Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20494

71 (2017) 233–243
April

The treatability of landfill leachate by direct contact membrane distillation and factors influencing the efficiency of the process

Ali Zoungrana*, İsmail Hakkı Zengin, Harun Elcik, Bestami Özkaya, Mehmet Çakmakci

*Environmental Engineering Department, Yildiz Technical University, 34220 Esenler, İstanbul, Turkey,
emails: zoungson1@gmail.com (A. Zoungrana), ismailhakkizengin@gmail.com (I.H. Zengin),
helcik2010@gmail.com (H. Elcik), bozkaya@yildiz.edu.tr (B. Özkaya), cakmakci@yildiz.edu.tr (M. Çakmakci)*

Received 11 August 2016; Accepted 7 January 2017

ABSTRACT

Landfill leachate is a high-strength wastewater with high concentration of harmful pollutants and is produced in almost all countries with high variation in constituents. In this study, a modified direct contact membrane distillation (DCMD) has been used to investigate the treatability of raw and pretreated landfill leachate. Two different hydrophobic membranes, polytetrafluoroethylene (PTFE) and polyvinylidene difluoride membranes with two different pore sizes (0.22 and 0.45 μm, respectively) were used and performed at three various delta temperatures (Δ*T*); 30°C, 40°C and 50°C. The rejection efficiencies for conductivity, COD, sulfate, alkalinity and hardness were approximately 85%, 99%, 95%, 90% and 98%, respectively, with raw leachate and 99%, 98%, 92%, 85% and 98%, respectively, with pretreated leachate, while NH_4^+–N removal efficiency was about 70% and 92% for raw and pretreated leachate, respectively. The highest transmembrane fluxes (TMF) were obtained at a Δ*T* of 50°C with 0.45 μm pore size of PTFE membrane. The highest TMF with raw leachate was 9.87 L/m^2 h while it was 15.54 L/m^2 h with pretreated leachate. Contact angles and Fourier transform infrared spectroscopy were used to evaluate the resistance of the membranes to wetting and fouling.

Keywords: Landfill leachate; Membrane distillation; Hydrophobic membrane

1. Introduction

The amount of solid wastes produced in the world exponentially increased with the population growth, industrialization and changes in consumption patterns. To face the impact of increasing waste amount, many countries are investigating environment-friendly manner of disposal strategies by means of Integrated Solid Waste Management (ISWM). Landfill disposal remains a major waste management option and is known worldwide as one of the most widely used techniques to dispose municipal solid waste (MSW) [1–7]. Despite the promotion of recycling and recovery [8], waste disposal as an old waste management technique still survives because of its simplicity and its suitability to less developed countries. Up to 95% of the total MSW collected worldwide is disposed of in landfills. More than 150,000 landfills have been built worldwide [6]. After being landfilled, residues decompose through series of combined physico-chemical and biological processes causing the formation of leachate when excess rainwater percolates through the waste layers in the landfill [6]. Landfill leachate is a complex wastewater with considerable variations in both composition and volumetric flow and has a varied composition and concentration depending on the deposited wastes type, moisture content, seasonal weather variation, degree of solid waste stabilization, hydrogeological factors, stage of decomposition and mainly the age of the landfill [2,9]. The leachate formation occurs when soluble components are dissolved out of a solid material by percolating water [5]. A combination of physical, chemical and microbial processes in the waste transfers pollutants from the waste material to the percolating water [10]. Besides causing malodors and aerosols, untreated leachates

---

* Corresponding author.

1944-3994/1944-3986

that seep from a landfill can permeate groundwater or mix with surface waters and contribute to the pollution of soil, groundwater and surface water [7,11]. It is a high-strength wastewater exhibiting acute and chronic toxicity. A landfill leachate where the acidic phase is dominant is termed young leachate, and this leachate has high biological oxygen demand (BOD) and chemical oxygen demand (COD) concentrations with BOD/COD rate up to 0.7 or higher. Due to the high concentration of volatile fatty acid (VFA) in young leachate, its pH is low [12]. Leachates older than 10 years, termed old leachates, are generally in methanogenic phase. The classification of landfill leachates according to their age is shown in Table 1.

Due to the complex nature of landfill leachate, different technologies have been developed to reduce its toxic constituents and make it suitable to be discharged into the receiving sewages and environment. Those technologies can be summarized in two main groups as conventional treatments (leachate transfer, biodegradation, chemical and physical methods) and new treatment by use of membrane processes (microfiltration, ultrafiltration [UF], nanofiltration and reverse osmosis) [2–5,14]. However, these technologies are either ineffective, expensive or use hazardous chemicals. Old leachates are not suitable for biological treatment due to low BOD/COD rate (<0.1). Recently, membrane distillation (MD) has been investigated as a possible alternative technique. MD is a thermally driven process, in which water vapor transport occurs through a non-wetted porous hydrophobic membrane. It operates on the principle of selection driven by the vapor pressure difference (ΔP) generated by the temperature difference (ΔT) between the two fluids on either side of the membranes [15,16], causing vapor molecules transportation from the warm feed side to the cold permeate side through the pores of the hydrophobic membrane. MD has several advantages compared with conventional techniques; it operates at lower temperature compared with conventional distillation process; it provides high treatment efficiency with very high rejection of ions, macromolecules, colloids, cells and other non-volatiles compounds; and it is more efficient and economical in terms of energy use especially when renewable energy is used [17,18]. Depending on the cooling side arrangement and the way effluent is collected from the MD module, there are four different configurations of MD including direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), vacuum membrane distillation (VMD) and air gap membrane distillation (AGMD) [15,16]. DCMD, in which condensed vapor on the filtrate side of the membrane is in direct contact with the membrane, is the most simple, cheapest and popular configuration of these configurations [15,19]. An air gap is interposed between the membrane and a condensation plate in AGMD configuration, and this helps reduce heat loss through conduction. For both above configurations, the condensation of the effluent takes place in the module. VMD uses a pump to create a vacuum at the permeate side where vapor or air under reduced pressure causes the condensation of the water vapor. SGMD uses an inert gas to carry or sweep the produced vapor that is further condensed outside the module as in VMD [20,21]. Because of the outside condensation and the requirement of an external condenser, these configurations seem more complex and expensive to implant compared with DCMD and AGMD. MD is responsible for high treatment efficiency with high rejection of pollutants but its performance is irreversibly connected to the structure of the membrane film in terms of thickness, porosity, mean pore size, pore distribution and geometry. A hydrophobic membrane, with high permeability, resistant to fouling and wetting, high chemical and thermal stability with low thermal conductivity, is ideal for MD application [22,23]. The main objective of this study is to investigate the treatability of solid waste landfill leachate with a modified DCMD and understand the factors that contribute to reducing the performance of the process.

Table 1
Classification of landfill leachate according to their age [13]

Leachate	Young	Middle age	Old
Age (year)	<5	5–10	>10
pH	6.5	6.5–7.5	>7.5
COD (mg/L)	>10,000	4,000–10,000	<4,000
BOD/COD	>0.3	0.1–0.3	<0.1
Heavy metals	Low-middle	–	Low
Biological treatability	High	Middle	Low

2. Materials and methods

2.1. Experimental setup

2.1.1. Laboratory-scale membrane distillation apparatus

A laboratory-scale modified DCMD apparatus with a flat-sheet membrane cell was used during this study (Fig. 1). In a regular DCMD configuration, both feed and permeate sides are in direct contact with the hydrophobic membrane, causing high transmembrane heat loss by conduction [24]. This issue together with temperature polarization caused by the difference between the bulk temperatures and the temperatures at the liquid–vapor interface on both sides of the membrane contributes to membrane wetting and fouling. A well-designed membrane module should provide high rates of heat and mass transfer between the bulk solution and the solution–membrane interface [25,26]. The modification in this study aimed to mitigate the thermal polarization and associated heat loss by conduction, by creating a gap (0.5 cm deep) that separate the cooling part of the module from the permeate side with a stainless steel plate. The plate is placed on the top of the gap, between the permeate water and the circulating cooling water. The cooling water flowed on the top of the plate

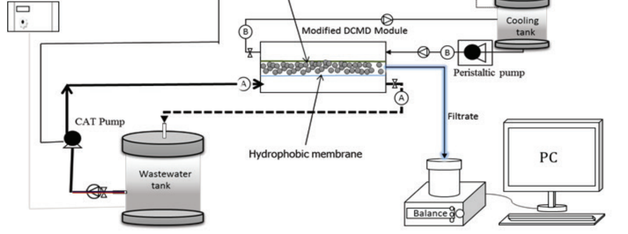

Fig. 1. Schematic flow diagram of the lab-scale modified DCMD.

causing the plate to cool and condense the water vapors that crossed the membrane. The feed tank (7.5 L) was wrapped and heated by 1 kW electrical heating elements. The membrane active area was 0.015 m^2 (0.1 m × 0.15 m). The flow rate, operating pressure and cooling temperature were kept constant at 3.5 LPM, 0.5 bar and 10°C, respectively, while the feed solution temperatures were varied between 40°C, 50°C and 60°C. A digital balance connected to a personal computer was used to measure the permeate water mass and to calculate the flux. A CAT Pumps 2SF35SEEL stainless steel direct-drive plunger pump and a Watson-Marlow peristaltic pump 323 Du/D were used to transfer heated wastewater and cooling water to the DCMD module, respectively. For each temperature, the membrane used underwent 2 h operation time. The membranes were changed once all the three various ΔT were tested.

2.1.2. Hydrophobic membranes

Two commercial membranes, hydrophobic polytetrafluoroethylene (PTFE) and polyvinylidene difluoride (PVDF) membranes manufactured by Membrane Solution LLC (Shanghai, China) were used during this study. Their main properties are summarized in Table 2. The bubble point and flow rate (membrane permeability) were tested with alcohol and the liquid entrance pressure (LEP) was tested with distilled water.

2.2. Wastewater source and characterization

Landfill leachates used during this study were collected from Odayeri sanitary landfill facilities plant in Istanbul. Two different leachates were used, raw leachate and leachate pretreated, with a membrane bioreactor (MBR), which consists of anoxic and aerobic reactors with UF membrane having 60 kDa molecular weight cut-off. Both raw leachate and pretreated leachate were stored at +4°C in wastewater laboratory cold room. The analysis results determined the characteristics of the leachates, and the results are presented in Table 3.

2.3. Analysis methods

Water quality analyses were mostly performed according to the standard methods (SM). pH and conductivity were measured at room temperature (24°C ± 1°C) using Thermo Scientific Orion 5-Star Plus pH/ORP/ISE/conductivity/DO meter, while hardness and alkalinity were measured according to SM 2340C and 2320, respectively. COD was analyzed using a closed reflux colorimetric method according to the SM 5220D. SO_4^{2-} analysis was performed according to the SM 4500-SO_4^{2-} E and NH_4^+–N was analyzed using a distillation apparatus according to the SM 4500-Nr-L C. Membrane surface properties were analyzed by contact angle (Attension, Theta Lite Optical Tensiometer) and Fourier transform infrared (FTIR) spectrometer (Agilent Technologies (California, United States), Cary 630 FTIR spectrometer).

3. Results and discussion

3.1. Treated leachate effluent quality

3.1.1. Conductivity, alkalinity and hardness rejection

Conductivity is related to the concentration of salts dissolved in water; therefore, it is connected to the total dissolved solids (TDS). Inorganic dissolved solids, mostly calcium and magnesium, are responsible for high conductivity in water. Conductivity is affected by temperature, being higher in warmer water [27]. Landfill leachates have high conductivity due to the presence of minerals. The initial conductivity of the raw leachate was around 35.800 µS/cm, and it has been reduced with more than 80% rejection efficiency (Fig. 2). The highest rejection efficiency (84.78%) was obtained with PTFE 0.22 µm at ΔT of 30°C, and this corresponded to 5,450 µS/cm in the permeate water. On the contrary to raw leachate, the highest rejection efficiency was obtained with pretreated leachate with similar membrane and ΔT. Conductivity rejection efficiency reached 98% in pretreated leachate with PTFE 0.22 µm at ΔT of 30°C, and some effluents conductivities were <400 µS/cm as shown in Fig. 2.

Table 3
Leachate characterization

Parameters	Raw leachate	MBR (anoxic + aerobic+ UF) pretreated leachate
COD, mg/L	10,500	2,440
Total solid (TS), mg/L	21,495	19,600
Total volatile solid (VSS), mg/L	6,370	6,045
Hardness, mg $CaCO_3$/L	7,500	1,250
Alkalinity, mg $CaCO_3$/L	15,500	2,440
NH_4–N, mg/L	2,800	1,193
Conductivity, µs/Cm	35,800	34,000
Sulfate, mg/L	313	277
pH	7.99	7.90

Table 2
Properties of the membranes

Membrane structure	Pore size (µm)	Thickness (µm)	Flow rate (mL/min/cm^2 at 0.7 bar)	Bubble point (bar)	LEP (bar)	Contact angles
PTFE 0.22 µm	0.22	180–240	11–14.5	1.1–1.5	4–5.5	127.61
PTFE 0.45 µm	0.45	170–220	63–74	0.5–1	4–5	124.91
PVDF 0.22 µm	0.22	140–180	4.5–6.3	1.1–1.4	3–4.5	128.99
PVDF 0.45 µm	0.45	120–180	10.5–16.5	1–1.2	3–3.5	123.59

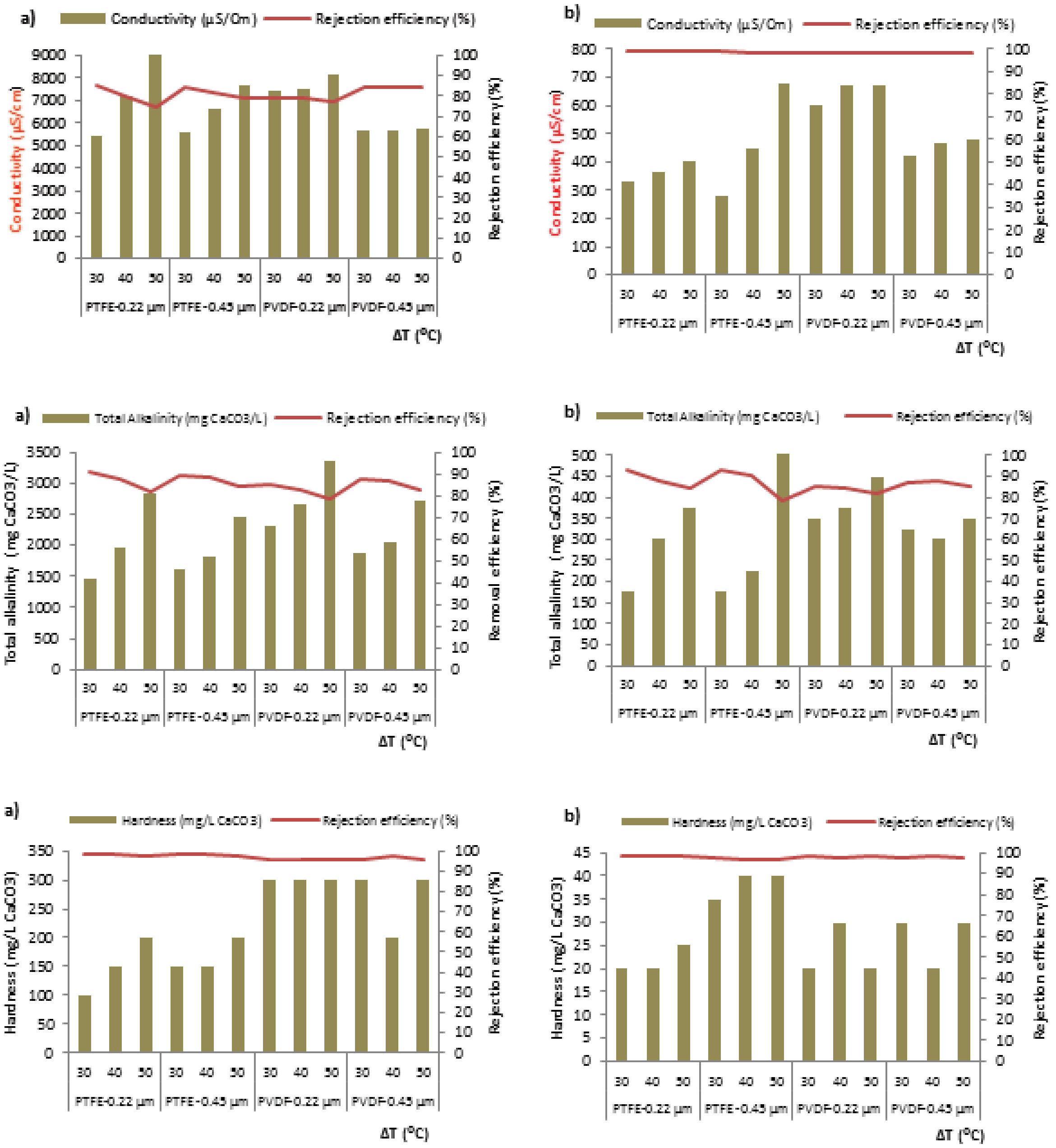

Fig. 2. Conductivity, total alkalinity and hardness of permeate water from various membranes at three different Δ*T* (30°C, 40°C and 50°C): (a) raw leachate and (b) pretreated leachate.

Effluent quality was affected by increasing Δ*T*; effluent conductivity increased with increasing Δ*T*, and this may due to high molecular mobility at high temperature forcing small inorganic dissolved ions to pass through the membrane pore. In addition, the presence of organic compounds in the feed solutions might contribute to the reduction of the solution surface tension and that increased the wetting power of the solution. Once the membrane is wetted, its contact angle drop and the passage of some minerals through its pores are inevitable. This may explain why conductivity is higher in the effluent from raw leachate, which initial COD concentration was the highest among the two feed solutions [28].

Raw leachate showed high alkalinity and hardness, 15,500 and 7,500 mg/L $CaCO_3$, respectively. In fact alkalinity and hardness usually derived from $CaCO_3$ or $MgCO_3$, it is then obvious to have high alkalinity and hardness when conductivity is so high. The effluents alkalinity and hardness are depicted in Fig. 2. Alkalinity and hardness rejection efficiencies reached 90.65% and 98.67%, respectively, in raw leachate. The lowest hardness in the effluent was 100 mg/L $CaCO_3$, characterizing a soft water. Results were better with pretreated leachate where the hardness was reduced up to 20 mg/L $CaCO_3$ (98.4% rejection efficiency) and the alkalinity up to 175 mg $CaCO_3$/L (92.83% rejection efficiency). Yildiz et al.

[29] used the membrane process as a posttreatment method to reject hardness of water in which beforehand lime soda and caustic soda (CS) were added. They reported a maximum 97.5% rejection with a chemical dosage of CS. In this study, desalination took place in a single step, and rejection efficiencies showed the success of the process. However, temperature and pore size influenced the rejection efficiencies of alkalinity and hardness. As observed with conductivity, and for the same reasons, hardness and alkalinity rejection followed the same trend, decreasing with increasing Δ*T*.

3.1.2. COD, NH_4^+–N and SO_4^{2-} rejection

According to Malaysia Environmental Quality (Sewage) Regulations 2009 PU(A) 432/2009 [30], the admissible concentration of COD in wastewater to be discharged must be <120 mg/L for Standard A and 200 mg/L for Standard B. Discharging wastewater with high COD concentration is toxic to biological life and affects aquatic environment in the receiving bodies. The MD process used was able to reduce the COD from 10,500 mg/L in raw leachate to below 100 mg/L and met Environmental Quality Standard A. The highest rejection efficiency was 99.44% corresponding to permeate COD concentration of 59 mg/L. COD was reduced up to 40 mg/L in the permeate of pretreated leachate. Similar to above-discussed parameters, the feed temperature influenced the COD rejection efficiency, with higher rejection at low feed temperature. The initial COD concentration as well influenced the rejection efficiency as shown in Fig. 3. Theoretically, no pollutant should pass through the membrane unless it could vaporize. It is assumed that some parts of COD might be volatile organic compounds under high temperature, and this favors the passage of some of these pollutants through the membrane pore. Though the

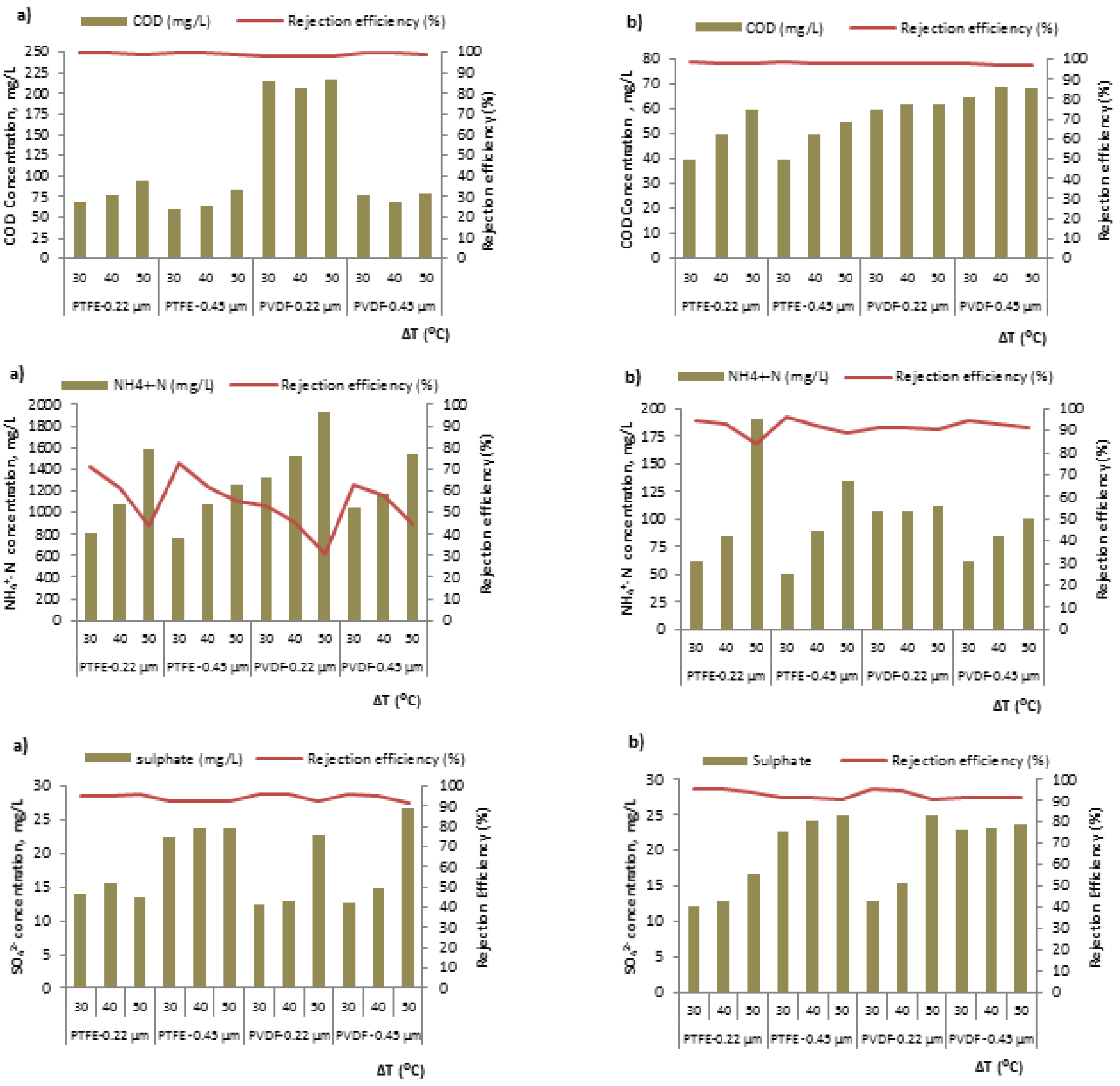

Fig. 3. COD, NH_4^+–N and SO_4^{2-} concentration of permeate from various membranes at three different Δ*T*: (a) raw leachate and (b) pretreated leachate.

effluents COD concentrations, as well as the rejection efficiency, are proof that MD can effectively remove COD with high rejection.

Ammonium nitrogen (NH$_4^+$–N) rejection efficiency, as well as its concentration in the permeate water from this study, is presented in Fig. 3. An initial raw leachate with NH$_4^+$–N concentration of 2,800 mg/L has been reduced to 767 mg/L as the lowest permeate NH$_4^+$–N concentration and corresponding to a rejection efficiency of 72.6%, while pretreated leachate has been reduced from 1,193 mg/L up to 50.4 mg/L (95.78%). In fact, NH$_4^+$–N rejection was the least successful among all the other contaminants. Regardless of membrane structure and pore size, NH$_4^+$–N rejection massively rose up with increased ΔT. Zhao et al. [31] faced the same issue during water regeneration from human urine by VMD. The rejection efficiency was very low at high ΔT, and they assumed that some part of the urea in the heated urine decomposed gradually into NH$_4^+$ and into NH$_3$ gas that could pass through membrane pores. Raw leachate is the result of a mixture of many different wastes that leached over time. It may contain NH$_4^+$–N-rich compounds and urea making raw leachate NH$_4^+$–N very high (2,800 mg/L). During the heating process of the alkaline feed solution (pH 8), ammonia gas (NH$_3$) formation is favored. In fact, any urea in the solution may have partially been converted into NH$_4^+$ and almost NH$_4^+$ present in the solution into the volatile NH$_3$ that undoubtedly continuously permeated through the membrane pores. Qu et al. [13] investigated the rejection of ammonia by DCMD, and they found similar results. They agreed that temperature as well as pH greatly impacts the process. They stated that the elevation of feed temperature from 30°C to 50°C caused an increase of 250% of ammonia permeation flux through 0.22 µm pore size PVDF membrane. Without a doubt, the feed leachate characteristics and concentration, the feed solution temperature and pH strongly influenced NH$_4^+$–N rejection during this study. The pollutants rejection was high when these parameters were moderate. Husnain et al. [32] investigated the performance of an integrated forward osmosis (FO) and MD process for wastewater reuse and reported over 99% NH$_4$ removal and almost 100% COD rejection. The high rejection achieved in their study was mainly due to the initial low concentration of NH$_4$ and COD together with the performance of the FO system. In our study, MD system was not able to reject ammoniacal nitrogen from raw leachate to Standard A (50 mg/L) set by Malaysia Environmental Quality (Sewage) Regulations 2009 [30]; however, this target was reached when the MD is used as a posttreatment technique to treat the leachate pretreated with MBR.

The initial raw leachate sulfate (SO$_4^{2-}$) concentration was 313 mg/L, and more than 95% rejection was achieved with PTFE 0.22 µm membrane and a little lower (about 92%) with the PTFE 0.45 µm membrane. Up to 95.67% SO$_4^{2-}$ was rejected from pretreated leachate; permeate water SO$_4^{2-}$ concentration was reduced to 12 mg/L. The membrane pore size importantly influenced the rejection efficiency; 0.22 µm pore size membranes showed better SO$_4^{2-}$ rejection performance compared with 0.45 µm pore size membranes. The rejection was higher at lower feed temperature but temperature effect on SO$_4^{2-}$ rejection was not as strong as its effect on conductivity, alkalinity hardness and ammonium rejections. The permeate SO$_4^{2-}$ concentration and rejection efficiency at different feed temperature are shown in Fig. 3.

3.2. Transmembrane flux

For an MD process to be implanted in a community, two key factors need to be addressed. After effluent quality is determined, the feasibility of the process depends on the flux. The importance of the flux is strongly connected to the operation cost. High effluent flux contributes to largely reduce operating cost. The flux vs. ΔT of different membranes used during this study is depicted in Fig. 4. The highest permeate fluxes of raw leachate and pretreated leachates are 9.87 and 15.54 L/m^2 h, respectively, with PTFE 0.45 µm membranes at ΔT of 50°C. The lowest fluxes were observed with PVDF – 0.22 µm membranes at a ΔT of 30°C. During the treatment of olive mill wastewater with PTFE membranes in a DCMD configuration, El-Abbassi et al. [33] reported an increase of permeate flux with the increasing membrane pore size, increasing feed temperature and ΔT. It is obvious from Fig. 4 that the flux increased with increasing ΔT and membrane pore size. The flux was highly influenced by ΔT. In fact, the temperature gradient between the feed and the permeate surface of the membrane increased the driving force at a higher temperature, which caused higher flux. Practically, a large amount of vapor is produced from the feed solution heated at high temperature, which created higher vapor pressure inside the channel, and may cause an increase of the flux through the membrane pores [34]. During the investigation of arsenic rejection by MD, Pal and Manna [35] reported the similarly remarkable influence of feed temperature on the permeate flux. They stated that the increase of temperature from 30°C to 61°C caused an increase in water vapor flux from 14.28 to 29.16 kg/m^2 h (104% flux increase) of PTFE 0.22 µm pore size. In the present study, Fig. 4 shows that when the feed inlet temperature increased from 40°C to 60°C (ΔT from 30°C to 50°C) using PTFE 0.45 µm membrane, permeate flux went up from 4.56 to 9.87 L/m^2 h and from 6.5 to 15.54 L/m^2 h with raw leachate and pretreated leachate, respectively. Such trend of exponential rise of the flux with increasing feed temperature has been reported in many

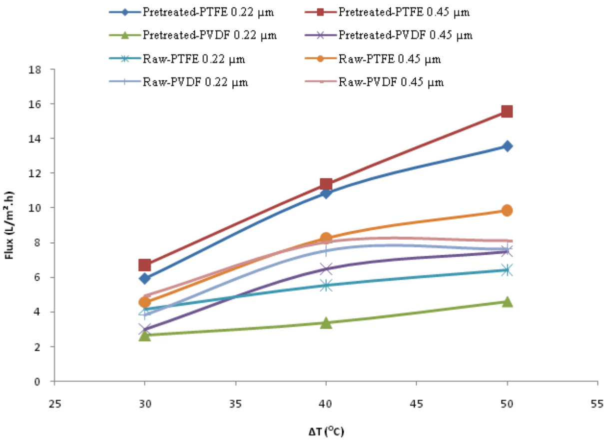

Fig. 4. Transmembrane flux of various membranes at three different ΔT: (a) raw leachate and (b) pretreated leachate.

MD studies [34–36]. In addition, regardless of feed temperature, PTFE membranes and 0.45 μm pores size membranes exhibited higher transmembrane flux (TMF) compared with PVDF membranes and 0.22 μm membranes, respectively. In fact, larger pores facilitated the passage of the water vapor allowing more vapor to condense in the filtrate side. PTFE membranes have an extremely low surface tension properties compared with PVDF membranes, for that reason, practically no materials stick to PTFE membranes surface, but as shown in Fig. S2, some pollutants were deposited. Pollutants accumulations on the PVDF membranes were higher than PTFE. It is assumed that the increase of feed temperature caused a rise of the pressure and consequently fastened the accumulation rate of pollutants on the PVDF membranes surface. The fluxes of PVDF membranes may be affected by this accumulation of pollutants. It is also reported in most MD literature that ΔT, feed concentration and flow rate as well as membrane characteristics such as membrane type, pore size and pore size distribution influence the TMF [32,37,38].

3.3. Membrane integrity; contact angle and FTIR

The main issues encountered by membrane processes are membrane wetting, fouling and damage. These influence the integrity of the membrane and contribute to worsening the distillate quality over time. Wetting is largely influenced by membrane pore sizes, larger pores being readily sensible to wetting [39]. By observation, used membranes seemed more damaged during the treatment of raw leachate than pretreated leachate. This may due to the complex composition of raw leachate, the high content of solid particles, organic and inorganic matters, that may scrub the membrane surface during the treatment process. But physical observation is far less efficient to examine the membrane integrity. The analyses of contact angles and FTIR of unused and used membranes were performed for a better understanding of membrane fouling and wetting. The contact angles of the membranes before and after being used have been determined and are shown in Table 4. After being used, the contact angle of PTFE membranes did not decrease significantly compared with PVDF membranes; they resisted more to wetting. For identical membrane structures (PVDF or PTFE) with different pore size, 0.22 μm pore size membranes resisted more to wetting. The wettability of the microporous membranes is a result of three main factors, which are the surface tension of the process solution, the membrane material and the membrane structure. Wetted membranes lose their hydrophobicity, being not able to prevent any more small substances from passing through their pores. Although membrane fouling is neglected during MD because of the vapor–liquid interface formed, it was obvious from the images presented in the supplementary information section that pollutant deposited in a great amount on the membrane surface; thus, fouling is a reality not to be ignored.

The change in the membranes structures and the deposition of external particles on the membrane surface and pores were examined with FTIR and depicted in Fig. 5. Unused PTFE and PVDF membranes showed the same peaks regardless of their pore size. Thus, only the FTIR spectra of unused PTFE and PVDF membranes having a pore size of 0.45 μm are presented, the FTIR spectra of these 0.22 μm pore size of these membranes are not presented. The unused PTFE membrane showed two characteristic peaks at 1,149 and 1,204 cm^{-1}, which are related to the stretching vibration of $–CF_2$ and $–CF_3$ groups, respectively [40,41]. On unused PVDF membrane, asymmetric and symmetric vibrations of CH_2 groups were shown by the peaks located at 3,022 and 2,980 cm^{-1}. The peak at 1,403 cm^{-1} was related to CH_2 wagging vibration, and a peak at 1,185 cm^{-1} represented C–C bands of PVDF membrane [42]. Some peaks observed in the range of 750–981 cm^{-1} were related to α and β phases of PVDF [43], and those observed at 878 and 839 cm^{-1} corresponded to C–C–C asymmetrical stretching and C–F stretching vibrations [41].

As depicted in Fig. 5, used membrane presented a peak at 3,393 cm^{-1} caused by intermolecular O–H stretching of the phenols, hydroxyls and carboxyls [44], and another peak located at 2,923 cm^{-1} and may represent the vibration of the –CH2 groups bound by the stretching of the –OH groups [45]. Some of the peaks were located in the range of 1,690–1,540 cm^{-1} and may be related to C=O stretching of amide groups (amide-1) and N–H bending vibration of amide groups (amide-2), indicating the possible presence of proteins in the leachate [46–48]. Some of the peaks were observed nearby 1,652 cm^{-1} and exhibited C=O stretching from aldehydes and ketones. Some peaks located at 1,540, 1,233 and 1,052 cm^{-1} may be attributed to C=O vibrations in the carboxylic acid dimer [44], the sulfate ester groups [9] and C–O–C vibrations of polysaccharides and polysaccharide-like substances, respectively [44,48]. A minor peak located at 871 cm^{-1} may be assigned to carbonates and $CaCO_3$ scale formation [44].

The characterizing peaks of the used PTFE and PVDF membranes were not present at the same intensity on the membranes after the treatment of the leachates. The membranes have lost some of their properties. The additional peaks appeared on the used membranes were the result of some inorganic and organic compounds (possibly proteins and polysaccharides) [48] deposited on the membranes

Table 4
Contact angles

Membranes	Contact angles			Contact angle reduction (%)	
	Unused	Pretreated	Raw	Pretreated	Raw
PTFE 0.22 μm	127.61	125.285	119.485	1.82	6.37
PTFE 0.45 μm	124.91	121.22	115.195	2.95	7.78
PVDF 0.22 μm	128.99	96.95	97.225	24.84	24.63
PVDF 0.45 μm	123.595	89.45	95.86	27.63	22.44

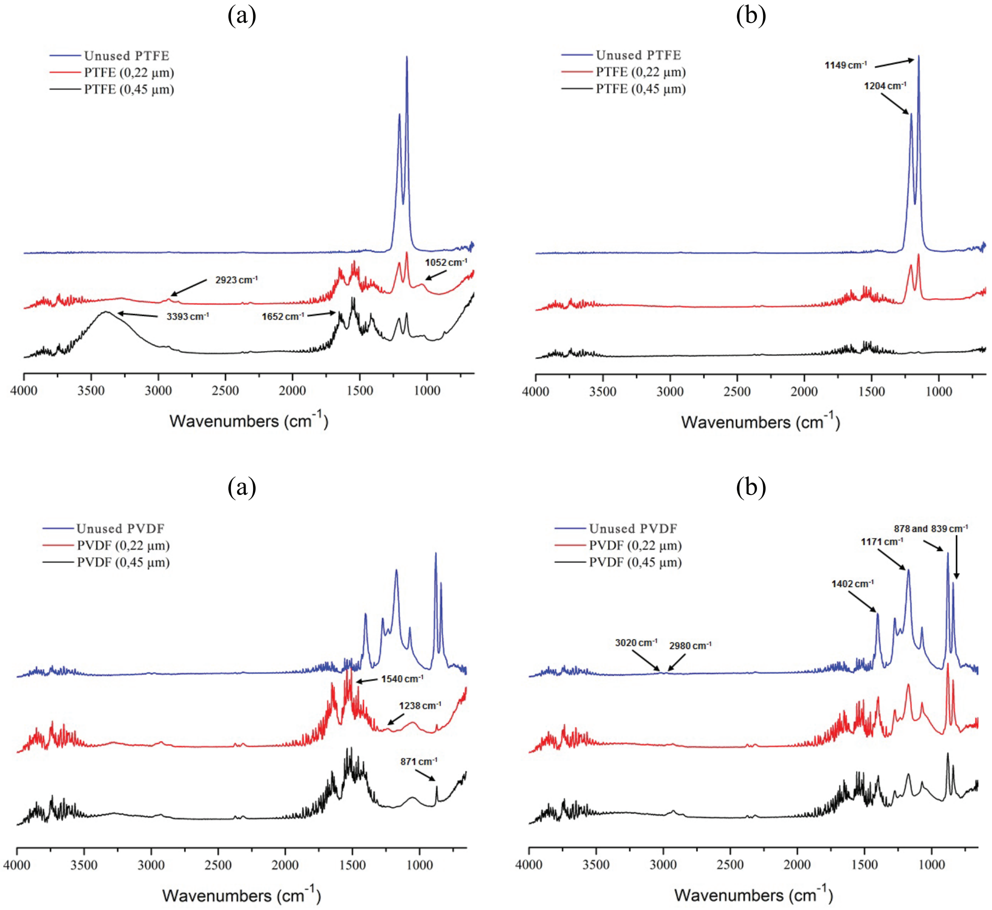

Fig. 5. FTIR spectra of PTFE and PVDF membranes before and after MD process: (a) raw leachate and (b) pretreated leachate.

surfaces. Used PVDF membranes presented denser extra peaks showing possibly more organic foulant deposition at a higher density compared with PTFE membranes.

4. Conclusion

The treatability of landfill leachate with a modified DCMD process was investigated. The permeate water quality has been accessed by the determination of the conductivity, COD, sulfate, ammonium, alkalinity and hardness content. The results of this study and some recommendations for future studies may be drawn as follows:

- The conductivity was rejected up to 98% in pretreated leachate. The conductivity of raw leachate was removed up to 80%, and the highest permeate water conductivity was observed at the highest ΔT (50°C).
- MBR pretreated leachate presented lower effluent hardness and alkalinity compared with raw leachate. The removal efficiencies of alkalinity and hardness were highly influenced by feed temperature and feed leachate concentrations, slightly by membrane structure and pore size.
- COD rejection efficiency reached approximately 99% in both leachates, and almost all permeate met Environmental Quality Standard A.
- An overall 90% sulfate was removed from raw and pretreated leachate.
- The ammonium nitrogen rejection efficiency was not a success when compared with all the other parameters; however, good rejection efficiency of 95.78% was observed with pretreated leachate at low ΔT (30°C).
- The highest TMF with pretreated and raw leachate were, respectively, 15.54 and 9.87 L/m^2 h with PTFE 0.45 membranes at ΔT of 50°C. The temperature was the most important parameter that affected the flux.
- From the effluent quality analyses, the MD application for landfill leachate treatment is possible with good result. However, a pretreatment to remove and reduce pollutants concentration could lead to better effluent quality and higher flux.
- Both PTFE and PVDF membranes presented good rejection of the pollutants, PTFE membranes, and however, presented better rejection of some pollutants compared with PVDF membranes.
- After being used, contact angles of the membranes did not change significantly; membrane wetting was negligible, but long-term pilot-scale study is necessary to follow the membrane behavior over time for better understanding of the membrane wettability and fouling, the flux and permeate quality.

- FTIR spectra showed that possibly proteins and polysaccharides were accumulated on the membrane surfaces.

Acknowledgment

This research was supported by the Ministry of Science, Industry and Technology (SAN-TEZ) Grant No: 0279. STZ.2013-2 in cooperation with İSTAÇ.

References

[1] C. Visvanathan, M.K. Choudharya, M.T. Montalboa, V. Jegatheesanb, Landfill leachate treatment using thermophilic membrane bioreactor, Desalination, 204 (2007) 8–16.

[2] T.A. Kurniawan, W. Lo, G.Y.S. Chan, Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate, J. Hazard. Mater., 129 (2006) 80–100.

[3] S. Renoua, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, J. Hazard. Mater., 150 (2008) 468–493.

[4] J. Bohdziewicz, E. Neczaj, A. Kwarciak, Landfill leachate treatment by means of anaerobic membrane bioreactor, Desalination, 221 (2008) 559–565.

[5] Z. Salem, K. Hamouri, R. Djemaa, K. Allia, Evaluation of landfill leachate pollution and treatment, Desalination, 220 (2008) 108–114.

[6] T.A. Kurniawan, W.-H. Lo, G.Y.S. Chan, Degradation of recalcitrant compounds from stabilized landfill leachate using a combination of ozone-GAC adsorption treatment, J. Hazard. Mater., 137 (2006) 443–455.

[7] H.-S. Li, S.-Q. Zhou, Y.-B. Sun, P. Feng, J.-D. Li, Advanced treatment of landfill leachate by a new combination process in a full-scale plant, J. Hazard. Mater., 172 (2009) 408–415.

[8] H. Scharff, Landfill reduction experience in The Netherlands, Waste Manage., 34 (2014) 2218–2224.

[9] D. Trebouet, J.P. Schlumpf, P. Jaouen, F. Quemeneur, Stabilized landfill leachate treatment by combined physicochemical–nanofiltration processes, Water Res., 35 (2001) 2935–2942.

[10] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate: a review, Crit. Rev. Env. Sci. Technol., 32 (2002) 297–336.

[11] Y. Deng, J.D. Englehardt, Treatment of landfill leachate by the Fenton process, Water Res., 40 (2006) 3683–3694.

[12] J. Bohdziewicz, A. Kwarciak, The application of hybrid system UASB reactor-RO in landfill leachate treatment, Desalination, 222 (2008) 128–134.

[13] D. Qu, D. Sun, H. Wang, Y. Yun, Experimental study of ammonia removal from water by modified direct contact membrane distillation, Desalination, 326 (2013) 135–140.

[14] M. Bilgili, A. Demir, B. Ozkaya, Quality and quantity of leachate in aerobic pilot-scale landfills, Environ. Manage., 38 (2006) 189–196.

[15] J. Koo, J. Han, J. Sohn, S. Lee, T.-M. Hwang, Experimental comparison of direct contact membrane distillation (DCMD) with vacuum membrane distillation (VMD), Desal. Wat. Treat., 51 (2013) 6299–6309.

[16] C. Huayan, W. Chunrui, J. Yue, W. Xuan, L. Xiaolong, Comparison of three membrane distillation configurations and seawater desalination by vacuum membrane distillation, Desal. Wat. Treat., 28 (2011) 321–327.

[17] A. Boubakri, S.A.-T. Bouguecha, I. Dhaouadi, A. Hafiane, Effect of operating parameters on boron removal from seawater using membrane distillation process, Desalination, 373 (2015) 86–93.

[18] K. Kezia, J. Lee, M. Weeks, S. Kentish, Direct contact membrane distillation for the concentration of saline dairy effluent, Water Res., 81 (2015) 167–177.

[19] S. Meng, Y. Yea, J. Mansouri, V. Chen, Crystallization behavior of salts during membrane distillation with hydrophobic and superhydrophobic capillary membranes, J. Membr. Sci., 473 (2015) 165–176.

[20] L.M. Camacho, L. Dumée, J. Zhang, J.-D. Li, M. Duke, J. Gomez, S. Gray, Advances in membrane distillation for water desalination and purification applications, Water, 5 (2013) 94–196.

[21] A. Alkhudhiri, N. Darwish, N. Hilal, Membrane distillation: a comprehensive review, Desalination, 287 (2012) 2–18.

[22] E. Drioli, A. Ali, F. Macedonio, Membrane distillation: recent developments and perspectives, Desalination, 356 (2015) 56–84.

[23] M. Khayet, Membranes and theoretical modeling of membrane distillation: a review, Adv. Colloid Interface Sci., 164 (2011) 56–88.

[24] P. Wang, T.-S. Chung, Recent advances in membrane distillation processes: membrane development, configuration design and application exploring, J. Membr. Sci., 474 (2015) 39–56.

[25] K.W. Lawson, L.D. Lloyd, Membrane distillation, J. Membr. Sci., 124 (1997) 1–25.

[26] J. Phattaranawik, R. Jiraratananon, A.G. Fane, Heat transport and membrane distillation coefficients in direct contact membrane distillation, J. Membr. Sci., 212 (2003) 177–193.

[27] E. Levlin, Conductivity Measurements for Controlling Municipal Waste-Water Treatment, Department of Land and Water Resources Engineering, KTH, S-100 44 Stockholm, Sweden.

[28] A.C.M. Franken, J.A.M. Nolten, M.H.V. Mulder, D. Bargeman, C A. Smolders, Wetting criteria for the applicability of membrane distillation, J. Membr. Sci., 33 (1987) 315–328.

[29] E. Yildiz, A. Nuhoglu, B. Keskinler, G. Akay, B. Farizoglu, Water softening in a crossflow membrane reactor, Desalination, 159 (2003) 139–152.

[30] Environmental Quality (Sewage) Regulations 2009, PU(A) 432/2009.

[31] Z. Zhao, L. Xu, X. Shang, K. Chen, Water regeneration from human urine by vacuum membrane distillation and analysis of membrane fouling characteristics, Sep. Purif. Technol., 118 (2013) 369–376.

[32] T. Husnain, Y. Liu, R. Riffat, B. Mi, Integration of forward osmosis and membrane distillation for sustainable wastewater reuse, Sep. Purif. Technol., 156 (2015) 424–431.

[33] A. El-Abbassi, H. Kiai, A. Hafidi, M.C. García-Payo, M. Khayet, Treatment of olive mill wastewater by membrane distillation using polytetrafluoroethylene membranes, Sep. Purif. Technol., 98 (2012) 55–61.

[34] M. Bhattacharya, S. Dutta, J. Sikder, M.K. Mandal, Computational andexperimental study of chromium (VI) removal in direct contact membrane distillation, J. Membr. Sci., 450 (2014) 447–456.

[35] P. Pal, A.K. Manna, Removal of arsenic from contaminated groundwater by solar-driven membrane distillation using three different commercial membranes, Water Res., 44 (2010) 5750–5760.

[36] C.K. Chiam, R. Sarbatly, Vacuum membrane distillation processes for aqueous solution treatment—a review, Chem. Eng. Process., 74 (2013) 27–54.

[37] A. Zoungrana, M. Çakmakci, I.H. Zengin, Ö. İnoğlu, H. Elcik, Treatment of metal-plating waste water by modified direct contact membrane distillation, Chem. Pap., 70 (2016) 1185–1195.

[38] A. Zoungrana, I.H. Zengin, H. Elcik, D. Yeşilırmak, D. Karadağ, M. Çakmakci, Arsenic removal from drinking water by direct contact membrane distillation, Membr. Water. Treat., 7 (2016) 241–255.

[39] T.-H. Khaing, J. Li, Y. Li, N. Wai, F. Wong, Feasibility study on petrochemical wastewater treatment and reuse using a novel submerged membrane distillation bioreactor, Sep. Purif. Technol., 74 (2010) 138–143.

[40] F. Wang, H. Zhu, H. Zhang, H. Tang, J. Chen, Y. Guo, Effect of surface hydrophilic modification on the wettability, surface charge property and separation performance of PTFE membrane, J. Water Process Eng., 8 (2015) 11–18.

[41] B.-Y. Wang, C.K. Tseng, C.-M. Shih, Y.-L. Pai, H.-P. Kuo, S.J. Lue, Polytetrafluoroethylene (PTFE)/silane cross-linked sulfonated poly(styrene–ethylene/butylene–styrene) (sSEBS) composite membrane for direct alcohol and formic acid fuel cells, J. Membr. Sci., 464 (2014) 43–54.

[42] H. Bai, X. Wang, Y. Zhou, L. Zhang, Preparation and characterization of poly(vinylidene fluoride) composite membranes blended with nano-crystalline cellulose, Prog. Nat. Sci., 22 (2010) 250–257.

[43] A. Alpatova, M. Meshref, K.N. McPhedran, M.G. El-Din, Composite polyvinylidene fluoride (PVDF) membrane impregnated with Fe_2O_3 nanoparticles and multiwalled carbon nanotubes for catalytic degradation of organic contaminants, J. Membr. Sci., 490 (2015) 227–235.

[44] Y. Xue, H. Zhao, L. Ge, Z. Chen, Y. Dang, D. Sun, Comparison of the performance of waste leachate treatment in submerged and recirculated membrane bioreactors, Int. Biodeterior. Biodegrad., 102 (2015) 73–80.

[45] L. Hu, G. Zeng, G. Chen, H. Dong, Y. Liu, J. Wan, A. Chen, Z. Guo, M. Yan, H. Wu, Z. Yu, Treatment of landfill leachate using immobilized *Phanerochaete chrysosporium* loaded with nitrogen-doped TiO_2 nanoparticles, J. Hazard. Mater., 301 (2016) 106–118.

[46] Z. Liu, W. Wu, P. Shi, J. Guo, J. Cheng. Characterization of dissolved organic matter in landfill leachate during the combined treatment process of air stripping, Fenton, SBR and coagulation, Waste Manage., 41 (2015) 111–118.

[47] M. Bis, A. Montusiewicz, J. Ozonek, S. Pasieczna-Patkowska, Application of hydrodynamic cavitation to improve the biodegradability of mature landfill leachate, Ultrason. Sonochem., 26 (2015) 378–387.

[48] Y. Dong, Z. Wang, C. Zhu, Q. Wang, J. Tang, Z. Wu, A forward osmosis membrane system for the post-treatment of MBR-treated landfill leachate, J. Membr. Sci., 471 (2014) 192–200.

Supplementary information

While raw leachate presented a black color, effluent was slightly blue, a color apparently indicating the presence of ammonium. Color changed into clear after titration with acid (precipitation of ammonia). On the other hand, pretreated leachate had dirty yellow color. After crossing the hydrophobic membrane, the effluent has been clarified as seen in Fig. S1.

The images below witnessed the damages the membranes underwent during the operation. Unused and used membrane surface can be seen in Fig. S2. Pollutants were accumulated on the membranes surface during the treatment process.

Fig. S1. (a) Raw landfill leachate (left) and permeate from MD (right), and (b) pretreated landfill leachate (left) and permeate from MD (right).

Fig. S2. Unused and used PTFE and PVDF membranes.