Conference: Sustainable Technologies in Water Treatment and Desalination

18th -19th December 2020, *National Institute of Technology Calicut, India*

Comparing nanofiltration membranes effectiveness for inorganic and organic compounds removal from a wastewater-reclamation plant's micro-filtered water

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Abstract

The study compared five NF membranes with varied water contact angles and molecular weight cut-off (MWCO) values for their effectiveness to remove dissolved organic carbon (DOC) and inorganic ions from micro-filtered water obtained from a wastewater-reclamation plant. The NF 90 membrane with the highest contact angle (79^0, least hydrophilic) and one with the lowest MWCO value ((90-200 Da) was the most efficient in removing DOC (88% rejection compared to 37-84% for the others) and inorganics (75% electrical conductivity rejection compared to 9-27% for the others). Of the 10 organic micropollutants in the feed water, more than 90% of 7 were removed.

Keywords: Wastewater treatment; organic micropollutants; nanofiltration; membrane; water quality

1 Introduction

Increasing shortage of natural water resources in many parts of the world is driving many countries to seek other sources of water such as wastewater. However, wastewater has many pollutants namely, dissolved organic matter (DOC) [1], organic micropollutants (OMP) [2,3] and inorganic salts [4,5]. These pollutants need to be removed before the treated wastewater can be reused. Of the many methods employed to treat wastewater for reuse, membrane process such as reverse osmosis (RO) and nanofiltration (NF) are attractive. Though RO removes dissolved organic and inorganic constituents at a higher efficiency than NF, the latter has other advantages such as higher water flux and uses lower pressure for its operation. This can cut down energy consumption and reduce treatment cost. NF process was tested in this investigation to determine whether the NF process can replace the RO process used in many water-treatment plants without scarifying the quality of the treated water.

The effectiveness of NF largely depends on the characteristics of the filtration membrane used, such as molecular weight cut off value (related to pore size), electric charge, degree of hydrophobicity and surface roughness. Several studies have been conducted comparing the different characteristics of membranes. However, these studies compared generally only two membranes in removing inorganic salts (conductivity) [6,7], OMP [8,9] or DOC [10]. To our knowledge, only two studies compared the effectiveness of three membranes [5,11] and no study reported comparing higher number of membranes. To obtain a better understanding of the various properties influencing the rejection of these pollutants it is necessary to compare a larger number of membranes with different properties.

The objectives of this study were to: firstly, compare the effectiveness of five NF membranes with different contact angles and molecular weight cut-off (MWCO) values to remove inorganic salts (conductivity) and DOC from a wastewater-reclamation plant's micro-filtered water; and secondly, use the most effective membrane from the first part of the study to determine its effectiveness in removing 10 OMPs present in this water; and thirdly explain the mechanisms of their removals.

2 Materials and methods

2.1 Feed solution and NF membranes

Microfiltered (MF) water from a wastewater reclamation plant located in Sydney, Australia, was used as the feed water in this investigation. This water contained high concentrations of inorganics (conductivity 0.9-1.2 mS/cm) and organics (DOC 4.5-6.0 mg/L) and a wide concentration range of 10 MOPs (concentrations presented in the last table in this paper). The NF membranes were supplied by Sterlitech Corporation, WA, USA. The membranes' properties are presented in Table 1. The MWCO values of the membranes ranged from 90 to 400 Da. On the other hand, the zero point of charge (ZPC, the pH at which the net surface charge is zero) of the membranes was nearly the same and ranged between 3-4, indicating that the membranes are all negatively charged.

2.2 NF membrane water contact angle measurement

To assess the hydrophilicity/hydrophobicity of the membranes, water contact angle of the membranes was determined using a Sessile drop Theta Lite Tensiometer (Model TL100). Contact angle of $<90^0$ is generally considered to indicate that the membrane is hydrophilic, and $>90^0$ hydrophobic. Details of this method are given elsewhere [12].

2.3 NF measurement

MF water of 2, 2.5 or 3.5 L was used as the feed water for NF treatment. The NF treatment unit had a rectangular cross flow cell containing the membrane (area 68 cm^2). A schematic of the NF unit is shown in Fig. 1. The operation was conducted at a transmembrane pressure of 2-5.5 bar and at a temperature of 25 ± 1^0C. Details of the treatment unit and method of operation are given elsewhere [12]. Permeate was constantly collected and at the completion of the process it was analysed. The NF rejected solution was constantly fed back to the feed solution. At the completion of the process the feed solution which contained the reject solution was also analysed.

2.4. Chemical analyses

The initial and final feed solutions and permeates were analysed for pH, conductivity, DOC and MOPs. pH was measured using a portable pH meter. Conductivity was measured using a conductivity meter (HQ 40d, HACH USA). DOC concentration was determined by a liquid chromatography-organic carbon detection unit (LC-OCD) (DOC-Labor Dr. Huber, Germany) [13]. Concentrations of MOPs were measured by employing solid phase extraction (SPE) and analysing the extracts by high performance liquid chromatograph with tandem mass spectroscopy (HPLC-MSMS) using isotope dilution. Details of the procedure are given elsewhere [12].

Table 1. Characteristics of the NF membranes

Membrane	Manufacturer	Material	MWCO (Da)	ZPC-pH	Contact angle (degrees)
NF 90	Dow	Polyamide TFC	200[4], 90-180[5], 200[6]	~3.5[5]	79
NF 270	Dow	Polyamide TFC	200-400[1], 150-340[5], 300-400[4], 270[3]	~3.0[5]	29
NP 030	Microdyn Nadir	Polyether sulfone	400[1]	~3.7[2]	58
NF-TS 80	Trisep	Polyamide TFC	150[1], 100-200[3], 200[7]	~3.0[3]	15
NF-Duracid	GE Osmonics	Polyamide TFC	150-200[1]	-	23

[1]https://www.sterlitech.com › flat-sheet-membranes; [2] Rezzadori et al. [14]; [3] Mullett et al. [6]; [4] Simon et al. [8]; [5] Imbrogno et al. [15]; [6] Yangali-Quintanilla et al. [9]; [7] Peiris et al. [10].

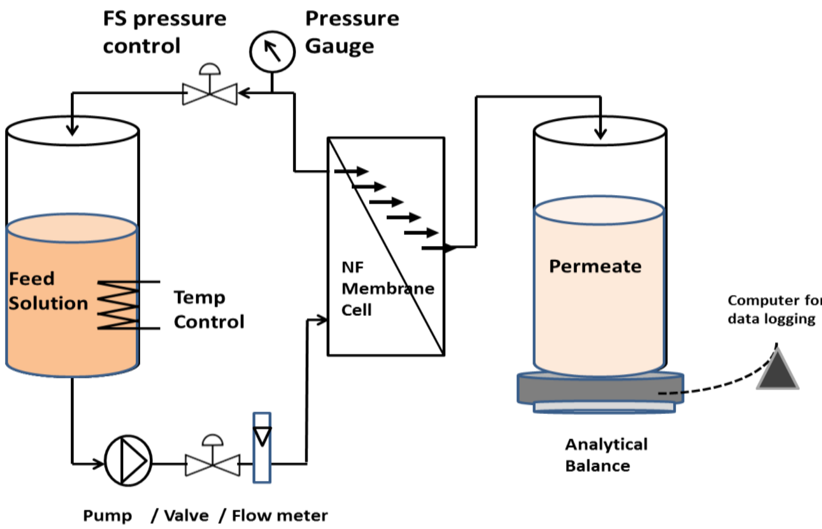

Fig. 1. Schematic of NF operation

3 Results and discussion

3.1 Membrane characteristics

The five membranes used in this study had widely different water contact angles (15-79^0) (Table 1). NF 90 with a contact angle of 79^0 is the least hydrophilic membrane, while others are highly hydrophilic. Others have also reported NF 90 with 63-65^0 contact angle as moderately hydrophobic (weakly hydrophilic) and NF 270 with contact angle of 30^0 as hydrophilic [8,11,16]. The membranes had different contact angles because their active layers had different polymer composition and morphology. NF 90 had higher contact angle than NF 270 because it has a rougher top layer whereas NF 270's top layer is smoother [17]. Increase in membrane roughness and hydrophobicity generally increases contact angle. Xu et al. [11] reported that NF 90 with the largest contact angle (63^0) out of the three NF membranes they tested was roughest (63 nm) as determined by atomic force microscopic measurement.

The MWCO value, which is directly related to the pore size of the membrane, is another property which controls solute rejection efficiency of membranes, based on size exclusion principle. However, sometimes, solutes of lower molecular weights than MWCO values are rejected more than expected, when processes other than size exclusion dominate, such as electrostatic repulsion and membrane/adsorption processes [18]. In this study, the MWCO values of NF 90, NF-TS80 and NF-Duracid were slightly lower than those of the other two membranes (Table 1). In contrast to the wide difference in contact angle and MWCO values, the ZPC values are nearly the same for all membranes (pH 3-4, Table 1). The very low ZPC indicates that all membranes are highly negatively charged at the pH 6.5-7.5 of MF water used for NF. An increase in pH would increase the membrane's negative charge density [19,20]. These ZPC values are consistent with those reported for these membranes by others [6,14,21].

3.2 Comparison of the membranes in removing inorganics and organics

Of the 5 membranes, NF90 which was least hydrophilic (highest contact angle, Table 1) removed the highest amounts of inorganics as measured by electrical conductivity (75% compared to 9-27% for others) (Table 2), and organics measured as measured by DOC in the permeate (88% compared to 37-84% for others) (Table 3). Inorganic cations in solution are hydrated with water molecules surrounding the ions and have high hydration energy, especially the higher valent ions, making it difficult to remove these water molecules [22]. These ions have less affinity towards negatively charged membranes with strong hydrophilicity for them to be removed by adsorption and, because the hydrophilic membranes have adsorbed water layers which weaken the binding efficiency of the hydrated cations [23]. NF 90, being the only weakly hydrophilic membrane, probably had very few water molecules attached to it, and this would have made the electrostatic attraction forces more dominant than the hydration force for cations to be adsorbed to this membrane leading to higher retention. Anions being negatively charged are electrostatically repelled by the negatively charged membrane and therefore rejected more than cations. However, some anions need to pass through the membrane to have electroneutrality on the permeate side and provide Donnan equilibrium throughout the NF operation [22].

Excessive salts in water (high conductivity) lead to physiological drought in plants affecting crop growth [7]. The MF water used for NF 90 membrane filtration had a conductivity value of 976 µS/cm (Table 2). This value is higher than the critical value of 650 µS/cm where crops very sensitive to salts suffer [4]. After the NF operation the permeate conductivity decreased to 240 µS/cm making the permeate water suitable for irrigating even for very sensitive crops. In comparison, the other membranes produced water that are not suitable for irrigating these crops because the permeate values (723-899 µS/cm) were higher than the critical value.

For the rejection of organic molecules, size exclusion through steric hinderance is the primary mechanism [24] in addition to charge exclusion (electrostatic repulsion) and membrane adsorption [8,11,20]. DOC rejection was generally higher than the inorganic ions rejection (conductivity) because the larger-sized organic molecules causing steric hinderance (Table 2, 3). NF 90 rejected the highest percentage of DOC (88% compared to 37-84% for others) (Table 3) because it has narrow pore sizes as indicated by its low MWCO value, and the membrane surface has high roughness (thicker active layer) [8,17]. Rough surface morphology was reported to have resulted in greater adsorption of organic molecules as a result of greater surface area, producing more chances for molecular interaction [19,25] and subjected to less hydraulic shear stress. Furthermore, this membrane being the least hydrophilic, would have had less water molecules attached to it and this might have helped some DOC molecules, especially the hydrophobic constituents, approach the membrane surface close enough for them to be adsorbed via hydrophobic interaction, π-π bonding and hydrogen bonding [20,23]. This resulted in rejection of the largest percentage of DOC. NF 90 was selected for the experiment on OMP removals because it was the most effective of the 5 membranes tested in rejecting both conductivity and DOC.

Table 2. Conductivity rejection by NF membranes at 2 bar applied pressure

	NF 90	NF 270	NP 030	NF TS80	Duracid NF
Initial/final feed solution (FS) conductivity, µS/cm	976/1590	1008/1062	793/878	1004/1330	1009/1044
Initial/final pH of FS	6.87/6.77	6.78/7.04	6.21/7.52	6.78/6.77	6.78/7.04
Final permeate conductivity, µS/cm	240	899	723	737	801
% Conductivity rejection[1]	75.4	10.9	8.9	26.6	20.6
FS/Permeate volume, mL	2000/883	3500/2935	2000/820	2500/1295	2000/73
NF operation duration, h	16.5	16.3	18.6	17.4	16.2
Feed volume factor (FVF)[2]	1.79	6.19	1.69	2.07	1.04

[1](1-permeate conductivity/initial feed conductivity) x 100
[2]FVF = Initial volume of FS/Final volume of FS

Table 3. DOC rejection by NF Membranes

	NF 90	NF 270	NF TS80	Duracid NF
FS, DOC, mg/L	5.09	5.09	5.09	5.09
Permeate DOC, mg/L	0.600	0.800	3.20	1.00
% DOC rejection	88.2	84.3	37.1	80.4
Treated feed solution, mg/L	11.43	19.65	7.4	6.68
Feed solution, mL	2500	2500	2500	2500
Permeate, mL	1620	2200	1400	1600
Applied Pressure, bar	2.5	1.5	2	5.5
NF operation duration, h	18.2	15.5	17.4	90
Feed volume factor (FVF)	2.84	8.33	2.50	2.78

3.3. Organic micropollutants rejection

NF 90 membrane rejected more than 90% of 7 out of the 10 OMPs identified in the MF water (Table 4). Diclofenac, gemfibrozil, ibuprofen, and naproxen, which have negative charges, were rejected by the negatively charged NF membrane via electrostatic repulsion, irrespective of their molecular weights. This mechanism of rejection was also reported by others [8]. Diclofenac with the largest molecular weight (296 g/mol, Table 4) among the MOPs tested might have been rejected by size exclusion mechanism. Triclosan and trimethoprim possessing neutral charge would have also been rejected >90% by size exclusion as their molecular weights were greater than the MWCO of the membrane (290 g/mol (Table 4) vs approximately 200 Da (Table 1)). Also, triclosan, being strongly hydrophobic (log Kow 4.76), would have adsorbed onto the moderately hydrophobic membrane contributing to the high rejection. Saccharin and benzotriazole also had neutral charge, but the rejection was not high (88% and 35% rejection, respectively). The reason for this is that they have the lowest molecular weights of 183 and 119 g/mol (Table 4), allowing them to pass through the membrane pores. The lower rejection rate of diuron (77%) is probably because it has a molecular weight (233 g/mol) value within the membrane's MWCO values range, which might have permited some of the diuron molecules to pass through the membrane's larger sized pores.

Table 4. Properties and removal of OMPs as a percentage (%) of their concentrations in feed solution

	Benzotriazole	Carbamazepine	Diclofenac	Diuron	Gemfibrozil	Ibuprofen	Naproxen	Saccharin	Triclosan	Trimethoprim
Molecular weight (g/mol)	119	236	296	233	250	206	230	183	290	290
Charge, pH 7.4	0[1]	0 [1,2]	- [1,2]	0[1]	- [1,2]	- [1,3]	- [2,3]	0[1]	0	0 [1,2,4]
LogKow, pH 7	1.44	2.45 [4,5]	4.5-4 [5,6]	3.49[1]	4.77[7]	3.5-4.5[2,5,6]	3.2 [6,8]	0.91	4.76	0.91 [5,9]
Feed concentration, ng/L	2020	191	54	70	76	38	188	131	48	136
[10]Removal, %	35	96	>93	77	>95	>90	>98	88	>92	>97

[1]Calculated with Advanced Chemistry Development (ACD/Labs) Software V9.04 for Solaris; [2]Shanmuganathan et al. [2]; [3]Hajibabania et al. [26]; [4]Ternes and Joss [27]; [5]Yang et al. [28]; [6]Serrano et al. [29]; [7]Westerhoff et al. [30]; [8]Yangali-Quintanilla et al. [9];
[9]U.S. National Library of Medicine (http://chem.sis.nlm.nih.gov/chemidplus/rn/52-53-9).
[10]Limit of quantification 4 ng/L for all OMPs except 10 ng/L for saccharin

3. **Conclusions**

Of the five negatively charged NF membranes tested with a MWCO range of 150-400 Da and water contact angles of 15-79^0, the NF membrane (NF 90) with the least hydrophilic characteristic (moderate hydrophobicity) (contact angle 79^0) and one of the three membranes having the lowest MWCO (90-200 Da) removed the largest amounts of salts (as measured by electrical conductivity) and DOC from the micro-filtered wastewater. DOC rejection was higher than the inorganic ions rejection (conductivity) because the larger organic molecules caused steric hinderance. The electrical conductivity of the MF water was very high making it unsuitable for irrigating crops that are very sensitive to salts. Only permeate water from the NF90 membrane was suitable for irrigating these crops. Permeate water from other membranes can produce adverse effects to these crops, if applied for irrigation. Of the 10 OMPs detected in the micro-filtered wastewater 7 were rejected >90% by the NF 90 membrane. The remaining three MOPs were poorly rejected because their molecular weights were equal or smaller than the MWCO value of the membrane.

Acknowledgements

We thank the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) (project number 4.1.10-14/15) for funding this research.

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