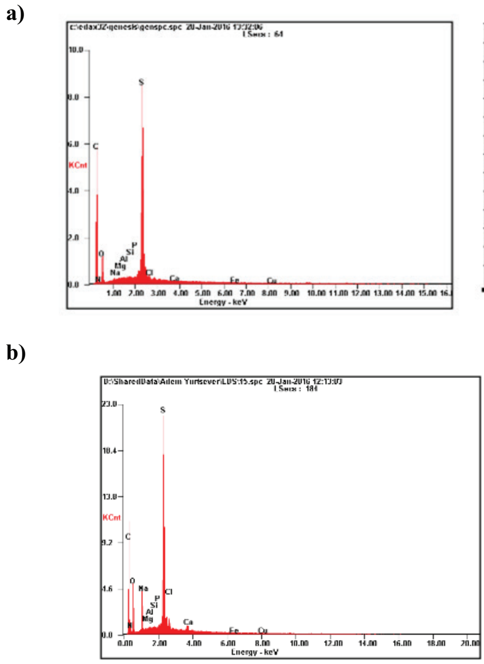
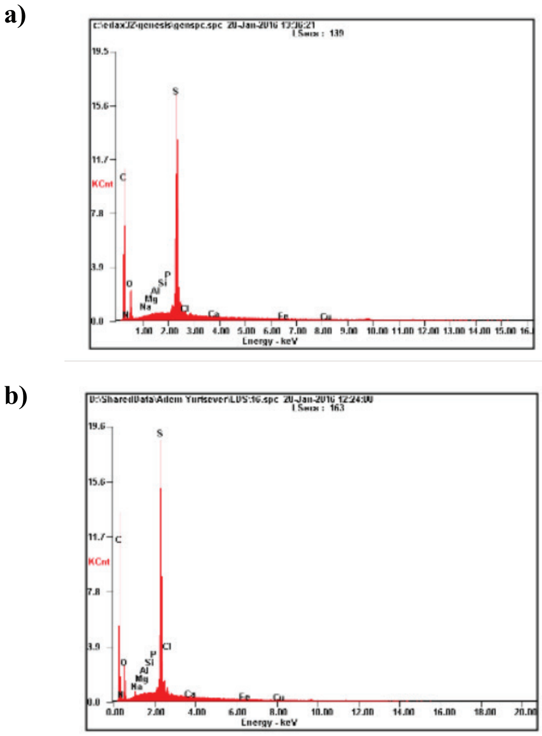
Supplementary



Element	Wt %	At %
C K	72.44	81.38
N K	01.50	01.45
O K	14.69	12.39
NaK	00.20	00.12
MgK	00.06	00.03
AlK	00.08	00.04
SiK	00.11	00.05
P K	00.04	00.02
S K	10.33	04.35
ClK	00.27	00.10
CaK	00.04	00.01
FeK	00.05	00.01
CuK	00.17	00.04

Element	Wt%	At%
CK	54.89	65.84
NK	06.35	06.53
OK	20.76	18.70
NaK	05.17	03.24
MgK	00.10	00.06
AlK	00.12	00.06
SiK	00.10	00.05
PK	00.16	00.08
SK	11.00	04.94
ClK	00.70	00.29
CaK	00.47	00.17
FeK	00.06	00.01
CuK	00.11	00.03
Matrix	Correction	ZAF

Fig. S1. SEM-EDS analysis of NF270 membrane: (a) clean membrane and (b) after wastewater filtration.



Element	Wt %	At %
C K	70.72	79.69
N K	03.15	03.04
O K	14.76	12.49
NaK	00.10	00.06
MgK	00.05	00.03
AlK	00.04	00.02
SiK	00.04	00.02
P K	00.07	00.03
S K	10.67	04.50
ClK	00.23	00.09
CaK	00.00	00.00
FeK	00.05	00.01
CuK	00.13	00.03

Element	Wt%	At%
CK	70.02	79.24
NK	03.34	03.24
OK	14.50	12.31
NaK	00.58	00.34
MgK	00.06	00.03
AlK	00.11	00.05
SiK	00.04	00.02
PK	00.03	00.01
SK	10.71	04.54
ClK	00.42	00.16
CaK	00.02	00.01
FeK	00.04	00.01
CuK	00.14	00.03
Matrix	Correction	ZAF

Fig. S2. SEM-EDS analysis of BW30 membrane: (a) clean membrane and (b) after wastewater filtration.