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The effects of pretreatment on membrane distillation of cooling tower blowdown water

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Abstract. In the membrane processes, pretreatment of the hardness is an effective way to minimize membrane fouling, and to increase the quality of the permeate. Many pretreatment methods can be applied for hardness removal in way of individual or combined before membrane processes. In this study, effects of pretreatment, pH adjustment, caustic soda (NaOH) softening and soda ash (Na_2CO_3) + caustic soda softening, on desalination performance of the coal fired power plant cooling tower blowdown water (CTBD) by membrane distillation (MD) was investigated.
By the MD system operated with hot feed (60°C) and cold permeate (20°C) sides of membrane, approximately 32 LMH permeate flux and more than 99.8% salt rejection were obtained in all experiments. While it was observed that the recovery rate of raw CTBD was 66.2%, recovery rate of pretreated CTBD with caustic soda was 79.4%. It was also found that pretreatment significantly reduces membrane scaling.
Keywords: cooling tower blowdown water; membrane distillation; pretreatment; scaling; softening

1. Introduction

Since only 2.5% of the world's water resources are freshwater and only 30% of freshwater is available, many regions of the world suffer from a severe water scarcity (Petersen *et al*. 2019). Traditional freshwater resources are decreasing due to overuse and brackish water inflow. Especially, the industries, using large amounts of fresh water contribute to the water scarcity. Among them, the industries with cooling towers occupy an important place due to the high water consumption and discharge of wastewater as CTBD form likewise, 70-80% of industrial water demand is used in cooling towers (Wang *et al*. 2006). According to the report of the United States Geological Survey, 41% of the total water consumption in the USA was used in the cooling towers of thermal power plants in 2015 (Dieter *et al*. 2015). As for Turkey, this value is emphasized as 45% in the report of Turkish Statistical Institute (TURKSTAT 2019).

Water plays critical role in the thermoelectric power industry due to using as physical source of energy conversion and heat exchange medium (Wolfe *et al*. 2009). In the thermal power plant with a steam turbine and wet cooling tower, two important water cycles are used. The first is the closed loop where the high quality boiler water is converted to steam and operates the turbine that supplies power to electric generator. The other is the recirculating water cycle that removes excess heat from the condenser on the low pressure side of the steam turbine and distributes it in the wet cooling tower. Therefore, a large amount of water is consumed to support energy production, the majority of which is stemmed from the recirculating cooling cycle (Feeley *et al*. 2008). Cooling tower water is usually drawn from a fresh water source. Due to water loss from the tower, by evaporation, leakage and wind, concentrations of pollutants such as Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, silica, microorganism increase in the cooling water cycle, and this can be leading to scaling and corrosion. Some of the water, concentrated with pollutants, in the cooling tower is discharged as blow down to prevent scaling and corrosion (Altman *et al*. 2012). Deficiency caused by blow down and evaporation is made-up with fresh water. For example, a 300 MW thermal power plant uses about 20,000 m^3/h of circulating cooling water and discharges about 98 m^3/h of blow down (Zhang *et al*. 2007). Typically, about 10-20% of the make-up water stems from blowdown, the rest from evaporation (Yu *et al*. 2013).

Desalination for fresh water production or reuse of wastewater is considered a key factor for sustainable development (Fritzmann *et al*. 2007, Greenlee *et al*. 2009). Reuse of CTBD to meet the high amount of water demand of cooling towers enables to save a large amount of fresh water (Zhang *et al*. 2007, Altman *et al*. 2012).

Compared to other industrial wastewaters, CTBDs have high volume and relatively less pollutants (You *et al*. 1999). However, they contain significant amount of particles, colloids, and salts. Also, some additive chemicals containing ammonium and phosphate for corrosion control are among typical components of CTBD (Mohsen 2004). High concentrations of ions especially Ca^{2+}, Mg^{2+}, CO_3^{2-} and HCO_3^- prevent direct reuse of blow down water and make be required various desalination technologies (Wang *et al*. 2006).

Up to now, the two main technologies used for the desalination of CTBD which are thermal processes and membrane processes. Thermal desalination technology is

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not preferred for the desalination of CTBD due to its high cost. Membrane technologies used for desalination can be divided into three categories as Electrodialysis (ED), Electrodialysis Reversal (EDR) and Reverse Osmosis (RO) (Fritzmann *et al*. 2007). In coal fired power plants, the application of RO technology is increasing for the treatment of CTBD. However, RO membranes are known to be sensitive to scaling and fouling and therefore requiring regular membrane cleaning. Currently, pretreatments such as coagulation, sedimentation, sand filtration, micro-filtration (MF) and ultrafiltration (UF) are increasingly used to remove suspended solids and biological material from CTBD. Combining RO process with these pretreatment processes forms integrated membrane systems (IMS) that have received great attention in recent years (Karakulski and Gryta 2005, Wang *et al*. 2006, Zhang *et al*. 2007). However, IMS has disadvantages such as high capital and energy costs, uneconomic water recovery rates, high treatment and maintenance costs. Also, RO membranes do not provide as high purity water as with thermal processes (Hanemaaijer *et al*. 2006). Therefore, MD composing of combining membrane process and thermal process is considered promising alternative process to treat CTBD.

In MD, water vapor is transported through a microporous hydrophobic membrane thanks to a vapor pressure difference created between the two sides of the membrane-self. The hydrophobic structure of the membranes and low operating pressure in MD provide less fouling problems compared to other membrane desalination technologies (Drioli *et al*. 2015, Wang and Chung 2015). While RO and ED use electricity to create a driving force, MD can also use waste heat, such as stemming from cooling towers, which makes the MD system advantageous, hence the option of using MD for the treatment of CTBD has been examined by several researchers (Yu *et al*. 2013, Koeman-Stein *et al*. 2016, Ince and Uslu 2019). MD can also decrease the required cooling capacity of cooling towers, resulting of using some of waste heat. Thus, the demand for make-up water, costs, and greenhouse gas emissions are reduced (Kuipers, Hanemaaijer, *et al*. 2015, Kuipers, van Leerdam, *et al*. 2015).

Majority of the problems encountered during the MD process are related to the hardness of the water (Gryta 2006, Karakulski *et al*. 2006, Singh 2006). Therefore, pretreatment of the hardness is an effective way to minimize membrane fouling in membrane processes, and also increase the quality of the permeate (Huang *et al*. 2009). Ineffective or incorrect pretreatment method can lead to significant operating problems, such as high membrane fouling, high membrane cleaning frequency, low recovery rate, high operating pressure, poor product quality, short membrane life (Wolf *et al*. 2005). In literature, pH adjustment (Karakulski and Gryta 2005), chemical softening (coagulation/flocculation) (Gryta 2008), thermal water softening (boiling) (Gryta 2010), membrane filtration (Löwenberg *et al*. 2015), chlorination (Friedler *et al*. 2008) etc. are used as pretreatment methods in desalination and water purification processes.

Many studies have investigated the feasibility of membrane distillation processes for the reuse of CTBD (Löwenberg *et al*. 2015, Davood Abadi Farahani *et al*. 2016, Koeman-Stein *et al*. 2016). However, there are very few studies in the literature about the direct comparison of different pretreatment techniques for increasing performance of the MD in terms of CTBD recovery and membrane fouling control (Wang *et al*. 2008). Therefore, the aim of this study is to investigate the effects of three different pretreatment methods (pH adjustment, caustic soda softening, soda ash + caustic soda softening) on performance of MD treating CTBD.

Table 1 CTBD characterization obtained from the coal fired power plant

Parameter	Unit	Value
TOC	mg/L	10.12
Conductivity	mS/cm	5.52
pH	-	8.05
Alkalinity	mg $CaCO_3$/L	790
Hardness	mg $CaCO_3$/L	4300.00
Sulfate	mg/L	4508.10
Chlorine	mg/L	104.30
Phosphate	mg/L	5.52
Silica	mg/L	35.83
Calcium	mg/L	355.30
Magnesium	mg/L	550.00
Sodium	mg/L	1.84
Potassium	mg/L	19.71
Iron	mg/L	0.04
Manganese	mg/L	0.23

2. Material and methods

2.1 Analytical methods and characterization

The CTBD used in this study was taken from the cooling tower of a 51 MW coal fired power plant discharging blowdown of 7 m^3/h and stored at 4°C. Conductivity and pH parameters were measured on site and the other parameters were analyzed in the laboratory. The characterization of the blowdown water is presented in Table 1.

Conductivity and pH measurements of CTBD were performed with the multimeter (WTW multiline P4). Alkalinity, hardness and phosphate analyses were done according to STM 2320-B, STM 2340-C, STM 4500-P-D, respectively (Clescerl *et al*. 1998). TOC concentration was determined in the TOC analyzer (Shimadzu, TOC-L) in accordance with the method of NPOC (non-purgeable organic carbon), and concentration of Ca, Mg, K, Na, Fe, Si and Mn were analyzed with ICP-OES (Perkin Elmer) instrument. Sulfate and chlorine concentrations were determined using ion chromatography (IC) (Shimadzu). IC analyzes were carried out with IC-SA2 column under 70 bar pressure at a flow rate of 1 mL/min. The all of these

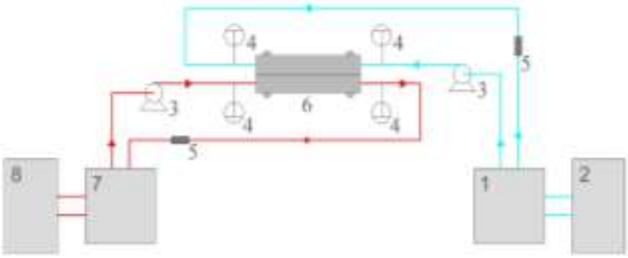

Fig. 1 MD experiment setup (1-Permeate tank, 2-Cooling system, 3-Peristaltic pump, 4-Thermocouples, 5-Conductivity and pH measurement probes, 6-DCMD Module, 7-Feed tank, 8-Water circulator)

analyzes were also done for distillates obtained in the MD process.

Morphological images of virgin and used membranes were obtained by scanning electron microscopy (SEM) (Philips XL 30 SFEG), and energy diffuse x-ray analysis (EDX). In addition, fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer) were used to detect reason of membrane fouling.

2.2 Membrane and membrane module

Microporous (0.2 µm), hydrophobic PVDF (Polyvinylidene Fluoride) membrane with pH range of 0-14 (Millipore) was used in the treatment of CTBD by MD. The porosity and thickness of the membrane are 75% and 200 µm, respectively. In each experiment, virgin membrane was used.

Direct contact membrane distillation (DCMD) module was made of teflon with 20 mm thickness to minimize heat interaction with the environment. It consists of two symmetrical layers for hot feed and cold permeate sides. Both layers of the membrane module have flow channels with width, length and height of 30, 105, 1 mm, respectively.

2.3 DCMD installation and test procedure

The schematic representation of the laboratory scale DCMD system used is shown in Fig. 1. Hot feed (60°C) and cold permeate (20°C) sides of membrane, determined as optimum temperatures for this blowdown water in another study (Ince and Uslu 2019), were kept at a constant temperature by means of the water circulator (Daihan Scientific Maxircu CL). The membrane module was operated cross-flow velocity of 0.75 m/s. The mass of the distillate was recorded by means of assay balance (AND EJ-6100) to calculate the mass flux. In each experiment, 11 liters of CTBD was used and the system was operated until a sharp drop in the flux, indicating the fouling of the membrane. Distillate conductivity was measured online with a multimeter (WTW multiline P4) for monitoring distillate quality.

2.4 Pretreatment of CTBD

As a thermally-driven membrane separation process, the implementation of MD encounters the obstacles of membrane scaling and fouling as applied to the purification of saline water (Yu *et al*. 2013). Generally, the recirculating cooling water is kept at a steady-state with relatively high concentration factor to minimize water usage and with moderate alkalinity to avoid corrosion. Under such operation conditions, blowdown water has a tendency of scaling. The scaling mainly includes inorganic hardness precipitations and silica scale. Therefore, before operation of MD pretreatment such as pH adjustment and softening were applied to the CTBD in order to increasing the recovery rate by reducing membrane fouling and preventing flux reduction. MD was also applied to raw CTBD (Run 1) under the same operating conditions in order to determine the effect of pretreatment processes.

In membrane application, if the pH, hardness and the alkalinity of the feed water to cause to scaling, in generally, acid is dosed to maintain carbonates in their soluble carbonic acid form (Bernardes 2016). Likewise, in the first pretreatment method (Run 2), the pH of CTBD was adjusted to 4 with HCl to prevent $CaCO_3$ precipitation.

The second (Run 3) and third (Run 4) pretreatment processes, used for softening, were caustic soda (NaOH) and soda ash (Na_2CO_3) + caustic soda (NaOH).

CTBD softening processes were carried out by jar test in which 1 min rapid mixing (100 rpm), 20 min slow mixing (30 rpm) and 45 min settling were applied.

3. Results and discussion

3.1 Pretreatments

Pretreatment is required to increase the efficiency and life expectancy of the membrane elements by minimizing fouling, scaling and degradation of the membrane.

In the first of the softening processes, due to its advantages such as forming less sludge and easier applicability compared to lime (Benefield *et al*. 1981), NaOH was added to the CTBD in doses ranging from 0 to 6 g/L. The hardness of the CTBD decreased by 91.2% according to Equation 1-3 at the dose of 3 g NaOH/L and decreased to 378 mg $CaCO_3$/L. Due to produced Na_2CO_3 (Equations 1-2), some of the external alkalinity requirement were met. After this value, it was observed that there was no significant hardness removal with increasing caustic soda dose. Considering caustic soda consumption and hardness removal rate, 3 g NaOH/L was determined as the optimum dose. With the caustic soda softening process, magnesium, calcium, and silica ions leading to significant scaling problems in the MD were removed by 99.9%, 68.0% and 93.6%, respectively.

$$\begin{aligned} &\mathrm{Ca^{2+} + 2HCO_3^- + 2Na(OH)} \\ &\leftrightarrow \mathrm{CaCO_{3(s)} + Na_2CO_3 + 2H_2O} \end{aligned} \tag{1}$$

$$\begin{aligned} &\mathrm{Mg^{2+} + 2HCO_3^- + 4Na(OH)} \\ &\leftrightarrow \mathrm{Mg(OH)_{2(s)} + 2Na_2CO_3 + 2H_2O} \end{aligned} \tag{2}$$

$$\mathrm{Mg^{2+} + SO_4^{2-} + 2Na(OH) \leftrightarrow Mg(OH)_{2(s)} + Na_2SO_4} \tag{3}$$

$$Ca^{2+} + SO_4^{2-} + Na_2CO_3 \leftrightarrow CaCO_{3(s)} + Na_2SO_4 \qquad (4)$$

In the third pretreatment, the soda ash + caustic soda, process (Run 4), after the determining of optimum Na_2CO_3 dose (10 g/L) which was added as a carbonate source to remove calcium hardness in accordance with Equation 4 (Benefield *et al*. 1981), various concentration of caustic was added to the CTBD

The NaOH was added at doses of 0.72, 1.20, 1.44, 1.68, 1.92, 2.16 g/L, and the hardness value of water decreased to 30.4 mg $CaCO_3$/L at 1.92 g NaOH/L dose, which was determined as the optimum dose. Thus, 99.3% hardness removal efficiency was obtained from raw CTBD by adding Na_2CO_3 + NaOH. Removal efficiency of calcium, magnesium and silica were 99.7%, 99.6%, 93.7%, respectively.

3.2 MD Process of CTBD

DCMD process was operated for raw and pretreated CTBDs in order to determine to effect of pretreatment process. During the study, flux and conductivity of distillate, important performance parameters for MD were constantly monitored. DCMD experiments were performed at the same temperature and cross flow rates and continued until sharp drops in fluxes were observed. The distillate flux graphs of four different DCMD studies are given in Fig. 2. In all experiments, the initial fluxes were very close to each other and range from 31.3 to 32.7 LMH. In the literature, a study investigating purified with DCMD, 30 LMH flux with temperature difference of 40°C was obtained (Yu *et al*. 2013) and 16.6 LMH distillate flux was obtained in another study with temperature difference of 10°C and 70°C feed temperature (Koeman-Stein *et al*. 2016). A rapid decrease in flux was observed after 70 hours of operating time in Run 1. These values for Run 2, Run 3 and Run 4 are 80, 92 and 84 hours respectively. The reason of the rapid reduction of the flux was that the blowdown water of 60ºC in the DCMD module reaches ionic saturation and fouls the membrane with forming of scale and salt crystals (Tijing *et al*. 2015).

In this study, the recovery rates were obtained as 66.2%, 70.6%, 79.4% and 76.4% for Run 1, Run 2, Run 3 and Run 4, respectively. In the first of the pretreatment processes (Run 2), pH of the CTBD was adjusted to 4. Controlling the pH of the feed solution is an effective pretreatment method to alleviate scaling in MD. Many researchers adjusted the pH of the feed water between 4-5 and found that $CaCO_3$ scaling was reduced effectively, but not silica (Karakulski and Gryta 2005). Compared to Run 1, there was only increase of about 4% in recovery rate. With regard to Run 3 and Run 4, there was a significant increase in water recovery due to removal of hardness in the CTBD. Although a higher recovery rate was expected from Run 4 due to be the most efficient pretreatment process considering hardness, the highest recovery rate was obtained from Run 3. Considering the recovery rate, one of the important performance parameters in MD, Run 3 was determined as the optimum operating condition with water recovery of 79.4%. Recovery rate obtained in this study is higher compared with the studies

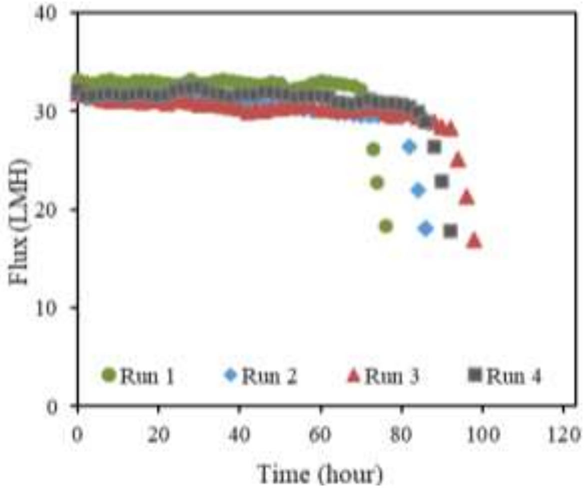

Fig. 2 Permeate flux during DCMD of pretreated and raw CTBD

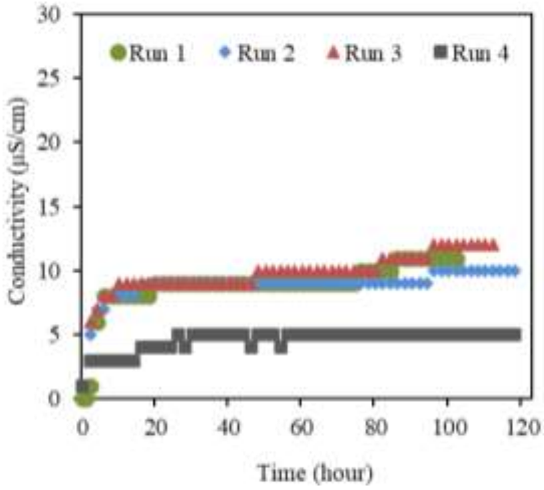

Fig. 3 Permeate conductivity during DCMD of pretreated and raw CTBD

Table 2 Permeate characteristics of DCMD

Parameter	Unit	Run1	Run 2	Run 3	Run 4
TOC	mg/L	0.44	0.11	0.14	0.33
Conductivity	µS/cm	11.00	11.00	13.00	7.00
pH	-	6.46	6.26	6.34	6.60
Alkalinity	mg $CaCO_3$/L	9.40	9.60	8.70	13.30
Hardness	mg $CaCO_3$/L	10.90	12.10	8.80	4.20
Sulfate	mg/L	0.16	0.72	1.22	ND
Chlorine	mg/L	ND	ND	ND	ND
Phosphate	mg/L	ND	ND	ND	ND
Silica	mg/L	0.34	4.85	0.82	0.35
Calcium	mg/L	0.88	3.50	0.31	0.25
Magnesium	mg/L	0.12	0.17	0.09	0.05
Sodium	mg/L	ND	ND	ND	ND
Potassium	mg/L	0.16	0.03	0.24	0.18
Iron	mg/L	ND	ND	ND	ND

ND: Not detected

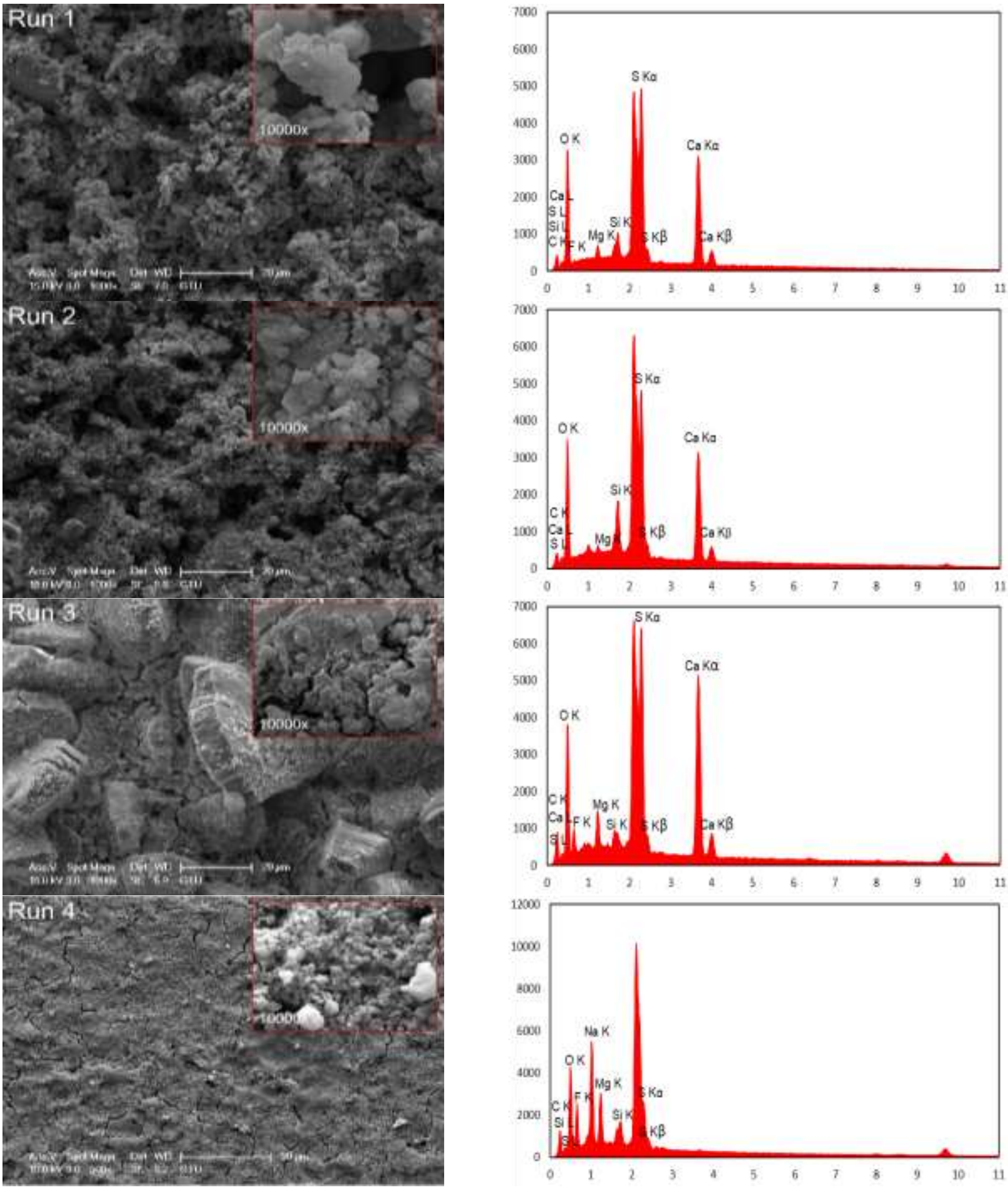

Fig. 4 SEM-EDX analysis results of PVDF membranes

implemented to treat cooling water by MD. In a case study, membrane distillation was applied to the cooling water to reduce the use of fresh water, and there was a reduction of up to 30% in freshwater use (Ma *et al*. 2018). Ricceri *et al.* (2019) prepared synthetic wastewater, containing paraffin, sodium dodecyl sulfate, and NaCl, and fed into the membrane distillation system. They observed that flux was around 20 LMH (Ricceri *et al*. 2019). In another study with poly-propylene membrane, approximately 57% water recovery factor was obtained with an initial volume of 5 L by using the first flue gas desulphurization wastewater (Ali *et al*. 2018).

In all DCMD studies (Run 1, Run 2, Run 3, Run 4), electrical conductivity of distillate was under 15 µS/cm (Fig. 3) and salt rejection was more than 99.8%. Also, the almost constant distillate conductivity throughout the four studies indicate that serious membrane hydrophilization did not occur in the whole DCMD processes. Of all the Runs, the lowest conductivity was observed in Run 4, since concentration of Ca^{2+}, one of the main ions forming scaling leading to wet of membrane, were the least after the pretreatment. Therefore, it is assumed that the wetting pores of the membrane in Run 4 were lower than ones of the other Runs, resulting in lower

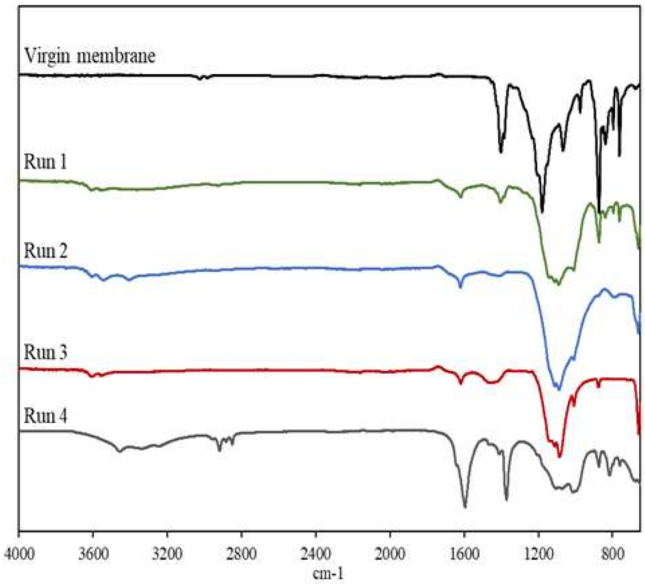

Fig. 5 FTIR spectra for virgin and CTBD scaled membranes

distillate conductivity.

Pollutant concentrations measured in distillates are given in Table 2. As can be seen in the table, chlorine, phosphate, iron and manganese cannot be detected, while the rejection rate for sulfate, calcium and magnesium was more than 99.9% for all four experiments.

3.3 Membrane fouling

The membrane surface can be covered with contaminants in MD, which reduces effective pore region and the temperature gradient between the feed and distillate sides (Kim et al. 2017). Therefore, membrane fouling leads to decrease in membrane flux and poor filtration quality. CTBD contains high concentrations of hardness, alkalinity and SO42- which enhance membrane fouling and wetting. Most of the fouling formation on the membrane is due to the soluble salts in the feed water and partly concentration polarization (Warsinger et al. 2015). There was a continuously increase in salt concentration of CTBD circulating through MD system, resulting in forming of salt crystals.

The structure of the virgin membrane and the composition of the fouling on the used membranes in MD experiments were examined by SEM, EDX and FTIR analysis. In the EDX analysis, on the virgin membrane, only C (44.7%) and F (55.3%) were found, while Ca, S, O, Si, Mg, Na and C elements were detected on the surface of the used membranes. SEM images and EDX spectrums of virgin and used membranes in the experiments are shown in Fig. 4.

As can be seen in Fig. 5, the peaks in the 1200 and 3025 cm^{-1} band in the FTIR analysis on the virgin membrane are the C-F bonds of the PVDF membrane (Liu *et al*. 2010). Observed peaks of FTIR spectrums wavelengths of used membranes were almost similar. The peaks in the 800 and 1100 cm^{-1} band show SiO_2 fouling on the membrane surface (Musić *et al*. 2011), which is also supported by EDX results. While gypsum (670, 1614 cm^{-1}) (Yu *et al*. 2013) and calcite (873 and 1543 cm^{-1}) (Yu *et al*. 2013) are seen in used membranes in Run 1, Run 2 and Run 3 experiments, these pollutants were not found on the membrane in Run 4, since almost all of the Ca^{2+} and Mg^{2+} ions were removed in the pretreatment process.

According to EDX and FTIR analysis in Run 1, membrane fouling was mostly caused by $CaCO_3$ and $CaSO_4$, and also slight contributed by the Mg and Si. In Run 2 experiment, the pH of the concentrated CTBD increased to 7.4 at the end of the experiment, which indicated that wastewater acidification only delayed membrane fouling, but with increase in pH during operation of the composition of the compounds leading to membrane fouling was quite similar to Run 1. The analyzes made on the membranes used in Run 3 and Run 4 experiments showed, unlike Run 1 and Run 2, fouling by silica decreased notably. However, in Run 4, $NaSO_4$ fouling was determined by EDX analysis. It is assumed that residual Na coming from Na_2CO_3 and NaOH added in the pretreatment and SO_4^{2-} formed $NaSO_4$ crystal on the membrane surface (Tun *et al*. 2005). Hence, considering SEM images and FTIR spectrums, it is clearly seen that the formation of fouling on the used membrane in Run 3 experiment is less than other experiments. The results obtained from EDX and FTIR analysis of all the Runs consistent with characterization of CTBD after each pretreatment: the hardness as 4300, 4300, 378 and 30.4 mg $CaCO_3$/L; silica as 35.83, 35.83, 2.29 and 2.26 mg/L; calcium as 355,3, 355,3, 113,7 and 1,07 mg/L; magnesium as 550, 550, 0.55, and 0.83 mg/L were measured for Run 1, Run 2, Run 3 and Run 4, respectively.

In the literature, concentration of both silica free and silica-containing simulated CTBD by the desalination process of a bench-scale DCMD was evaluated in a study. While silica, calcium carbonate and sulfate scaling precipitated together for silica-containing simulated CTBD, insoluble calcium carbonate scale formed on membrane for silica free simulated CTBD. The authors reported that the scales resulted in the drop of both permeate flux and salt rejection (Yu *et al*. 2013). In another study, pretreatment CTBD water was purified with MD system and SEM images of the membrane surface were given. According to the SEM images, no $CaCO_3$ scaling was observed, possibly because of the short duration of the experiment (about 30 hours). Wang *et al*. (2008) desalinated CTBD with MD process after pretreated by coagulation, precision filtration, acidification and degassing. The results showed that magnesium-calcite scale formed on the membrane surface when coagulation pretreatment was employed. However, the deposited magnesium-calcite on the membrane surface was loosely packed with particles of much smaller size when CTBD without pretreatment (Wang *et al*. 2008).

4. Conclusions

CTBD treatment with DCMD is an advantageous process due to produce high-quality distillate and the ability of using waste heat as an energy source. The DCMD system obtained approximately 32 LMH permeate flux and more than 99.8% salt rejection at a temperature difference of 40°C. In addition, caustic soda softening as pretreatment was very effective since it increased the water recovery rate up to 79%. It was also found that pretreatment significantly reduces membrane scaling.

Since approximately 10%-20% of the make-up water requirement in cooling towers is caused by blow down, the recovery of CTBD can reduce the need for cooling water up to 20% theorically. In this study, 5.5 m^3/h water can be recovered from 7 m^3/h blow down water at 79% water recovery rate for the thermal power plant where CTBD is taken. In addition, the amount of water lost by evaporation can be reduced because of using some of the waste heat in the DCMD.

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