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Research Article / Araştırma Makalesi

TREATABILITY OF MUNICIPAL WASTEWATER WITH DIRECT CONTACT MEMBRANE DISTILLATION

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ABSTRACT

In this study, the treatability of raw and biologically pretreated municipal wastewater (MWW) by direct contact membrane distillation (DCMD) was investigated. The treatment was performed at three various feed temperatures, 40, 50 and 60 ^{0}C and at constant 10 ºC cooling water, with two hydrophobic membranes made of polytetrafluoroethylene (PTFE) and Polyvinylidene difluoride (PVDF). Both membranes had a pore size of 0.45 µm. The conductivity, COD, alkalinity and hardness were highly rejected over 98 % while ammonium nitrogen (NH_4-N) rejection efficiency was low; up to 60 %. The highest transmembrane flux (TMF) approximately 16 L/m^2.h was obtained at 60 ^{0}C feed temperature with PTFE membrane and pretreated solution as feed. The membranes used in this study were effective for the treatment of MWW. Checking the contact angles of the PTFE membranes after the treatment and the quality of the treated effluent showed that membrane is effective for this process.
Keywords: Hydrophobic membrane, membrane distillation, municipal wastewater.

1. INTRODUCTION

The amount of municipal wastewater (MWW) released per capita increased up to more than 200 L per day and its composition varied widely with increasing population, urbanization, industrialization and changes in consumption patterns. MWW is mostly rich with microorganisms, biodegradable organic compounds, nutrients, inorganic materials and metals [1]. Once released into the environment MWW is a source of aesthetic problems, malodors, surface water pollution (eutrophication) and ground water infiltration.

The membrane processes used in MWT treatment and reclamation include membrane bioreactor (MBR), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis and they have competitively proven their effectiveness [2], [3], [4]. These processes, however, require external energy to pressurize the water through the membranes, and they suffer from membrane fouling when the feed solution is too much rich with organics or scaling compounds [5]. Biological treatments have efficiently been used to remove nutrients and biodegradable organic compounds from MWW. Biological treatments suffer the problem of complexity and are

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unable to treat certified harmful inorganic compounds and metals found in wastewaters. Alternative technologies such as membrane distillation (MD) have been used and are qualified as efficient technologies for wastewaters treatment.

Membrane distillation (MD) has been investigated as a possible alternative technique for water treatment capable of removing in a single step all pollutants and theoretically produce a pure effluent [6]. It is a thermally driven process using vapor pressure difference as the driving force to transport molecules from the high vapor pressure side to the low vapor pressure side through the membrane pores [7]. Mokhtar et al. investigated the treatment of wastewater from rubber industry in Malaysia using MD technology. The authors reported an efficient rejection of almost pollutants in the solution and resulted to high-quality permeate, however, they pointed the decline of the TMF as a result of membrane fouling to be the main limitation of the process [8]. In fact, MD process is associated with several advantages. It provides high treatment efficiency with the very high rejection of ions, macromolecules, colloids, cells and other non-volatiles compounds. In addition, the possible operation at low temperature and very low pressure together with the possible use of alternative energy sources, such as sun or waste heat energy for heating in MD process can significantly reduce the operating cost [6], [9]. 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) are generally the main configurations used [9], [10], [11], but some modifications to improve these configurations are wide and mostly concern the reduction of heat loss by conduction [7]. DCMD, in which condensed vapor (usually water) on the filtrate side of the membrane is in direct contact with the membrane is the simplest, cheapest and popular configuration of these configurations [6], [7]. The aim of this study is to investigate both polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) hydrophobic membrane effectiveness in raw and biologically pretreated MWW treatment in a DCMD module. The membranes performance and the effects of the feed solution pollutants nature and concentration on the treatment performance will be accessed.

2. MATERIALS AND METHODS

2.1. Membrane Distillation Apparatus and Membranes

The schematic representation of the MD module used in this study is shown in figure 1. The cooling side of the module was separated with a stainless plate in order to reduce the heat loss by conduction, refer to Zoungrana et al. [7] for more details. The volume of the feed tank was 7 L. The flow-rate, temperatures and operating pressures were monitored by a flow-meter, digital temperature probes and manometers, respectively. A digital balance connected to a personal computer was used to measure the permeate water mass and to calculate the flux. A CAT pump 2SF35SEEL-stainless steel direct-drive plunger pump (Minneapolis, MN, USA) and Watson Marlow peristaltic pump 323 Du/D (Ringsted, Denmark) were used to transfer the feed heated wastewater and the cooling water to the DCMD module, respectively. CAT Pump 2SF35SEEL-Stainless Steel Direct-Drive Plunger Pump and Watson Marlow Peristaltic pump 323 Du/D were used to transfer the heated wastewater and the cooling water to the DCMD module, respectively. The effective membrane surface area was 0.015 m^2.The study was carried out at three different heating temperatures (40 ^{0}C, 50 ^{0}C and 60 ^{0}C). The cooling temperature was maintained constant at 10 ^{o}C during the whole study. For each heating temperature the membrane was used during 90 minutes operation time. Membranes are changed once all three different delta temperatures are tested. Two commercial hydrophobic membranes made of PTFE and PVDF with 0.45 µm pore sizes manufactured by Membrane-Solution-LLC were used for this study.

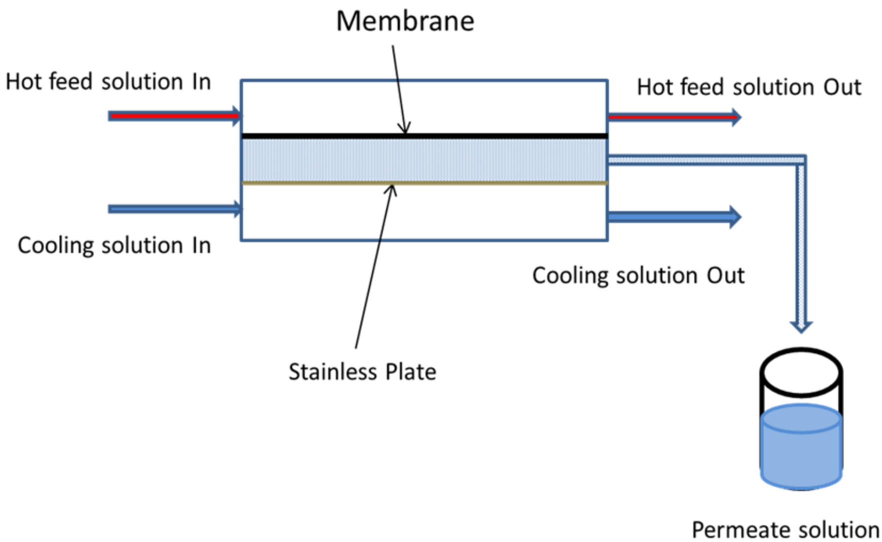

Figure 1. Schematic representation of the MD module

2.2. Wastewater Source and Characterization

The MWW used for the experimental study were collected from İSKİ/Istanbul. Two different wastewaters were used, raw wastewater undergoing no pretreatment and advanced biologically pretreated effluent. Both wastewaters have been analyzed and characterized as shown in table 1.

Table 1. Estimated percentage content of the waste

Parameters	Raw wastewater	Pretreated wastewater
Conductivity, µs/Cm	1672	1042
COD, mg/L	345	45
Hardness, mg $CaCO_3$/L	248	235
Alkalinity, mg $CaCO_3$/L	330	155
NH_4-N, mg/L	81.2	61.6
pH	5.9	6.2

2.3. Analysis Methods

All characteristics related to leachate quality as well as treated permeate quality have been accessed using standard methods (APHA, 2005). pH and conductivity were measured at room temperature (24±1 ^oC) using Thermo Scientific Orion 5-Star Plus pH/ ORP/ ISE /Conductivity /DO Meter, while hardness and alkalinity were measured according to standard methods 2340 C (APHA, 2005) and 2320 (APHA, 2005) respectively. COD was analyzed using a closed reflux colorimetric method according to the standard method 5220 D (APHA, 2005) and $NH4^+$-N content was carried out by 4500-Nr-L C standard method (APHA, 2005) using distillation apparatus. The membrane wettability was analyzed by contact angle device Attension Theta Lite (TL 100).

3. RESULT AND DISCUSSION

The effluent from both raw and pretreated MWW presented different quality and this quality was as well influenced by the membrane type and the feed heating temperature. Initial pH of both solutions was slightly acidic, approximately pH 6, and effluent show varied pH but mostly around pH 6.5. Conductivity, COD, alkalinity, hardness, NH_4-N and transmembrane flux (TMF) of different permeate were investigated in order to access the quality and the reusability of the treated effluents.

3.1. COD, Alkalinity and Hardness Rejection

Table 2 shows the COD, hardness and alkalinity values of different permeates of raw and pretreated MWW treated with PTFE and PDVF membranes at different feed temperatures. The COD was very low in all effluents. Both membranes rejected COD in the MWW to a minimal value lower than 5 mg/L in most of the cases studied. Same results were observed for hardness and alkalinity. These compounds are mostly not evaporable, so there were retained in the feed solution while vaporized water molecules passed through the membrane. COD of MWW is not evaporable at 60 ^oC, hardness as well as alkalinity usually derived from $CaCO_3$ or $MgCO_3$ and are also not evaporable, so they are not able to cross the hydrophobic membrane. As a result, the rejection was high with the PTFE membrane for both feed solutions. However, at high temperature, the increase of molecules motility and the fragility of the membrane caused some of the components to escape through the PVDF membrane by forcing the hydrophobic barrier. In addition, the pretreated MWW presented much better rejection compared to raw MWW with PVDF membrane. This may due to the low concentration of pollutants in the pretreated solution, minimizing the negative effect of the feed solution on the membrane such as wetting and fouling. PTFE membrane resisted more to the negative effects caused by the increase of the feed solution temperature. This is due to the structure of this membrane.

Table 2. MD treatment effluents COD, alkalinity, and hardness content

Parameters	Raw MWW	PTFE			PVDF		
		40 ^oC	50 ^oC	60 ^oC	40 ^oC	50 ^oC	60 ^oC
COD, mg/L	345	<5	<5	<5	<10	<10	<10
Hardness, mg $CaCO_3$/L	248	3	3	4	42	66	83
Alkalinity, mg $CaCO_3$/L	330	<20	<20	<20	120	125	155

Parameters	Pretreated MWW	PTFE			PVDF		
		40 ^oC	50 ^oC	60 ^oC	40 ^oC	50 ^oC	60 ^oC
COD, mg/L	45	<5	<5	<5	<5	<5	<5
Hardness, mg $CaCO_3$/L	235	2	3	3	40	48	55
Alkalinity, mg $CaCO_3$/L	155	<20	<20	<20	35	33	55

3.2. Conductivity

Conductivity is an important water parameter, simple to measure and determine the amount of dissolved matters in the water solution [12]. Inorganic dissolved solids, mostly calcium and magnesium are responsible for high conductivity in water. Conductivity is affected by temperature, being higher in warmer water [12]. Figure 2 shows conductivity values and rejection efficiencies in raw and pretreated MWW effluents from MD. PTFE membranes showed very high conductivity rejection and resulted to a very soft water after the treatment of both raw and pretreated MWW. PVDF membrane, however, showed less efficient rejection. The temperature effect on the rejection is obvious on the graphs; 40 ^{O}C heating feeding solutions presented lower conductivity and the conductivity increased when the feed temperature increased to 60 ^{o}C. A similar result was reported by Zoungrana et al. [7]. In fact, the membrane pores become fragile and vulnerable to some pollutants at higher temperature, causing some tiny dissolved matters to escape and increase the conductivity of the effluent. However, it is worth to mention that the conductivity in all treated effluent was low enough for water to be reused.

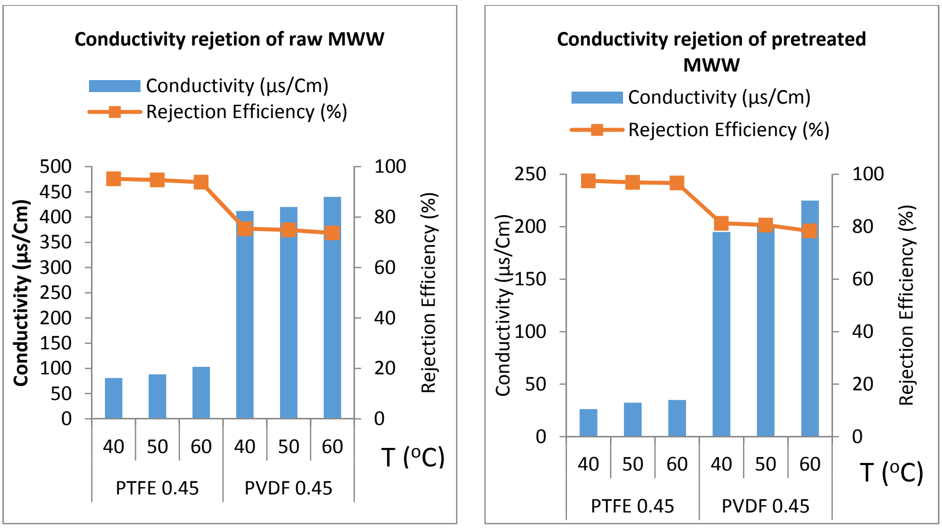

Figure 2. The conductivity of the MD permeate solution and the rejection efficiency with raw and pretreated MWW

3.3. Ammonium nitrogen (NH_4-N) Rejection

Ammoniacal nitrogen is responsible for eutrophication in wastewaters and causes potential toxicity to fish and other aquatic life when discharged without meeting the required standard [13]. Figure 3 shows the rejection efficiency of NH_4-N in the present study and its concentrations in the permeate water. NH_4-N rejection was the less efficient among all the parameters studied. The highest rejections were observed with PTFE membranes and pretreated MWW as feed solution where the highest rejection efficiency was 60%. The rejection was low with raw MWW and PVDF membranes. For the same membrane and feed solution, the rejection decreased with increasing feed heating temperature. Ammonium is an unstable compound and varies from gaseous (NH_3) to liquid (NH_4^+) depending on the solution state, the temperature and the pH. During the heating process of the feed solution, the ammonium (NH_4^+) in the solution may be converted into ammonia gas (NH_3) that can easily cross the hydrophobic membrane pores. Qu et al. reported a similar result during the investigation of the rejection of ammonia by DCMD. They agreed that temperature as well as pH greatly impact the process efficiency. They stated that the elevation of feed temperature from 30 to 50 °C caused an increase of 250% of ammonia transport through 0.22 µm pore size PVDF membrane [14]. Husnain et al., however, reported up to 99% NH_4 rejection and almost 100% COD rejection during a study of an integrated forward osmosis (FO) and MD process for wastewater reuse. The very high rejection in their study was mainly due to the initial low concentration of NH_4 (300–495 mg/L NH_4Cl) and COD together with the performance of the FO system [4]. In the present study, despite the low rejection of NH_4-N, the effluent NH_4-N content is low enough to be considered for some re-utilization.

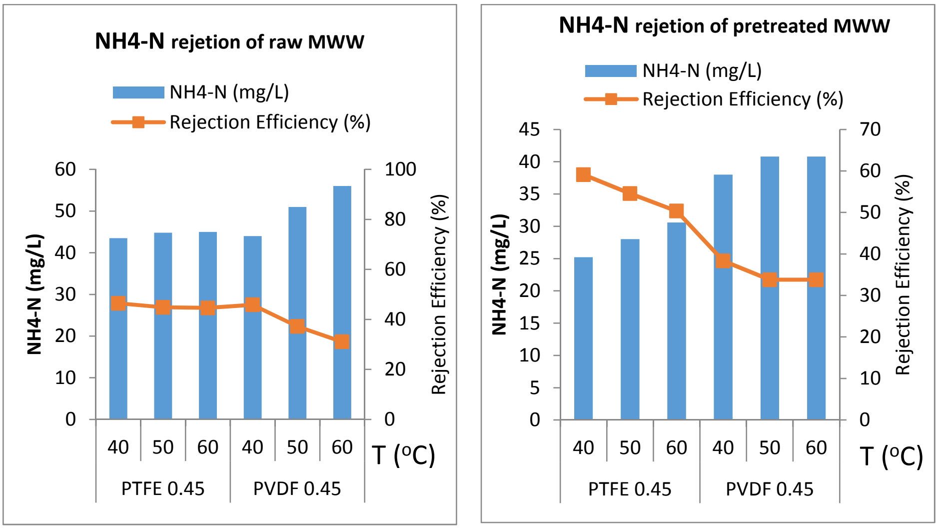

Figure 3. NH_4-N content of the MD permeate solution and the rejection efficiency with raw and pretreated MWW

3.4. Transmembrane Flux (TMF)

The TMF is one of the limiting factors of the commercial applicability of MD treatment technology [15]. Once effluent quality is certified, the flux remains critical for an economical acceptance of the process [11]. The TMF of both PTFE and PVDF membranes at different operating conditions are depicted in the graphs in Figure 4. The highest TMF observed for PTFE and PVDF membranes were 16.4 and 8.16 $L.m^{-2}.h^{-1}$ for pretreated MWW, 13.5 and 8.6 $L.m^{-2}.h^{-1}$ for raw MWW, respectively. These highest TMF were all obtained at the highest feed temperature (60°C). MD is a thermally driven process; the TMF is highly dependent on membrane pore size and feeds solution temperature as reported by El-Abbassi et al. [16]. In practice, a high amount of vapor is produced from the feed solution when it is heated at high temperature, and this cause higher vapor pressure inside the channel, and may cause an increase of the flux through the membrane pores [17]. An increase of the feed temperature from 40°C to 60 °C caused the flux to increase from 6 to 16.4 $L.m^{-2}.h^{-1}$ and from 2 to 8.16 $L.m^{-2}.h^{-1}$ with PTFE and PVDF membranes respectively, during the treatment of pretreated MWW. Similar result is observed with raw MMW treatment, and many researchers as well reported results alike [6], [7] [17], [18], [19]. Pretreated MWW has the advantage of containing less fouling components and particles that may harm the membrane surface, as a result, the water vapor flows easily and is not obstructed when crossing the membrane; this may explain the obtained higher flux compared to raw MMW. Regarding membrane structures, PTFE membranes have an extremely low surface tension properties [20], [21] compared to PVDF membranes, for that reason, practically no materials stick on PTFE membranes surface, and this minimize membrane fouling and result to higher membrane flux.

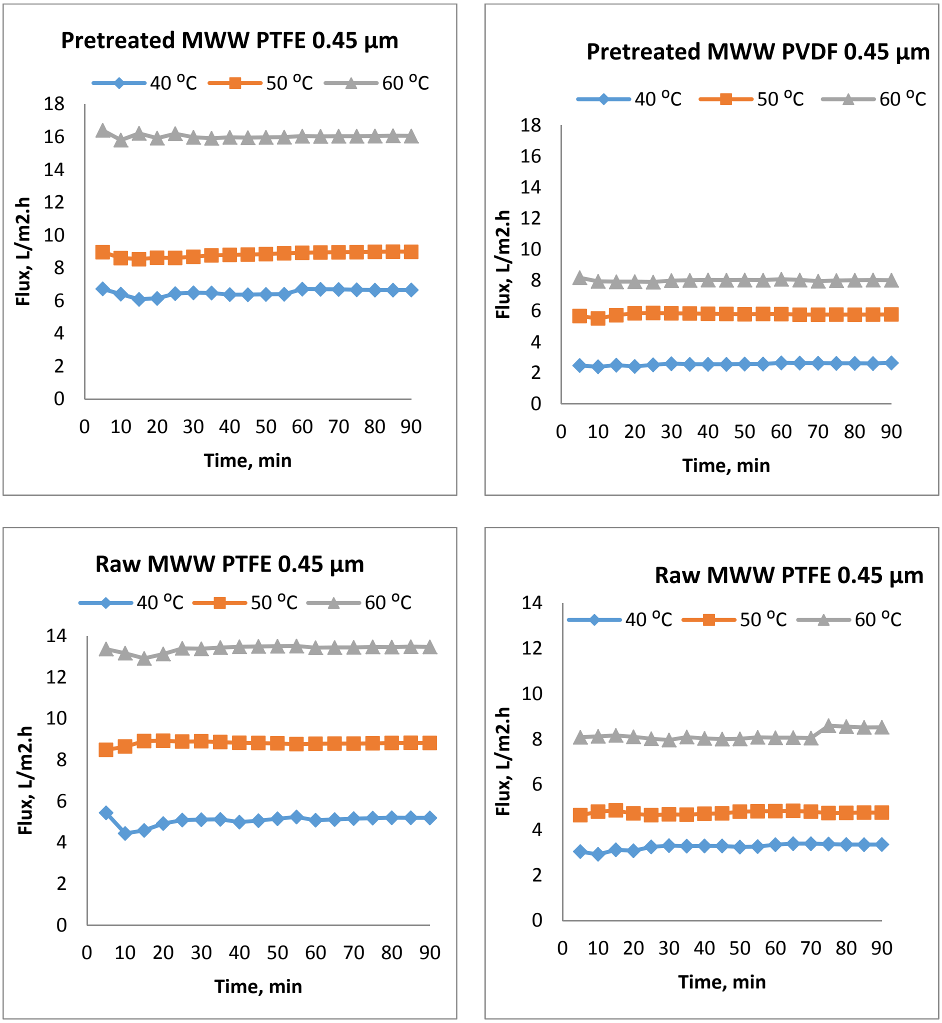

Figure 4. The TMF behavior with raw and pretreated MWW at different feed temperature with PTFE and PVDF membranes

3.5. Membrane Fouling and Contact Angle

As reported by Mokhtar and his coworkers [5], the decline of the flux is mainly caused by the concentration polarization, temperature polarization and membrane fouling. In fact, these elements participate to membrane wetting as well and contribute to worsening the quality of the permeate water. Besides those parameters, membrane wettability can be associated with the membrane liquid entrance pressure (LEP), structure and pore sizes, larger pores being readily sensible to wetting [22]. Table 2 shows the contact angles of the membranes before and after being used. Both PTFE and PVDF membranes showed high hydrophobicity, being the result of high contact angle. After being used, the contact angle of both membranes decreased, but the decrease was high when the membranes were used to treat raw MWW, and for the same feed solution the decrease was higher with PVDF membranes; PTFE 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. Though membrane fouling is neglected during MD due to the formation of the vapor-liquid interface, it was obvious when checking the membrane surface that some pollutant deposited on the membrane surface during raw MWW treatment.

Table 3. Contact angles of PTFE and PVDF membranes before and after treatment

Membranes	**Unused**	**After Raw MWW treatment**		**After Pretreated MWW treatment**	
Part measured	**All part**	**Corner**	**Center**	**Corner**	**Center**
PTFE 0.45 µm	124.91	109.21	91.01	118.25	108.43
PVDF 0.45 µm	123.595	76.66	66.79	80.22	74.87

4. CONCLUSION

The treatability of raw and biologically pretreated MWW by DCMD was investigated with success. The rejection of the conductivity, COD, alkalinity and hardness were high, up to 98%. Low rejection of NH_4-N approximately up to 60 % was achieved. This low rejection of NH_4-N is mostly related to the feed solution pH, initial high NH_4-N content and the increased heating of the feed solution. A high flux approximately 16 $L.m^{-2}.h^{-1}$ was obtained with pretreated feed solution with PTFE membrane at 60 ^oC heating temperature. The effluent quality shows that MD can be used for MWW recycle to supply some industrial water demand. The PTFE membrane produced better effluent quality and higher TMF compared to PVDF membrane. The contact angles showed that PTFE membranes resisted more to fouling and wetting and seemed to be the best membrane for MWW treatment with MD process. Membrane wetting was much intense in the centers than the corners, and this may be due to the higher water pressure in the center than the corner of the membrane. Further studies using membrane support may be needed to investigate the possible reduction of this negative effect on the TMF.

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