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Laboratory Scale Applications of Membrane Treatment Systems for Organized Industrial Zones

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Abstract – Organized Industrial Zones (OIZ) are growing in number since the year 1962, and as of 2018, the number of mixed, specialized and rehabilitated OIZs is more than 300. In these regions, wastewater management is mostly contracted with the municipality and in 46% of the regions have a treatment plant. Wastewater treatment plants (WWTPs) in Turkey have usually conventional WWTPs (only carbon removal) while some large-scale OIZs have advanced treatment plants that removes nitrogen and phosphorus besides carbon (Adana, Antalya, Balikesir OIZs).
Turkey's textile, metal, food and recycling industries are using excessive water in their processes. New technologies need to be developed in order to protect the existing water resources and to reuse water. Membrane treatment systems are among the best available techniques for water reuse. In this study, laboratory scale studies were performed with different membranes for reuse of wastewater from OIZ. Membrane bioreactors (MBRs) and membrane filtration systems are studied with different molecular weight cutoff values. As a result of the studies, treatment of OIZ raw water by MBR, nanofiltration (NF) and reverse osmosis (RO) membranes were investigated and the best membrane configuration was determined. In addition, the treatment of OIZ effluent water with UF and NF-RO membranes was investigated and the membrane pairs were determined to give the best results. In both studies, both the efficiencies and the performance of the membranes were evaluated by evaluating the compliance with the irrigation water criteria specified in Turkish Irrigation Water Standards.

Keywords – *Organized industrial zones, membrane filtration, reuse.*

Özet – Organize Sanayi Bölgeleri (OSB) 1962 yılından beri sayıları giderek artan ve 2018 yılı itibariyle karma, ihtisas ve ıslah OSB'ler olmak üzere sayıları 300'ü aşan bölgelerdir. Bu bölgelerde atıksu yönetimi çoğunlukla belediye ile sözleşmeli olarak yürütülmekte olup bölgelerin %46'sında arıtma tesisi bulunmaktadır. Türkiye'deki atıksu arıtma tesisleri genellikle karbon giderimi yapan klasik biyolojik atıksu arıtma tesisleri olup bazı büyük ölçekli OSB'lerde karbonun yanı sıra azot ve fosfor giderimi de yapılmaktadır (Adana, Kayseri, Balıkesir OSB'ler).
Türkiye'de tekstil, metal, gıda ve geri dönüşüm sektörleri proseslerinde aşırı su kullanmaktadırlar. Aşırı su tüketen OSB'lerde mevcut su kaynaklarının korunması ve suların yeniden kullanımı için yeni teknolojilerin geliştirilmesi gerekmektedir. Membranlı arıtma sistemleri suyun yeniden kullanmımı için mevcut en iyi teknikler arasındadır. Bu çalışmada, OSB atıksularının yeniden kullanımı için farklı membranlar ile laboratuvar ölçekli çalışmalar yapılmıştır. Farklı moleküler ağırlık engelleme sınırı değerlerine sahip membranlar, membran biyoreaktör (MBR) ve membran filtrasyon sistemleri için çalışılmıştır. OSB ham suyunun MBR ile arıtılması çalışmaları sonucunda oluşan süzüntünün nanofiltrasyon (NF) ve ters ozmoz (TO) membranları ile arıtımları incelenmiş ve en iyi membran konfigürasyonu belirlenmiştir. Ayrıca, OSB çıkış suyunun UF ve NF-RO membranları ile arıtımları da incelenmiş olup en iyi sonuçları veren membran ikilileri belirlenmiştir. Her iki çalışmada da hem giderim verimleri, hem akılar hem de Atıksu Arıtma Tesisleri Teknik Usuller Tebliğinde belirtilen sulama suyu kriterlerine uygunluğu değerlendirilerek membran performansları değerlendirilmiştir.

Anahtar Kelimeler – *organize sanayi bölgesi, membran filtrasyon, yeniden kullanım,*

I. INTRODUCTION

In Turkey, industrial enterprises are organized in certain regions and these regions are called organized industrial zones. The purpose of the organized industrial zones is development of the industry for these reasons: to guide the urbanization, to support the regular development of the cities and to use the resources efficiently. The wastewater of the companies in organized industrial zone is treated in a central treatment plant in these zones.
There are hundreds of studies, especially made on membrane systems for food, textile, paper, pharmaceutical, oil and leather processing wastewaters [1-11]. Although these studies have identified systematic disadvantages for different membrane systems or operating conditions, new studies are needed to ensure system stability for mixed industrial wastewater. In particular, wastewater management in organized industrial zones in Turkey is being studied as a whole, and mixed industrial wastewater is being treated or mostly inefficiently treated.
Membrane technology has been preferred in wastewater

treatment for reuse of water in recent years. There are many advantages of membrane treatment systems over the conventional treatment methods. The most important of these are i) better water quality, ii) less space needed, and iii) less sludge generated [12].

Membrane configurations have been established in the literature for different types of wastewater and membrane systems of different pore diameters. Membranes are used either singly or in combination of two and three in accordance with the quality of water desired to be obtained. The use of reverse osmosis membranes is more common for waters where monovalent ions and some micropollutants are desired to be removed. As an alternative to RO membrane, NF and UF membranes can be preferred because they provide higher removal efficiencies at higher flux and lower pressure. Different types of membranes are used in different industrial areas. In a study of the UF membrane treatment of industrial park wastewater for reuse purposes, it was reported that the fouling mechanisms of pretreatment with UF membranes before RO membranes were revealed and the most suitable process was obtained with 1μ filter-UF-RO sequences [13].

One of the biggest operational problems in membrane systems is membrane fouling. Membrane fouling; reduce the flux, decrease membrane lifetime, increase operating cost and reduce system efficiency. There are many parameters defined up to now that cause membrane clogging. The most important ones are micropollutants (colloidal organic or inorganic), organic substances (humic acid, fulvic acid, protein etc.), inorganic substances (iron, manganese, silica etc.) and microbiological organisms (algae, bacteria etc.) [14].

Membrane bioreactors and membrane materials have been studied under different operating conditions in many countries for the reuse of wastewater. With an increasing tendency in recent years more than 400 publications have been published annually on MBR. Of the 800 full-scale MBR facilities in Europe, 566 are used for industrial wastewater treatment. The total number of publications on MBRs are less than 5% for the treatment of mixed industrial wastewater [15].

In this study, the effect of fouling propensities of membranes used in an integrated MBR and NF/RO filtration system in the treatment of mixed industrial wastewaters with different membrane modules was investigated.

II. MATERIALS AND METHOD

In this study, real wastewater of Kayseri OIZ wastewater treatment plant (WWTP) was used. It was produced about 1000 companies and the daily average flow was 30.000 m3. Industrial wastewater mainly comes from textile, paper, recycling and domestic sources. However, considering the characterization of wastewater, it is similar to a domestic wastewater in terms of biological treatability. Physical, chemical and biological treatment is carried out in WWTP. The effluent of WWTP provides discharge standards; however reuse is not possible because of irrigation water standards.

A. Membrane Bioreactor

The lab-scale MBR has an active volume of 20 liters. The MBR system has been inoculated with activated sludge, taken from return activated sludge in the OIZ WWTP. Flat-sheet modules made of two different membrane types are used in MBR. The surface area of the membrane modules are ranged from 690 to 1100 cm^2. The membrane types used in this study and the MBR operating conditions are shown in Table 1. Temperature, pH and the dissolved oxygen concentration in both MBR systems were equal. A diffuser was placed at the bottom of the reactor to prevent fouling of the submerged membrane module and to allow mixing in the reactor. The dissolved oxygen (DO) concentration was kept over 3 mg O_2/L during aeration. The system was operated for 6 months and the solids retention time was adjusted to 20 and 40 days.

Table 1. Membranes and MBR operating conditions.

Module	Material	Pore size (μ)	Oper. Days	SRT (day)
MF	PVDF	0.24	60	40
			30	20
UF	PVDF	0.44	60	40
			30	20

B. Nanofiltration and reverse osmosis experiments

In order to improve the effluent quality of the MF and UF modules, permeates were treated by NF and RO membranes. Three NF (NF90, NF270 and TM610) and RO (BW30, XLE and GE) membranes were used. The specifications of those membranes are given in Table 2. Only TM610 membrane was polyvinylidene fluoride (PVDF), the rest of the membranes were polyamide (PA). The experimentation setup consist of a nitrogen gas tank, 300 mL stainless steel pressure resistant cell (HP4750 Sterlitech, USA) and a weighing scale connected to the computer where the data recorder software is located. The diameter of the stainless steel cell is 47 mm and the effective area is 14.7 cm^2.

Table 1. Membranes characteristics of NF and RO membranes

Parameters/Membranes	Membrane material	Salt rejection
NF90	PA	85-95
NF270	PA	40-60
TM610	PVDF	80-97
BW30	PA	99,5
XLE	PA	95
GE	PA	99.3

Experiments were carried out at pressures 3, 6, 9 and 12 bars. The experiments were started with 12 bar pressure and the filtration was terminated at the pressure below 2 LMH, therefore experiments were not performed at lower pressures. Recovery rates of 70% for NF membranes and 50% for RO membranes were selected. The permeate samples were stored at +4 ° C in beaker covered with parafilm until analysis. Permeate analysis was carried out for conductivity, turbidity and flux parameters.

RESULTS

A. MBR Performance

Basic parameters of the 2 different membrane types, operated in the MBR system, were shown in Table 2. COD and BOD removal efficiency were obtained in both membrane modules. COD removals were over 91% on both membranes. Electrical conductivity (EC) of the influent was lower than the effluent. Influent EC of the wastewater was between 4.1 to 5.1 ms/cm; however effluent EC was between 4.2 to 5.9 ms/cm. This was due to oxidation of some pollutants that was ionized. The oxidation reduction potential (ORP) of the reactor remained relatively stable at -403±79 and -390±90 mV for MF and UF (250 kDa) membranes, respectively.

Table 2. MBR performance of FS membrane modules

Parameters	MF module		UF module	
	Influent	Influent	Influent	Effluent
pH	6.5 ± 0.4	6.9 ± 0.4	8.4 ± 0.2	7.9 ± 0.4
EC (ms/cm)	5.0 ± 0.8	5.9 ± 0.7	4.1±0.6	5.1 ± 1.1
COD (mg/L)	430 ± 110	34.5 ± 14.7	618 ± 155	39.5± 22.3
BOD (mg/L)	310 ± 68	0	345 ± 78	0
NO_2-N (mg/L)	<0,01	0	<0,01	0
NO_3-N (mg/L)	<0,01	2.6 ± 2.3	<0,01	3.5 ± 2.1

B. NF-RO results

All filtration experiments were conducted as the recovery rates were reached to 70 % for NF membranes and 50% for RO membranes. TM610 membrane filtrations were not consistent as the fluxes were not as low as it was expected. These filtrations were repeated many times but the membrane was fragile that it teared when the filtration was started. Data of this membrane was not shown elsewhere through the text.

Flux-pressure profiles of NF-RO membranes were shown in Figure 1. No significant flux difference was observed in the experiments made with effluent of the MF and UF membrane modules. However, NF-RO fluxes were differed from each other as the NF membranes showed higher fluxes as shown in Figure 2.

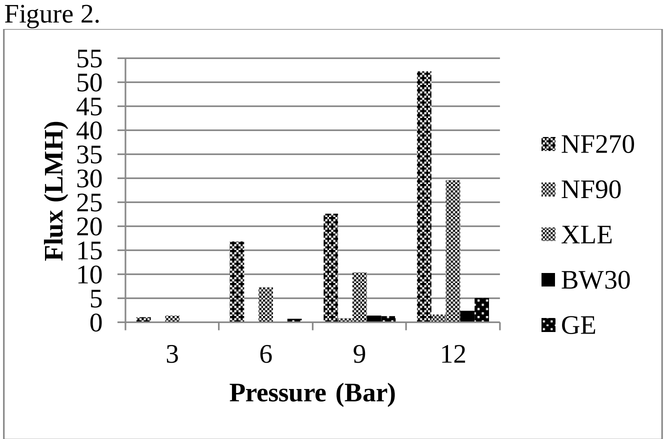

Figure 1. Flux-pressure profile of nanofiltration/reverse osmosis membranes for MF module effluent

When the removal efficiencies were examined, the membranes RO membranes showed higher performance as they showed low conductivity (as ms/cm).

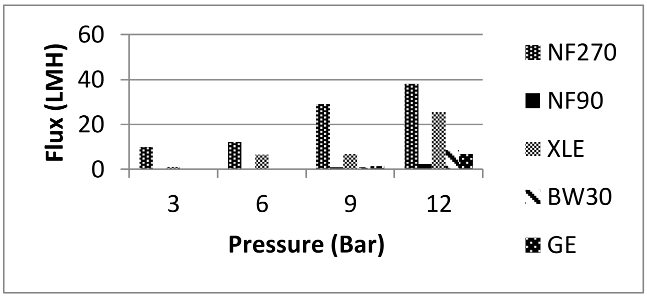

Figure 2. Flux-pressure profile of NF-RO membranes for UF module effluent

NF270 membrane showed very high flux values. NF90 and GE membranes were the worst membranes in terms of flux values. At 12 bars pressure, flux was as high as 38 LMH for NF 270 membrane while it was as low as 2.5 LMH for NF90 membrane.

III. Discussion

MBR results showed that polyvinylidene fluoride (PVDF) membranes could be used with flat sheet (FS) modules. However, one of the PVDF membranes used in the operation of the MBR showed low performance in terms of cleaning. MF membrane illustrated high tendency to irremovable fouling since it was not performed the same after physical cleaning operation.

UF membrane showed fewer tendencies to fouling. The physical cleaning of the membrane showed better results as the flux was recovered after cleaning operation. Therefore, it could be said that although the membrane material was the same, the fouling tendencies could be different. This could be due to both the membrane manufacturers and membrane manufacturing process as their contact angles and production process could be different.

The cleaning differences of the membranes were differed since both the pore sizes and fouling mechanisms of the membranes were different. Hydrophobicity could be the other reason in terms of fouling behavior.

Flux pressure profiles of the NF & RO membranes showed significant results in terms of membrane type. Some of the NF membranes have very high flux values while NF90 membrane showed very little flux value which is lower than some RO membranes. This was due to both MWCO values and membrane material. For example, TM610 membrane has very high flux values which are made of PVDF material, NF90 membrane showed, PA material, very low fluxes. Fouling profiles of these membranes should be searched in further studies.

Permeate qualities of the NF and RO membranes showed also different results in terms of conductivity values. RO membranes rejected almost all salinity while NF membranes could not reduce the conductivity values. XLE membrane permeate has very low conductivity values compared to other RO membranes. However, NF270 membrane has very little conductivity reduction which is around 1 ms/cm.

The best membrane performance should be determined with both good effluent quality and high flux values. If low flux membranes were eliminated there is only four membranes left: NF270, BW30, XLE, and GE. NF270 membrane should also be eliminated since the effluent quality is not good in terms of conductivity. The other membranes left were easily eliminated since BW30 and GE membranes have very low flux values. Therefore XLE membrane was found to be optimum for the operation of the organized industrial zone wastewater treatment and reuse together with the MBR, operated with a UF membrane.

IV. CONCLUSION

In this study laboratory scale evaluation of Kayseri OIZ wastewater is conducted. For this purpose, a laboratory scale MBR is designed to further treat with NF and RO membranes. MBR results showed that water quality is stable in optimum operational conditions. However, the conductivity of effluent of MBR is high as it could not be used for irrigation according to limit values in Turkey. NF and RO experiments showed that only RO membranes showed low conductivity values that are below 1.0 ms/cm. As a result, MBR-RO is a good solution for an industrial zone wastewater to reuse the water for irrigation purposes.

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