Chapter 1

Effects of High Concentrations of Organic and Inorganic Pollutants in Waste Water and Drinking Water on Nanofiltration Membrane Behavior

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Additional information is available at the end of the chapter

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Abstract

Removal possibility of high concentrations of organic and inorganic matter from aquatic solution using "Crossflow" spiral wound nanofiltration membranes was investigated on a self-made semi-industrial pilot plant, capacity 800 L/h. Natural organic matter, ammonia ions, and total arsenic removal were examined using concentrates—waste water obtained from industrial nanofiltration plant. Nanofiltration of waste water provided conclusions that arsenic was better removed in higher organic concentration environment rather than in lower. Also, membranes removed organic carbon with high efficiency and produced drinking water quality permeate. Removal of high concentrations of total iron, manganese, calcium, and magnesium was conducted using natural groundwater with and without the presence of complexing agent. Obtained results show that molecular weight cutoff, as well as quantity and type of complexing agent, had an influence on measured parameter removal. Also, electrostatic forces influenced separation of investigated ions.

Keywords: organic matter, arsenic, metal ions, complexing agent, asymmetric polyamide nanofiltration membranes

1. Introduction

Nanofiltration (NF) is a widely used type of membrane process in the world for undesirable constituents' removal from various types of water due to its characteristic pore size that is between ultrafiltration (UF) and reverse osmosis pore size. Besides, NF membranes operate with no phase change and typically have high rejections of multivalent inorganic salts and small organic molecules at modest applied pressures [1]. This chapter is dedicated to better understanding of nanofiltration membrane process in order to further resolve waste water treatment problems, especially waste water form nanofiltration plants. The aim of this investigation was to examine the behavior of nanofiltration membranes when exposed to high concentrations of natural organic matter (NOM) and arsenic originated from waste water. Additionally, nanofiltration process was monitored in the presence and absence of complexing agent in the environment of elevated iron, manganese, calcium, and magnesium ion concentrations originated from well water. The highlight of this work can be presented in the way that no model solution was used and that nanofiltration membranes were tested in situ allowing precise deduction and report of complex removal mechanisms that undergo in nanofiltration process. Natural drinking water resources are continuously reducing, and with regard to increasing demand for clean drinking water, it presents a great problem for the society. Large amounts of waste water are produced during drinking water production using membrane processes. The goal of waste concentrate treatment using membrane processes is firstly protection of natural drinking water resources. Nanofiltration concentrate discharge presents great problem in the means of quantity and quality. Even though NF membrane's characteristics such as materials, resistance, and efficiency are quickly improving [2–4], the question of NF concentrate discharge into the environment is still present. NOM and arsenic found in water present great problem all around the world. Elevated concentrations of NOM expressed as dissolved organic carbon (DOC) can be found in natural water in concentrations of 2.3 up to 11.90 mg DOC/L [5–9]. DOC-elevated content can also be found in waste water originated from technological processes for organic matter removal from aquatic influents [10] or in municipal waste water with up to 51 mg/L of total organic carbon (TOC) [11]. Arsenic is usually found in natural water in concentrations of 1–2 μg/L [12]; however, several countries such as Bangladesh [13, 14], China, the USA, and Taiwan [15] can be excluded from this statistics because arsenic content in these countries in great deal exceeds maximum tolerable value determined by the World Health Organization in drinking water of 10 μg/L where Argentina is the country with largest reported arsenic content in groundwater with up to 7550 μg/L [16]. Nanofiltration is especially suitable for arsenic and NOM removal from different types of natural water in the process of drinking water preparation [17, 18]. Survey of previous investigations has shown that nanofiltration [19, 20] can successfully be used for arsenic removal under normal or higher pressures [21]. Besides, addition of lime to nanofiltration of NF and reverse osmosis concentrates secured arsenic concentration of less than 10 μgAs/L in the permeate [22]. Also, it has been reported that arsenic removal efficiency is higher in the presence of humic acid [23]. Nanofiltration can be used for arsenite and arsenate removal with size exclusion [24] in molar mass range of 200–2000 Da. Electrically charged particles, especially anions, with the process of electrostatic repulsion is typical for NF membranes [25]. Pentavalent arsenic removal is significantly larger than As^{3+}, 95% and 20–50%, respectively [26, 27]. Arsenic in organic form can be removed from water with greater efficiency than nonorganic arsenic. It is found that arsenic in natural organic matter-rich environment has the ability to form complex chemical compounds with NOM anions as ligands [28]. Natural water NOM has significant influence on arsenic compound reduction and complexing [29]. Examinations of ionic force and NOM concentration influence on As(V) removal using four types of NF membranes under different transmembrane pressures (TMP) were conducted [30].

Results have shown that TMP, NOM, and several other ions' presence has an influence on arsenic removal efficiency. The degree of arsenic removal depends on organic matter concentration because the permeate flux is smaller when humic matter content is greater [30]. Secondary NF treatment of concentrate from nanofiltration plant for groundwater filtration from the city of Kikinda and Zrenjanin region has shown that large concentrations of NOM and arsenic can be removed with high efficiency [31]. It is reported in many studies that iron, manganese, calcium, and magnesium can be found in natural and waste water around the globe. Iron can be found in groundwater in concentrations smaller than 1 mg/L as well as >1 mg/L, and those are called "macro" concentrations [32]. Extremely high iron and manganese content found in the literature was in Vietnam (48 mg/L) [33] and in Cambodia (3.1 mg/L) [34], respectively. Water hardness may cause many problems in the means of calcium carbonate and magnesium hydroxide precipitation, especially in hot water systems [35–37]. Water hardness can be removed with traditional methods like ion exchange resins and lime softeners and membrane processes like electrically charged NF membranes [38, 39].

It is known that metal chelates can be successfully removed from aquatic medium using membrane processes. Membrane process technologies are proven suitable for metal separation from corresponding chelate ligands from waste water treatment-originated compounds [40]. In addition, gadolinium (III) and lanthanum (III) ethylenediaminetetraacetic acid (EDTA) complexes were successfully concentrated using nanofiltration [41].

Investigations of manganese and humic acid removal with nanofiltration have shown manganese retention from 45 to 96% with regard to pH value and HA removal efficiency of 80%. Manganese removal efficiency is the best in pH value range of 10–12. Complexation model has shown that when pH value is larger than 7, complexes of Mn and humic matter are created [42]. A group of authors has investigated combined UF-NF process for dissolved organic pollutant removal from River Huangpu in China. Turbidity, iron, manganese, and large molar mass NOM were removed using ultrafiltration, while NF process was used for smaller molar mass NOM and inorganic salt removal. Manganese and iron ion concentration in river water were up to 0.72 mg/L and up to 5.5 mg/L, respectively, while UF and NF effluents contained 0.01–0.1 mg Mn/L and 0.001–0.07 mg Mn/L, as well as 0.01–0.12 and 0.01–0.03 mg Fe/L, respectively [43]. Investigations have shown that spring water containing low iron (0.09–0.26 mg/L) and manganese (0.05–0.1 mg/L) content in the presence of NOM (2–34 mg TOC/L) can be successfully treated with nanofiltration [44]. Oxidation, coagulation, flocculation, and sedimentation can be used as UF and NF pretreatments for water that contains iron and manganese [45]. NF is also proven as a promising technique for removal of large manganese quantities from mine waste water. Dissolved manganese concentration of 115 mg/L in waste water was reduced in the permeate for 98% [46].

2. Materials and methods

Investigations of NF membrane behavior when exposed to large quantities of organic and inorganic pollutants from aqueous solution were conducted on a self-made semi-industrial pilot plant (PNF). NOM, arsenic, and ammonium ion originated from industrial NF plant waste water concentrate and removal possibilities of stated pollutants were examined in NFCP experiments. NFWP experimental series was conducted for membrane behavior investigations when exposed to high concentrations of calcium, magnesium, total iron (Fe_t), and manganese originated from natural groundwater. Main components of the PNF are presented in **Table 1**. All presented components of industrial pilot plant were identical for both experiments. Only difference was chemical dosing device (DP) installed for NFWP experimental series. Schematic of the PNF used in the experiment series NFCP and NFWP is given in **Figure 1A** and **B**, respectively.

2.1. NF membrane configuration

Nanofiltration membranes retain substances with molar masses higher than ~300 g/mol (300 Da) and multivalent ions [47]. Retention characteristics depend on the membrane type and the amount of free volume in the membranes that is most commonly influenced by flux. As the flux increases, retention of the membrane is decreased. Membrane surface can obtain surface charge via different mechanisms such as surface functioning group ionization, ion adsorption from the solution and polyelectrolyte, ion surface matters, and charged molecule adsorption [48]. Aromatic composite thin-film membranes that are used in this paper can contain carboxyl and amino functional groups [49]. Membrane surface can be positively charged in the low pH environment, as well as transformed to negatively charged with pH value rise [48].

Component	Characteristics	Manufacturer
Microfilter for inlet water pretreatment	Polypropylene filter cartridge of 5 μm with housing	“Atlas”
Booster pump	Centrifugal multistage pump CR1-23; $Q = 1.8\ m^3/h$; $H = 104\ m$	“Grundfos”
Nanofiltration modules	NF membranes $\Phi = 0.102\ m$; $L = 1.02\ m$	“Torey-Korea Inc”
Instantaneous inlet water, permeate and concentrate flow meter	Polysulfone rotameter F1 300–3.000 L/h F2 and F3 200–2.000 L/h F4 100–1.000 L/h	“IBG-Praher”
Water pressure meter	Pressure gauge 0–10 bar (M1, M2 and M5) 0–20 bar (M3 and M4)	“Wika”
Solenoid valve	EV220A NC; ¾”	“Danfoss”
Dosing pump for chemicals dosage	Dosing pump DDC 6-10	“Grundfos”
Electric control unit	Programmable logic controller (PLC)	“Omron”

Table 1. Main components of nanofiltration pilot plant.

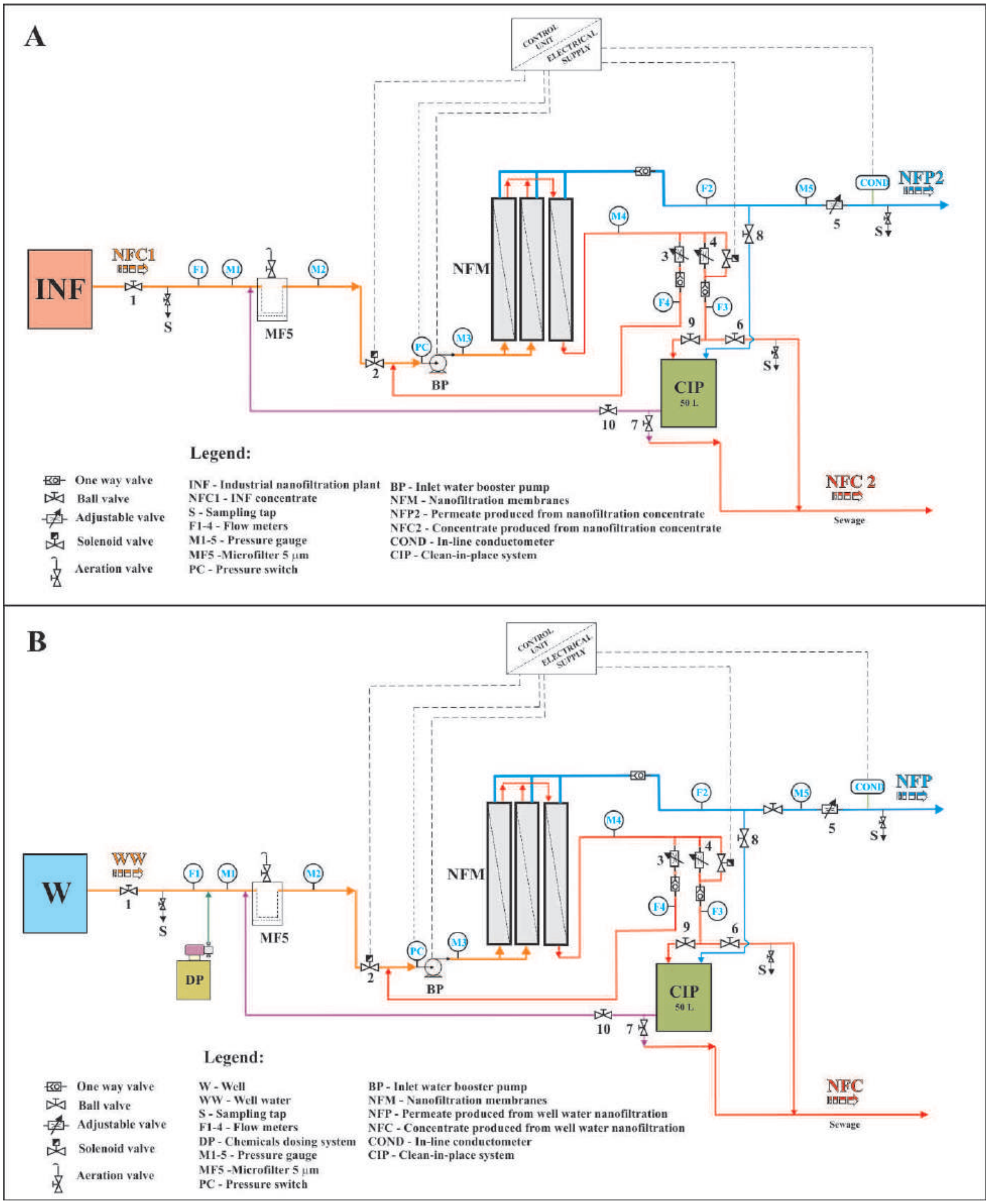

Figure 1. Pilot plant schematic diagram used in NFCP experiment series (A) and NFWP experimental series (B).

For the purpose of examination of membrane behavior, commercial spiral-wound membranes, manufacturer Toray Chemical Korea Inc., type CSM-NE 4040-70 (NE70), and CSM-NE 4040-90 (NE90) were chosen. Membrane type CSM-NE 4040-70 removes approximately 70%

and modules CSM-NE 4040-90 ~ 90% of all inorganic dissolved substances from water solution. Data obtained by the manufacturer show that membranes NE70 and NE90 possess different pore sizes and substance removal capabilities (molecular weight cutoff, MWCO). NE70 membrane type can remove substances with molar mass larger than 250 [50], i.e., 350 Da [47], while NE90 membranes remove molecules with molar mass larger than 200 Da [51]. Membrane MWCO represents molecular molar mass that can be removed using distinct type of membrane in the percentage of 90% [52]. MWCO concept is based on the constatation that molecule size grows with molar mass increase [53], and MWCO shows membrane retention characteristic prediction through separation mechanisms by size [54]. PNF was designed as two-stage membrane filtration, and different, theoretically possible, combinations of NE70 and NE90 membranes were used in the NFWP experiment (**Table 2**). MWCO value for the first membrane configuration was calculated from NE 4040-70 and NE 4040-90 membrane data sheets. Pilot plant contained three membranes, two in the first stage and one membrane in the second stage. Three NE90 membranes were used for NFCP concentrate filtration experiments.

2.2. NFCP experiment series

NFCP experiment series were conducted on two locations:

- Public pool complex, J.P. “Sportski objekti,” Zrenjanin (BZR)
- Public pool complex, S.R.C. “Jezero,” Kikinda (BKI)

An industrial nanofiltration plant type ET-NF-12000/A (INF1) is installed on BZR premises with permeate production capacity of 12,000 L/h, while industrial nanofiltration plant (INF2), type ET-NF-10000/A, that produces 10,000 L/h of permeate is functioning in BKI. Produced permeate is used as hygienically clean water for drinking, pool filling, and refilling on both locations. Waste water nanofiltration concentrates from both INF1 (NFC1-ZR) and INF2 (NFC2-KI) are discharged into local sewage systems. The goal of NFCP investigations was to explore nanofiltration removal efficiency when exposed to high organic and inorganic containing NF concentrates. Physicochemical composition of investigated NFC1-ZR and NFC1-KI concentrates is shown in **Table 3** with presentation of national maximum acceptable concentrations (MAC). INF1 and INF2 industrial plants have secured enough amount of concentrate for normal PNF operation. Both NFC1-ZR and NFC1-KI were transported

Experiment name	First stage	Second stage	MWCO (Da)
NF90-70-90	NE90 and NE70	NE90	~217
NF3-90	NE90 and NE90	NE90	200
NF3-70	NE70 and NE70	NE70	250

Table 2. Membrane configurations used in the NFWP experimental series.

Parameter	Unit	MAC	NFC1-ZR	NFC1-KI
pH	/	6.8–8.5	8.42	8.64
Electrical conductivity (EC)	μS/cm	1,000	3.380	4.650
Permanganate consumption (COD)	mg/L	8	224.40	43.10
Total organic carbon (TOC)	mg/L	/	60.98	19.50
Ammonium ion, NH_4^+-N	mg/L	0.1	1.54	2.70
Arsenic—total	μg/L	10	451.26	45
Sodium, Na^+	mg/L	150	652.94	387.80
Bicarbonates, HCO_3^-	mg/L	/	3621.14	1,171.57

Table 3. Selected physicochemical parameters of nanofiltration concentrates.

to PNF's buster pump (BP) under the pressure they obtained on INF1 and INF2 and then to NF membrane pilot plant. Part of newly produced concentrate from INF2-NFC2-KI was recirculated to PNF inlet in order to increase recovery and to reduce the amount of waste water. Flow of the recirculated concentrate was kept constant during the experiments. Newly produced concentrate from INF1, NFC2-ZR, in the BZR experiment series, was not recirculated due to the enormous pressure increase.

Investigations were conducted in a way that concentrate flow rates were changed which had an effect on permeate flow rate and consequently permeate flux, thus providing experimental points. Obtained results present average value of three experimental cycle repetitions for every measuring point.

2.3. NFWP experimental series

NFWP experimental series were conducted on the "Envirotech" d.o.o. company premises, located in the city of Kikinda, province Vojvodina, Serbia. This location is equipped with groundwater well "Sterija" drilled in the second aquifer layer on the depth of 52 m. Physicochemical composition of investigated groundwater is presented in **Table 4**.

Well water was distributed to BP under the submersible well pump pressure and subsequently to the NF pilot plant. At the place where well water is inserted into microfilter MF5, a dosing system DP was used for chemical dosage (**Figure 1B**). This was done with the purpose of calcium, magnesium, iron, and manganese ion complexation. Experimental procedure regarding recirculation flow, permeate flux, and pressures was identical to one described in Section 2.2 of this paper for NFCP experiment series.

Citric acid (CA) and Na4EDTA solutions, both added with dosing speed of 240, 480, and 720 mL/h, were introduced to the inlet well water during the NFWP investigations, and initial CA and Na4EDTA concentrations, determined on the basis of self-made preliminary experimental data, were 0.4164 mol/L (80 g/L) and 25 mg/L, respectively. Grundfos DDC 6–10 dosing pump was used for precise dosage regulation and adjustment of solution quantity with accuracy of 1% where desired solution concentration could be monitored via dosing pump LCD display. NFWP experiments were repeated three times for every membrane configuration (**Table 2**) and every concentration of both complexing chemicals. Obtained results present average value of three experimental cycle repetitions for every measuring point. Names of the experiments in the NFWP series with regard to membrane configurations and CA and Na4EDTA dosage quantity are presented in **Table 5**.

2.4. Analytical methods used for selected physicochemical parameter determination

Preliminary physicochemical analysis of groundwater that presented inlet to PNF, as well as permeates and concentrates produced during NFCP and NFWP experiments, was conducted in “Envirotech” laboratory. Selected parameters were determined with the use of standard methods as follows: pH (pH-meter Hanna Instruments HI 98,150), electrical conductivity (conductometer Hanna Instruments HI 9811-5), and ammonium ion and total dissolved iron and manganese (spectrophotometer Hanna C200). Obtained results were used for instantaneous nanofiltration process monitoring.

Selected parameters of inlet water, permeates, and concentrates produced during the experiments were analyzed by accredited body “Institute for work safety,” Novi Sad. Samples were tested for following parameters: pH (WTW InoLab, Germany); electrical conductivity (Crison Instruments Basic 30 conductometer); total arsenic, iron, and manganese (atomic absorption spectrophotometry Shimadzu Japan, type AA-7000 with GFA); TOC (Analytik Jena/Multi N/C 2100 Instrument); ammonia, sodium, calcium, and magnesium (Ion chromatograph, DIONEX, USA, type IC/ICS 3000); and COD and HCO_3^- using standard analytical methods [55].

Parameter	**Unit**	**MAC**	**Well water**
pH	/	6.8–8.5	7.39
Electrical conductivity	μS/cm	1,000	780
TOC	mg/L	/	7.22
Ammonium ion, NH_4^+-N	mg/L	0.1	3.24
Sodium, Na^+	mg/L	150	80.67
Iron, total	mg/L	0.3	1.79
Manganese, Mn^{2+}	μg/L	50	332
Total hardness	°dH	/	19.77
Calcium, Ca^{2+}	mg/L	200	80.08
Magnesium, Mg^{2+}	mg/L	50	37.11

Table 4. Selected physicochemical parameters of groundwater from “Sterija” well in the city of Kikinda.

Experiment name	Membrane configuration	Dosage quantity (moL/h)	Substance
EX3-1	NF90-70-90	/	/
EX3-2	NF90-70-90	0.1	CA
EX3-3	NF90-70-90	0.2	CA
EX3-4	NF90-70-90	0.3	CA
EX3-5	NF90-70-90	0.016	Na4EDTA
EX3-6	NF90-70-90	0.032	Na4EDTA
EX3-7	NF90-70-90	0.047	Na4EDTA
EX3-8	NF3-90	/	/
EX3-9	NF3-90	0.1	CA
EX3-10	NF3-90	0.2	CA
EX3-11	NF3-90	0.3	CA
EX3-12	NF3-90	0.016	Na4EDTA
EX3-13	NF3-90	0.032	Na4EDTA
EX3-14	NF3-90	0.047	Na4EDTA
EX3-15	NF3-70	/	/
EX3-16	NF3-70	0.1	CA
EX3-17	NF3-70	0.2	CA
EX3-18	NF3-70	0.3	CA
EX3-19	NF3-70	0.016	Na4EDTA
EX3-20	NF3-70	0.032	Na4EDTA
EX3-21	NF3-70	0.047	Na4EDTA

Table 5. NFWP experiments with regard to membrane configurations and CA and Na4EDTA dosage quantity.

3. Results and discussion

Hydraulic parameters such as permeate flux and pressures were monitored during the experiments that lead to transmembrane pressure [56] and membrane efficiency [57] calculation.

3.1. NFCP series experimental results

Transmembrane pressure influence on COD, TOC, arsenic, bicarbonate, ammonia, and sodium removal efficiency is presented in **Figure 2**. Removal of easily oxidizable matter expressed via COD was more efficient during EX1 (**Figure 2A**), while total dissolved organic matter showed better removal rate in EX2 experiment. COD and TOC values decreased in average 190 and 57 times, respectively, with regard to inlet water concentration in EX1, and

37 and 18 times, respectively, in EX2. Dissolved organic matter concentration in all the experiments was below MAC [58]. Total organic carbon separation was very efficient in both EX1 and EX2 from 96.74 to 99.10% and 97.88 to 99.70%, respectively. Removal of organic matter expressed via COD was very efficient as well with ξ values of 99.33 to 99.60% in EX1 and 96.49–99.00% in EX2 (**Figure 2A**). The largest portion (> 98%) of dissolved organic matter has MWCO larger than 200 Da, and this is the reason for NOM excellent separation on NF membranes (**Figure 2A**). NOM is removed by NF membranes on two principles, size exclusion and electrostatic repulsion, considering the fact that membranes are in most cases negatively charged [59]. During EX1 investigations arsenic was removed with 98.86–99.38% efficiency, while in EX2 this number was a little lower and valued 94.63–98.75% (**Figure 2A**) where arsenic concentration decreased in average ~115 and ~17 times with regard to inlet concentrations. Obtained total arsenic values were below MAC in all produced permeates [58]. Significantly higher and better arsenic ion retention, with regard to permeate flux, was observed in organic matter-rich environment (EX1). Due to the high organic content, arsenic ions were probably bonded with NOM functional group complex compounds, which could be referred as organoarsenic compounds. These findings of extremely good organoarsenic removal in organic-rich environment confirm previous results [60, 61]. Sodium ion retention was reported with lower efficiency than organic matter and total arsenic in both experiments (**Figure 2B**), with ξ values of 92.25–93.93% in EX1 and 90.44 to 94.51% in EX2. Investigated NF membranes were surrounded with influent that contained dissolved salts where dynamic equilibrium occurred. Concentration of positively charged sodium ions as opposed to negatively charged membrane was greater as long as the concentration of ions of the same charge, like membranes, was less in membrane phase than on the membrane surface. Created Donnan potential prevents equally charged ion diffusion from membrane phase to membrane surface as well as diffusion of oppositely charged ions from membrane surface to membrane phase [62]. Experimentally obtained data for sodium ion rejections can lead to the conclusion that ions were probably rejected from the filtration membrane layer by Donnan effect.

Bicarbonate ions are separated to the concentrate steam with great percentage, in average ~96% in EX1 and ~97% in EX2. Separation of bicarbonate ions on membranes is followed by their decomposition to CO_2 and water via carbonic acid as intermediate compound. Bicarbonate decomposition is generated by electrostatic phenomenon and steric effects under elevated pressure in membrane pores. Complete bicarbonate buffer system is present in NF system. Reaction equilibrium is preferentially shifted to the right side in concentrate phase, where bicarbonate and hydronium ions dominate, while opposite occurs in permeate phase where reaction equilibrium is shifted left where weak carbonic acid and carbon (IV)-oxide and water are present. Ammonium ion separation from water solution was the least efficient of all observed parameters (**Figure 2B**). Ammonium ion was most successfully removed in EX1 with average permeate value of 0.2 mg/L, where this value presents reduction of inlet concentration ~9 times. TMP increase had positive effect on ammonium ion removal with significant increase in removal efficiency. Low ammonium ion removal rate is typical for nanofiltration membranes due to the ammonium MWCO of ~18 Da that is value similar to one that water molecule possesses. At the influent pH > 8.40, most of NOM carboxyl groups are deprotonated, while amino groups, i.e., ammonium ions, are protonated [63]. This phenomenon has an effect on weak electrostatic attraction occurrence and ammonium ions binding on carboxyl groups which, as a constitutive part of heterogenic humic and fulvic acid solution, are rejected to the concentrate. In this way, small ammonia ions are assimilated into NOM macromolecules with average MWCO values of 500–1500 Da [64], which are building elements of supramolecular structures. Detected ammonium ion concentration in both experiments was above MAC [58], with exception in EX1 where these concentrations were in accordance with EU recommendations for quality of water intended for human consumption [65].

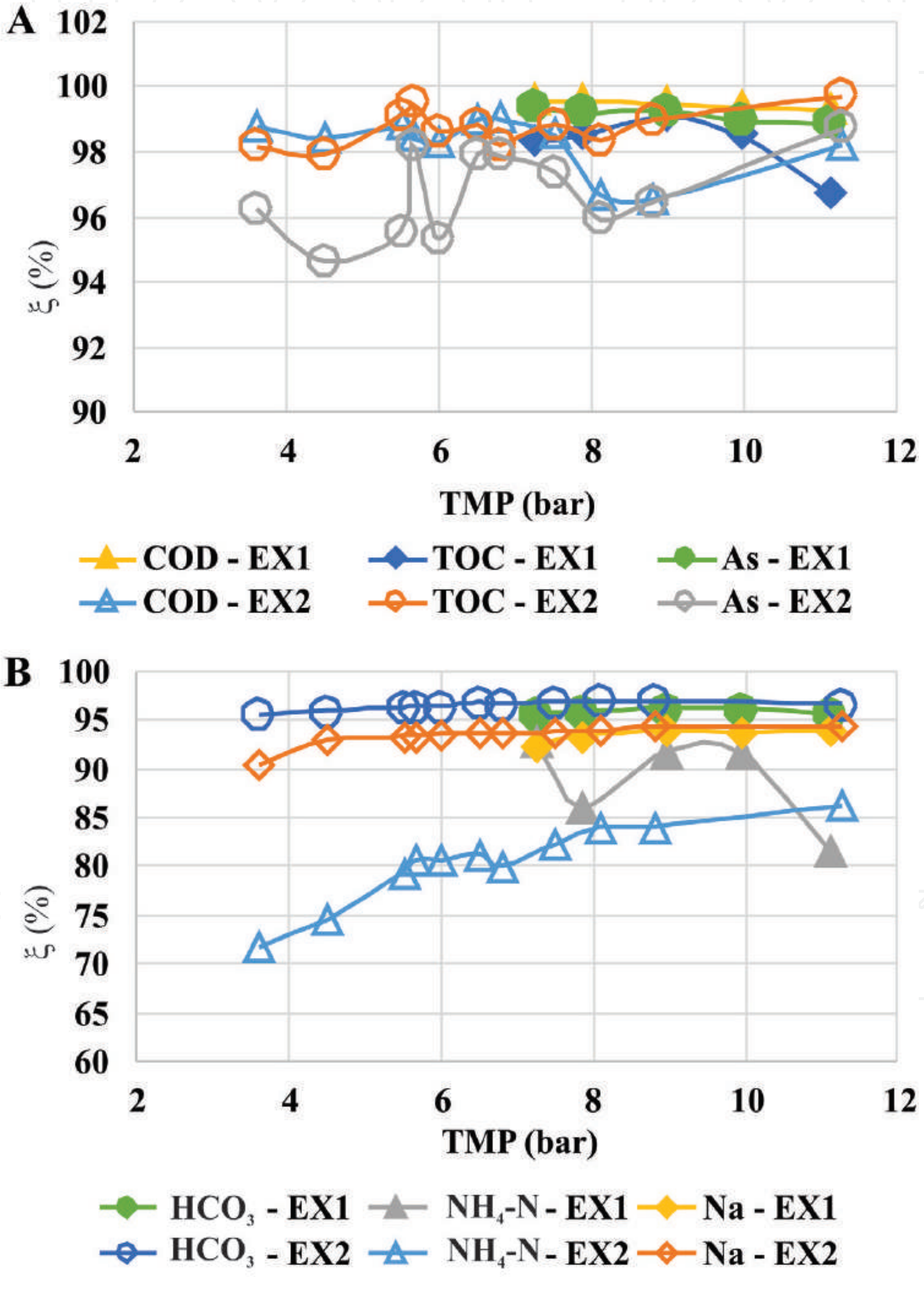

Figure 2. Transmembrane pressure influence on (A) COD, TOC, and total As and (B) bicarbonate ion, ammonium ion, and sodium ion removal efficiency.

3.2. NFWP experimental series results

NFWP experimental series included simultaneous comparison of observed metal ion separation efficiency with regard to applied NF membrane configuration and complexing chemical compound dosing concentrations. Fe_t ion, Mn(II), Ca(II), and Mg(II) removal efficiency was calculated and presented in **Figures 3–6** in the dependence of transmembrane pressure. Observed permeability changes of different membranes and their different position arrangement in the system were especially discussed with regard to atomic radius dimension (AR), presented in Å, of investigated metal ion hydrates [66], molecular topological polar surface area (TPSA) in $Å^2$ [67], their complexes with CA and Na4EDTA and maximal projection area (MPA) in $Å^2$, of metal ions. Metal ions in aquatic solution are through ion-dipole bonds of mainly electrostatic character bound with water molecules [68]. Certain ion hydration process depends on electrostatic attraction of water molecule and that ion. Considering that attraction of water molecules in the ion environment depends on ion charge density, smaller ions, i.e., ions with larger ionic potential, attract bigger number of water molecules [69]. Radii of hydrated iron, manganese, calcium, and magnesium ions equal 6, 6, 6, and 8 Å, respectively, and MPA of the same ions equals 12.57, 12.57, 15.74, and 15.74 $Å^2$, respectively. If organic substances like citric acid or EDTA are added to aquatic solution, substitution of one or more water molecules from hydrated metal ion environment with chelate groups occurs, thus producing coordinative compounds, i.e., complex ions.

Total iron ions are removed with excellent efficiency with 99.77% regardless of applied pressure (**Figure 3A**) in EX-8 experiment without dosage and in EX3-9 to EX3-11 with the dosage of CA solution. NF90-70-90 membrane configuration in EX3-1 and EX3-2 reduces Fe_t concentration from ~85 to ~93%. Addition of larger amounts of CA influences the increase of ξ in EX3-3 and EX3-4 to ~97%. ξ_{Fet} exhibits decrease with TMP increase only in EX3-15 and EX3-18, while simultaneously in EX3-16 and EX3-17 increases to ~5 bar and then decreases again. The lowest removal rate is observed in experiments with NF3-70 membrane configuration. The size of probably created iron and citrate complexes, such as iron (III) citrate (M_i = 244.94 g/mol, TPSA = 141 $Å^2$) and iron(II) citrate (M_i = 245.95 g/mol, TPSA = 138 $Å^2$), suggests the possibility of steric and electrostatic competitions in molecule transport through the limited space of curvaceous channels in membrane material. This is especially pronounced in NF3-70 configuration in **Figure 3A** where the largest difference in coordinative iron and citrate compound retention was observed. Iron ions are removed with great efficiency (**Figure 3B**), while this percentage is significantly lower in investigations with three NF 4040-70 membranes. Removal efficiency is decreasing with TMP increase in Na4EDTA dosage experiments where NF3-90 configuration was used. Increase in Na4EDTA dosage concentration in EX3-5 to EX3-7 influences increase in iron removal efficiency by ~10% in regard to EX3-1. Competition during retention on membranes is also observable, especially in NF3-70 in complexes iron(III)-EDTA (M_i = 366.98 g/mol, TPSA = 167 $Å^2$) and iron(II)-EDTA (M_i = 346.0 g/mol, TPSA = 167 $Å^2$). The highest Mn(II) removal of average 97.36%, regardless of CA dosage, was done by membranes with MWCO of 200 Da (**Figure 4A**). Manganese ion separation process in other two series is more efficient with the addition of CA complexing agent. Manganese removal efficiency was increased for ~15% with membrane configuration NF90-70-90 with the addition of CA. The lowest Mn^{2+} removal rate of ~70% was observed

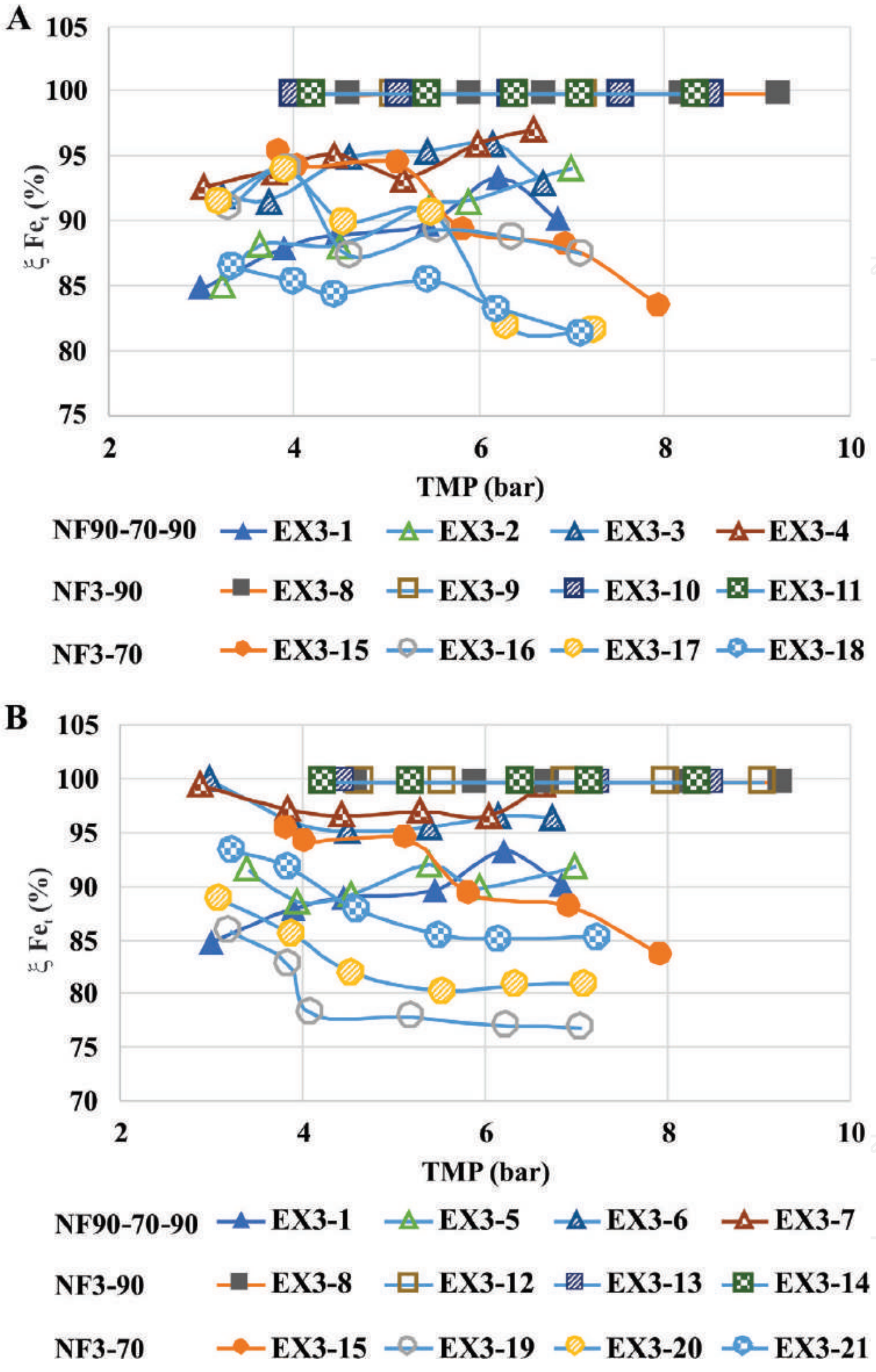

Figure 3. Influence of transmembrane pressure on iron removal from groundwater water (EX3-1, EX3-8, and EX3-15) and from groundwater with addition of CA solution (A) and Na4EDTA (B) with regard to NF membrane configuration.

in experiments EX-16 to EX3-18. Manganese(II) citrate molar mass (M_i = 244.94 g/mol) and TPSA of 138 Å^2 follow, to a high degree, separation by size with regard to MWCO of investigated membranes (**Figure 4A**).

The best manganese removal with the addition of Na4EDTA solution was reported in experiments with NF3-90 membrane configuration with average efficiency of 97.36% (**Figure 4B**). Other two membrane configurations showed excellent ability for $\xi_{Mn(II)}$ increase proportional

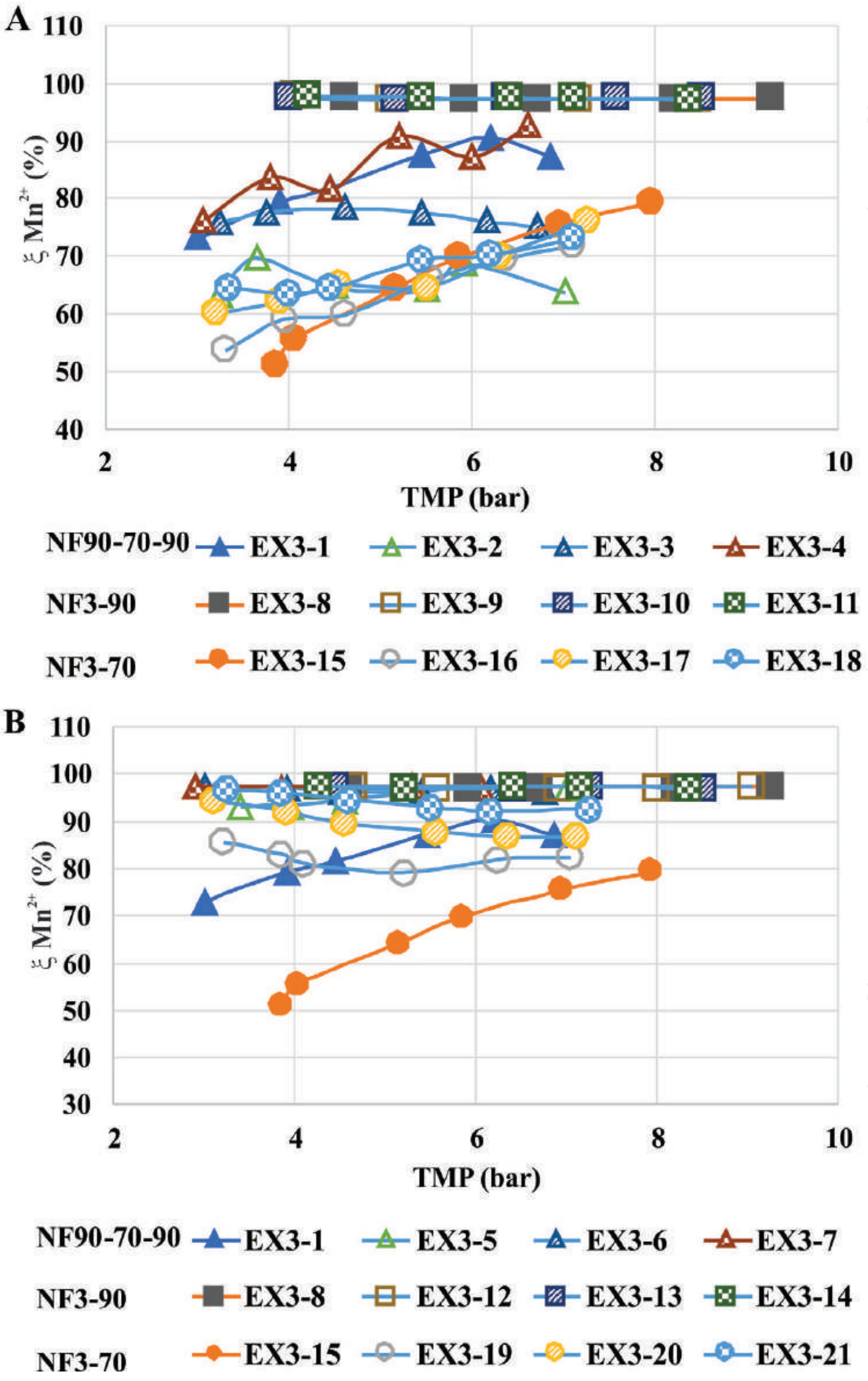

Figure 4. TMP influence on manganese removal from well water (EX3-1, EX3-8, and EX3-15) and well water with addition of CA solution (A) and Na4EDTA solution (B) in all experimental membrane configurations.

to Na4EDTA dosage concentration. Average increase in removal efficiency to 85.34% was observed in membrane system with 217 Da MWCO with the highest concentration of chelate agent, while MWCO of 250 Da membrane configuration has, proportionally to Na4EDTA concentration increase, enabled $\xi_{Mn(II)}$ increase from 66 to 96.65%. In EDTA, manganese(II) complex (M_i = 345.01 g/mol, TPSA = 167 Å^2) retention on the membranes was significantly increased with regard to citrate manganese complexes, even in the membrane configuration with the highest MWCO. This can be contributed to electrostatic forces and Donnan potential difference that obviously were preferential over separation by size.

Fe_t and Mn(II) ions' AR and MPA values are identical, but retention of these ions is significantly altered with addition of complexing ligands into the influent, except in 200 Da MWCO membrane configuration. Increase in TMP values has affected the most $\xi_{Ca(II)}$ increase in NF3-70 membrane configuration (**Figure 5A**) where this value was increased from ~40 to ~70% in the range of investigated pressures. It is evident that increase in CA dosage influenced removal efficiency value rise to TMP of ~5 bar. Obtained values for removal efficiency were in the range of ~75 to ~90%, where better values were obtained with CA dosage in membrane configuration with MWCO of 217 Da. NF3-90 membranes have removed Ca(II) ions with the highest removal efficiency, regardless of TMP values and CA dosage concentration. Average $\xi_{Ca(II)}$ for membranes with MWCO of 200 Da equaled 97.26% (**Figure 5A**). Ca(II) ion rejection was 40 to 50% more pronounced than the results observed in previous investigations [70] in experiments with NF90-70-90 and NF3-90 membrane configurations. Dimensions of probably formed tricalcium dicitrate of M_i = 467.89 g/mol and TPSA = 281 Å^2 were convenient for separation by size for all three MWCO dimensions. Lower $\xi_{Ca(II)}$ is evident from EX3-19 to EX3-21 investigations comparing to Ca(II) removal efficiency from well water (**Figure 5B**), while Na4EDTA dosage did not have any effect on calcium ion retention with NF90-70-90 membrane configuration. Average removal efficiency calculated in NF3-90 experiments with addition of Na4EDTA was 97.54%. The greatest $\xi_{Ca(II)}$ value increase with TMP rise was recorded in the NF3-90 investigations and the least in NF3-70 experiments. Even though Ca(II)-EDTA complex is smaller (M_i = 330.04 g/mol, TPSA = 161 Å^2) than citrate calcium ion complex, their retention on the membranes is reduced probably due to the electrostatic repulsion, especially in NF3-70 experiments with regard to EX3-15. AR and MPA values for calcium ions are identical to corresponding values for Fe_t and Mn(II) ions. Calcium ion retention is, however, quite different from iron and manganese removal efficiency changes.

CA dosage did not have any significant effect on removal of magnesium ions with regard to removal efficiency with no dosage (experiments EX3-15 to EX3-18). Observed oscillations in ξ values with TMP changes are recorded in experiments with NF90-70-90, especially in EX3-2 where lower values of removal efficiency were calculated with regard to well water filtration with no complexing agent addition. The tightest NF membranes removed magnesium ions with approximately equal ξ, and TMP or CA had negligible effect on these values that were ~95%. Tangential filtration of complex trimagnesium dicitrate molecule (M_i = 449.96 g/mol, TPSA = 281 Å^2) with MWCO of 200 and 217 Da affected significant dispersion of retention experimental results in the dependence of CA dosage concentration. Influence of membrane charge and steric effects on the attraction of these complex molecules is evident.

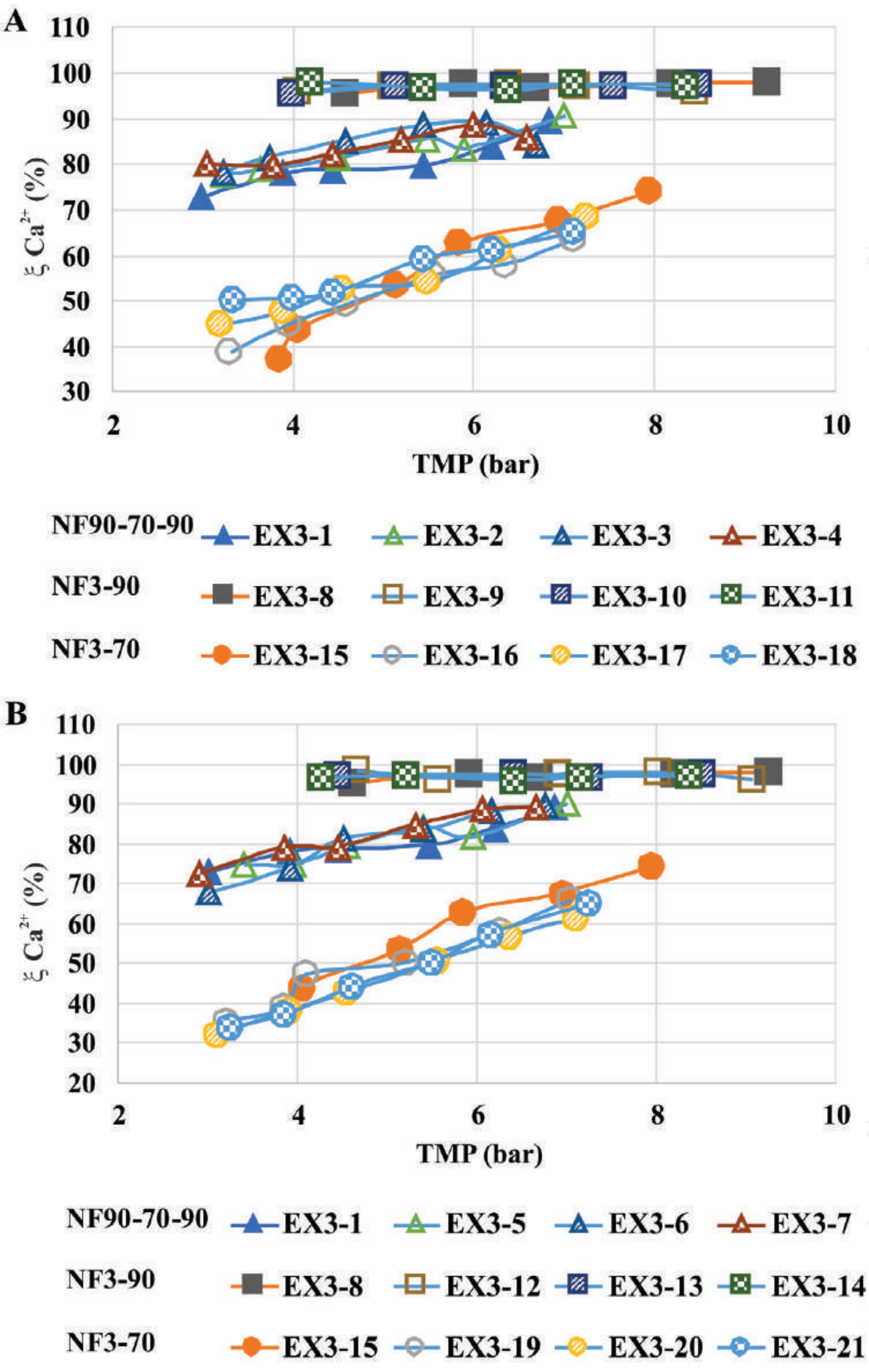

Figure 5. Influence of NF configuration on calcium ion removal efficiency from raw water (EX3-1, EX3-8, and EX3-15) and from raw water with addition of CA solution (A) and Na4EDTA (B) in the dependence of TMP.

Less values of Mg(II) ion removal efficiency were observed in experiments EX3-19 to EX3-21 with Na4EDTA addition with regard to EX3-15 with well water. Similar to results from **Figure 6A**, the highest $\xi_{Mg(II)}$ values were obtained in the experiments with NF3-90 configuration (**Figure 6B**). With the highest Na4EDTA concentration, magnesium ion removal was the lowest in EX3-7

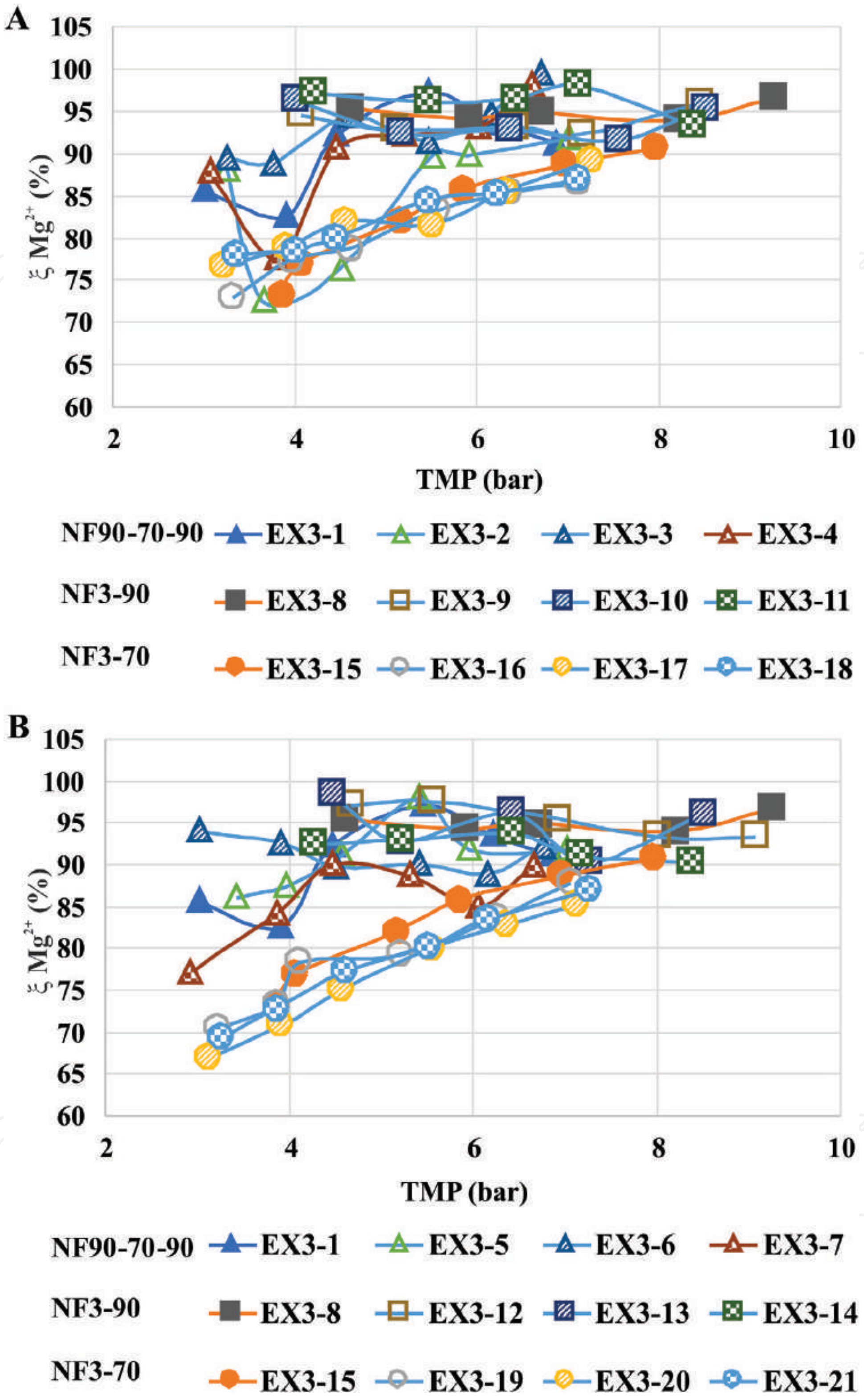

Figure 6. Transmembrane pressure influence on magnesium ξ changes with regard to NF membrane configuration. Experiment with well water: EX3-1, EX3-8, and EX3-15. Experiments with well water + CA solution (A). Experiments with well water + Na4EDTA (B).

experiments. Magnesium(II)-EDTA complex (M_i = 358.02 g/mol, TPSA = 167 $Å^2$) is significantly smaller than magnesium citrate complex ion. Retention results are coherent and almost identical to results obtained in membrane configurations with MWCO of 200 and 217 Da with regard to Mg(II) citrate complex, where Mg(II)-EDTA complexes are removed with lower efficiency with 250 Da MWCO membranes. Magnesium(II) ion's AR is larger and MPA is equal to one of Ca(II) ions. Mg(II) ion retention is characterized by significant dispersion of $\xi_{Mg(II)}$ values in the experiments with organic ligand dosage with regard to experiments with well water, except when MF3-70 configuration was used (**Figure 6**).

4. Conclusions

Semi-industrial investigations of high concentration of dissolved organic matter, total arsenic ions, ammonium ions, $Na^+_{(aq)}$, and bicarbonate separation presented in NFCP experiment series showed nanofiltration ability for good removal efficiency of stated parameters from waste water. Arsenic ions were chemically bonded with NOM anions into organoarsenic complexes. Applied membranes with 200 Da MWCO removed with greater efficiency higher NOM and total arsenic ion concentrations providing permeates that contained arsenic and NOM in concentrations below maximum tolerable concentrations. It was found that organic matter concentration can be of essence when designing arsenic removal drinking water and waste water plant.

Metal ion separation by different types of nanofiltration membranes and their different configurations with and without addition of citric acid and Na4EDTA as complexing agent provided several conclusions on membrane behavior. NF3-90 membrane configuration has proved extremely suitable for iron and manganese ion separation regardless of CA and Na4EDTA solution dosage. Removal of Fe using membrane configuration with higher MWCO (NF90-70-90) showed more intensive separation in addition of complexing agents, while using NF3-70 membrane combination, total iron ion retention was very poor. Probably, coordinative iron and manganese compound separation mechanism to concentrate is a complex one and is not based entirely on size exclusion, but electrostatic forces play a significant role too.

Calcium(II) separation, both with and without organic compound dosage, was very efficient at MWCO of 200 Da and exclusively depends of particle sizes. Retention of magnesium(II) ions shows particle size separation only at MWCO of 250 Da. Significant effect of CA dosage was not recorded, but addition of Na4EDTA had negative influence on Mg(II) ion separation. Electrostatic effects are dominant in membrane separation of Mg(II) at MWCO of 217 Da.

Obtained results in semi-industrial scale are practically applicable on the large-scale plants for drinking water preparation from deep wells, as well as from shallow aquifers.

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Chapter 2

Nanofiltration for the Treatment of Oil Sands-Produced Water

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Additional information is available at the end of the chapter

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Abstract

This chapter summarizes nanofiltration (NF) studies focused on the treatment of thermal in-situ steam-assisted gravity drainage (SAGD)-produced water streams in the Alberta, Canada, oil sands industry. SAGD processes use recycled produced water to generate steam, which is injected into oil-bearing formations to enhance oil recovery. NF has potential applications in the produced water recycling treatment process for water softening, dissolved organic matter removal, and partial desalination, to improve recycle rates, reduce make-up water consumption, and provide an alternative to desalination technologies (thermal evaporation and reverse osmosis). The aim of this study was to provide proof-of-concept for NF treatment of the following produced water streams in the SAGD operation: warm lime softener (WLS) inlet water, boiler feed water (BFW), and boiler blowdown (BBD) water. Commercial NF membranes enabled removal of up to 98% of the total dissolved solids (TDS), total organic carbon (TOC), and dissolved silica, which is significant compared to the removal achieved using conventional SAGD-produced water treatment processes. More than 99% removal of divalent ions was achieved using tight NF membranes, highlighting the potential of NF softening for oil sands-produced water streams. The NF process configurations studied provide feasible process arrangements suitable for integration into existing and future oil sands and other produced water treatment schemes.

Keywords: nanofiltration, produced water treatment, oil sands, SAGD, membrane processes

1. Introduction

A significant amount of research and development is currently underway to improve oil sands water treatment processes to allow for higher levels of water recycle and to reduce the energy associated with water treatment and steam generation. Part of this water use reduction effort is focused on water consumption in the steam-assisted gravity drainage (SAGD) process. SAGD is a thermally enhanced heavy oil recovery method, which is widely practiced for bitumen extraction from oil sands in Alberta, Canada. In this process, steam is injected through a horizontal well into the bitumen-containing formation to decrease the viscosity of the bitumen and allow its extraction. An emulsion of steam condensate and heated bitumen flows down the periphery of the steam chamber to the production well, which is located below the injection well. This emulsion is pumped to the surface where the bitumen and water are separated, and the water subsequently treated for reuse as boiler feed water for steam generation.

In a typical SAGD plant (**Figure 1**), the produced emulsion is first sent through a series of gravity separation vessels to remove gases and separate the bitumen and water. The de-oiled produced water is mixed with make-up water (fresh and/or brackish) and recycled boiler blow-down (BBD) prior to treatment in a warm lime softener (WLS) to remove silica. Treated fluids from the WLS are further processed through ion exchangers (IX) to remove Ca^{2+} and Mg^{2+} to generate boiler feed water (BFW) suitable for steam generation. Unlike power generation and utility steam drum boilers, SAGD plants use robust, oilfield-style once-through steam generators (OTSG’s), which can tolerate high amounts of TDS (8000–12,000 mg/L) and TOC (300–1000 mg/L). Only hardness and silica removal are necessary for OTSGs, not desalination. To compensate for the relatively low-quality feedwater, OTSG’s typically produce a low-quality steam (75–80% steam), resulting in a large volumetric rate of boiler blowdown (BBD). A portion of the BBD is recycled back to the WLS, while the balance is sent to deep disposal wells, third-party waste disposal operators, or processing in zero liquid discharge (ZLD) facilities.

The conventional WLS-IX water treatment configuration does not reduce the amount of dissolved organic matter (DOM) or total dissolved solids (TDS) in the boiler feed water, and only partially removes silica. In spite of the robust nature of SAGD OTSGs, high levels of DOM and TDS in OTSG feed water can cause operational and maintenance problems due to fouling and scaling of steam generators and disposal wells [1–3]. Boiler feed water from WLS-IX processes requires blowdown rate management to mitigate scale formation; this causes a higher recycle of low-quality BBD water back to the process [3]. To reduce the volume of disposal water, evaporators are sometimes used as a downstream BBD water recovery process [4]. Evaporators are also used in SAGD to directly desalinate produced water for higher-quality BFW, allowing the use of more efficient, smaller oilfield drum or hybrid boilers. However, evaporation results in high operational costs (chemical cleaning and electrical energy). In light of the above, industry is pursuing replacement of the WLS-IX and produced water evaporator schemes with emerging membrane-based processes, which can separate almost all silica and divalent ions, and reject more than 90% of DOM and TDS in a single step, while consuming less energy than if desalination evaporators were used.

Membrane separation processes are an emerging technology for oil sands-produced water treatment due to their distinct advantages over traditional processes, primarily lower operating

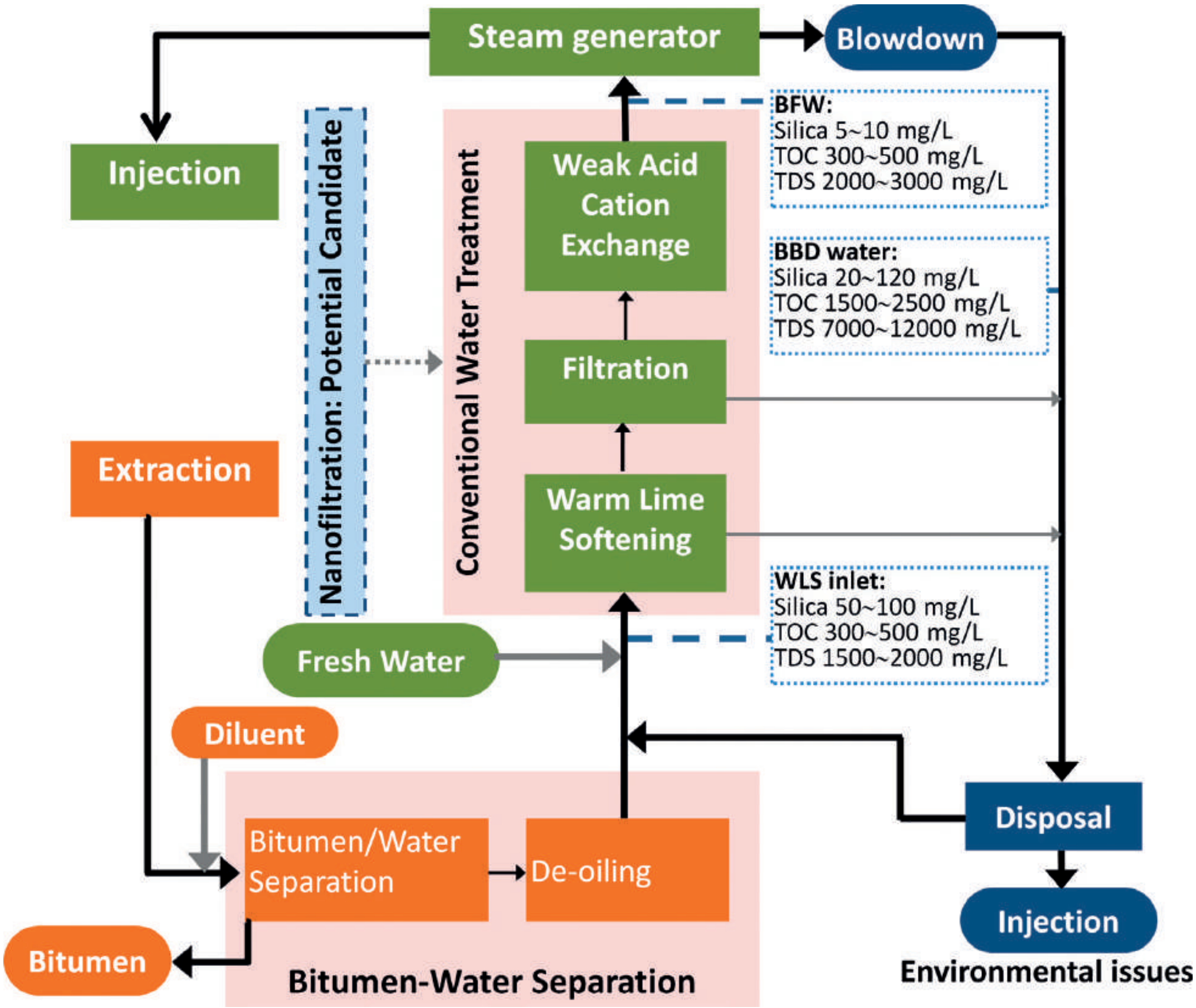

Figure 1. Main steps in SAGD-produced water treatment operations.

costs, compact design, and high filtrate quality [5]. Among membrane processes, nanofiltration (NF) is increasingly deployed for the removal of solutes ranging from colloidal particles and organic molecules to salts in a single unit operation. NF membranes provide a higher water flux and lower rejection of monovalent ions (<90%) as compared to reverse osmosis (RO) membranes. Tight NF membranes are similar to RO membranes, while loose ones can be categorized as ultrafiltration (UF) membranes [6]. NF membranes are the best candidates for water softening as they provide a high rejection of divalent ions (>99%). For SAGD-produced water or blowdown treatment, removal of scale-forming divalent ions such as hardness and silica is more important than NaCl removal when OTSG's are used. Treatment with NF membranes may reduce operational costs of operating OTSG's and WLS-IX processes, and also enable direct blowdown reuse as BFW instead of requiring disposal. Further treatment to drum boiler quality requires further research, but will likely require RO treatment to reach required TDS levels like those achievable by evaporators.

In this chapter, we aim at evaluating the performance of NF processes for the treatment of SAGD-produced water and blowdown streams. First, all emerging technologies that can be applied for the treatment of oilfield-produced water are presented. Then, a critical literature review on the application of NF for the treatment of oil sands-produced water is provided. After that, the methodology for a typical NF experiment and analysis of results are described. Finally, membrane permeation results are discussed on the basis of membrane characteristics including hydrophilicity, zeta potential, and roughness.

2. Emerging technologies for the treatment of oilfield-produced water: overview and perspective

The potential technologies for oilfield-produced water treatment can be classified into five main groups [7–9]:

i. *Physical treatment* such as adsorption, media filtration (anthracite, sand, walnut shell), evaporation, distillation, gas floatation, and hydrocyclones

ii. *Chemical treatment* such as precipitation (WLS), chemical oxidation (by chlorine, hydrogen peroxide, ozone, and permanganate), and electrochemical processes (electrocoagulation)

iii. *Biological treatment* such as activated sludge, anaerobic reactors, aerated lagoons, and wetlands

iv. *Membrane filtration* such as microfiltration (MF), ultrafiltration (UF), NF, RO, and electrodialysis (ED)

v. *Hybrid processes* such as membrane bioreactor (MBR), micellar-enhanced UF (MEUF), coagulation/MF, and oxidation/flocculation/membranes

Among these processes, adsorption (by activated carbon, zeolites, clays, resins, and synthetic polymers) [10–12], oxidation (chemical, photocatalytic, and sonochemical) [12–14], biological treatment [15–17], and membrane processes [18–20] represent emerging technologies in Canada’s oil sands industry. Adsorption processes are used for the removal of a broad range of compounds in oilfield-produced water, including DOM, oil, and heavy metals [21]. The principal shortcomings noted for adsorption processes are low adsorption capacity and the high costs for disposal, cleaning, and regeneration of spent media [7, 21]. In oxidation process, pollutants are degraded through a series of direct oxidation and radical reactions. Radicals are produced by using chemicals like ozone (ozonation), hydrogen peroxide (Fenton), chlorine, and permanganate. The formation can be intensified by UV light (photocatalytic oxidation) and ultrasound (sonochemical oxidation). The application of oxidation in oilfield water treatment is limited by inefficient radical generation, poor reaction kinetics, and interference from background TOC concentrations and high concentrations of salt and radical scavengers (chloride and bicarbonate) in oilfield-produced water. Incomplete pollutant removal and high energy costs limit the application of oxidative treatment [7, 21]. Biological treatment, primarily activated sludge, is widely used in the treatment of municipal and refinery wastewaters, but its application is limited for the treatment of more complex industrial effluents, especially those with high salinity high temperatures, and the presence of inhibitory organics [21]. Membrane processes have been broadly applied in industrial and municipal wastewater treatment. Numerous previous studies have mainly considered the use of looser MF and UF membranes for oily produced water treatment [22–24]. For the separation of DOM, salt, and silica from oil sands-produced water, it is essential to use tighter NF and RO membranes [25].

3. Oil sands-produced water treatment by nanofiltration

An overview of published studies on oil sands-produced water treatment using NF membranes is presented in **Table 1**. Although NF membranes are widely applied in water softening, there are few records in the literature for their application in oil sands-produced water treatment. This is mainly due to the high susceptibility of these membranes to fouling by the high TDS and TOC of oilfield-produced water. Meanwhile, these waters are mostly at high temperature and pH, which can affect the membrane integrity of current commercial membranes. In some applications, these streams must be cooled or pH tuned solely to accommodate a membrane separation process, after which the processed fluid will be readjusted back to an initial condition (e.g., pH) to optimize steam production reliability [26–28]. This temperature and pH adjustment requires a significant amount of energy and chemicals. Applying hydrophilic membranes with antifouling properties as well as thermal and chemical resilience (up to 70°C and pH 2–11), for example, sulfonated polyethersulfone (PES) developed by hydranautics, will facilitate the practice of NF in the oil sands-produced water treatment.

From the data presented in **Table 1**, it can be seen that NF was studied for the treatment of produced water generated from two main oil sands operations, namely open-pit mining and SAGD [5, 25, 29–31]. Sadrzadeh et al. [5] and Hayatbakhsh et al. [25] treated SAGD WLS

Ref	**Produced water**	**Feed characteristics**				**Contaminant removal**
		pH	**TDS (mg/L)**	**TOC (mg/L)**	**Ca/Mg (mg/L)**	
[5]	SAGD BFW	9.8–10.5	1800	500	0.84	Up to 98% TOC, TDS, and silica rejection
[25]	SAGD WLS inlet	9.0	1200	420	2.5	>86% rejection of the salt, silica, and DOM
[29]	SAGD BBD	11.6–12.2	14,900–36,200	2480–5060	Up to 700	Up to 80% DOC and 45% TDS removal
[30]	Mining OSPW	7.3–8.5	1549–4920 μS/cm	46–85	30–80	>95% rejection of TOC and divalent ions.
[31]	Mining OSPW	8.0–9.0	2477	48.3	73	~69% and 82% NaCl removal w/ and w/o pretreatment

Table 1. Overview of earlier studies on oilfield-produced water using NF membranes.

inlet and BFW using various types of NF membranes. TOC, TDS, and silica rejection of up to 98% and divalent cation removal greater than 99% was obtained at different pH values from pH 7.0 to pH 10.5. Pulsation of pH was proposed as an effective technique for mitigation of membrane fouling and water flux recovery. Hurwitz et al. [29] investigated NF processes with and without upstream coagulation and pH adjustment for the treatment of SAGD BBD water. Dissolved organic carbon (DOC) and TDS removal as high as 80 and 45%, respectively, were obtained. It was also found that neither coagulation nor acidification as pre-treatment processes improved the separation performance of the NF process. Peng et al. [30] and Kim et al. [31] worked on oil sands process-affected water (OSPW) associated with surface mining extraction of bitumen. OSPW is the water contained in tailings ponds in oil sands mining operations. Significant reductions in permeate hardness, TOC (>95%), and NaCl (up to 82%) was reported. In contrast to the Hurwitz et al. [29] study, Kim et al. [31] demonstrated that applying pre-treatment methods, for example, coagulation, resulted in improved desalination performance. As will be discussed further in subsequent sections of this chapter, the high native pH of the BBD stream (>11) compared to the lower pH of the OSPW streams (<9) was likely the main reason for the differences in the effectiveness of pretreatment. However, differences in the nature of the DOM may also have been important. Earlier studies revealed that the DOM in mining OSPW consists primarily of naphthenic acid-like compounds [32–34]. The type of DOM present is different for in situ processes compared to mining OSPW, likely due to the different water temperatures and pressures, as well as solvents used (diluent versus naphtha or paraffins). It was shown that the DOM in SAGD-produced water are more representative of humic acids than naphthenic acids [3, 35]. Each organic matter fraction has specific physicochemical properties, for example, charge and molecular conformation, which governs the fouling rate and thus the performance of membrane processes [36]. Hence, membrane fouling propensity changes vastly from mining to SAGD water treatment as the type and concentration of organic matter and produced water chemistry are significantly different.

Here we present the materials and methodologies (sections 4), as well as, experimental results (section 5) related to the treatment of SAGD produced water which have been already published in peer-reviewed journals [5, 25, 29].

4. Summary of NF experiments on SAGD water treatment

4.1. Produced water

SAGD-produced water was obtained from different SAGD water treatment plants located in the Athabasca oil sands region of Alberta, Canada. Concentrations of salt, organic matter, silica, and other inorganic ions were measured in the samples. **Table 2** presents the properties of BFW, WLS inlet, and BBD as the main process-affected streams in a SAGD water treatment plant (**Figure 1**).

4.2. Nanofiltration membranes

Commercial NF membranes are mostly thin film composite (TFC) membranes consisting of three layers: a thin polyamide (PA) or sulfonated polyethersulfone (PES) active layer (100–300 nm), an intermediate microporous layer (~40 μm), and a mesoporous polyester fabric

Elements	Units	WLS Inlet	BFW[ξ]	BBD[ς]
pH	—	9	10.5	11.9
Conductivity	mS/cm	1.68	3.50	15.4
TDS	mg/L	1200	1800	14,900
TOC	mg/L	420	500	2890
Dissolved Silica (Si)	mg/L	89	21	331
Sodium (Na^+)	mg/L	350	880	2980
Calcium (Ca^{2+})	mg/L	1.9	3.30	490
Magnesium (Mg^{2+})	mg/L	0.59	0.37	212
Iron (total Fe)	mg/L	0.39	2.12	11.4

[ξ] Model BFW is prepared by the dilution of BBD.

[ς] Plant 1 in Hurwitz et al. study [29], Silica in this study is total silica.

Table 2. Properties of WLS inlet water, BFW, and BBD water [5, 25, 29].

support (~100 μm) [37]. The active layer of TFC membranes governs the membrane separation performance and fouling behavior. The top active layer is typically synthesized by an interfacial polymerization reaction between two monomers (e.g., m-phenylenediamine and trimesoyl chloride for the synthesis of polyamide), which are dissolved in two immiscible solvents [38, 39].

Membrane properties	NF270 (Filmtec) [25]	NF90 (Filmtec) [25]	ESNA (Hydranautics) [25]	HYDRACoRe[ξ] (Hydranautics) [40]
Membrane type	TFC-PA	TFC-PA	TFC-PA	TFC-Sulfonated PES
Maximum operation pressure (kPa)	4136	4136	4136	4136
Maximum operation temperature (°C)	45	45	45	70
pH range	2.0–11.0	2.0–11.0	2.0–10.0	1.0–13.5
Salt rejection (%)	40–60	85–95	75–92	10–70
MWCO (Da)	330 ± 48	201 ± 25	223 ± 37	720–3000 [29]
Contact angle (θ°)	34 ± 5.5	62 ± 6.7	60 ± 6.2	62 ± 3.0 [41]
Zeta potential (mV)	−12.1 at pH 4, −21.6 at pH 7, −24.0 at pH 9	5.1 at pH 4.5, −24.9 at pH 7, −27.3 at pH 9	0 at pH 4.5, −11.5 at pH 7, −11.0 at pH 9	−85 mV over a pH range of 3–11 −36.8 at pH 7 [41]
Isoelectric point (IEP, KCl 10^{-3} M)	3.0 ± 0.2	4.0	4.9 ± 0.1	N/A
Mean roughness (nm)	5 ± 0.25	65 ± 2.2	50 ± 3.5	9.8 [41]

[ξ] The properties of this membrane are obtained from the membrane manufacturer's published literature [40] unless otherwise stated.

Table 3. Properties of NF membranes tested for SAGD-produced water treatment.

The main characteristics of NF membranes, which have been used for SAGD-produced water treatment are summarized in **Table 3**.

The fouling propensity of a membrane primarily depends on its surface charge, roughness, hydrophilicity. The hydrophilicity and surface charge of membranes are obtained by measuring their zeta potential and contact angle. In general, more hydrophilic and more negatively charged membranes are less susceptible to fouling by more hydrophobic DOM and negatively charged organic and inorganic dissolved materials present in water. The surface roughness of a membrane also plays a significant role in fouling. Rougher surfaces cause the entrapment of more foulants in the eddy zones created behind the peaks. The blockage of valleys on the surface of NF membranes results in a substantial loss of water flux [25].

4.3. Nanofiltration test apparatus

The NF experiments were conducted using bench scale cross-flow filtration systems (**Figure 2**). A typical system consisted of a feed tank, a membrane cell, a pump, a temperature controller to keep the feed temperature at a specific value, a back pressure regulator, and a bypass valve to adjust the applied pressure and cross-flow velocity. A weighing balance or a digital flowmeter were utilized to measure the permeate flow rate. Permeate and retentate are recycled to the feed tank to maintain a constant feed concentration over time.

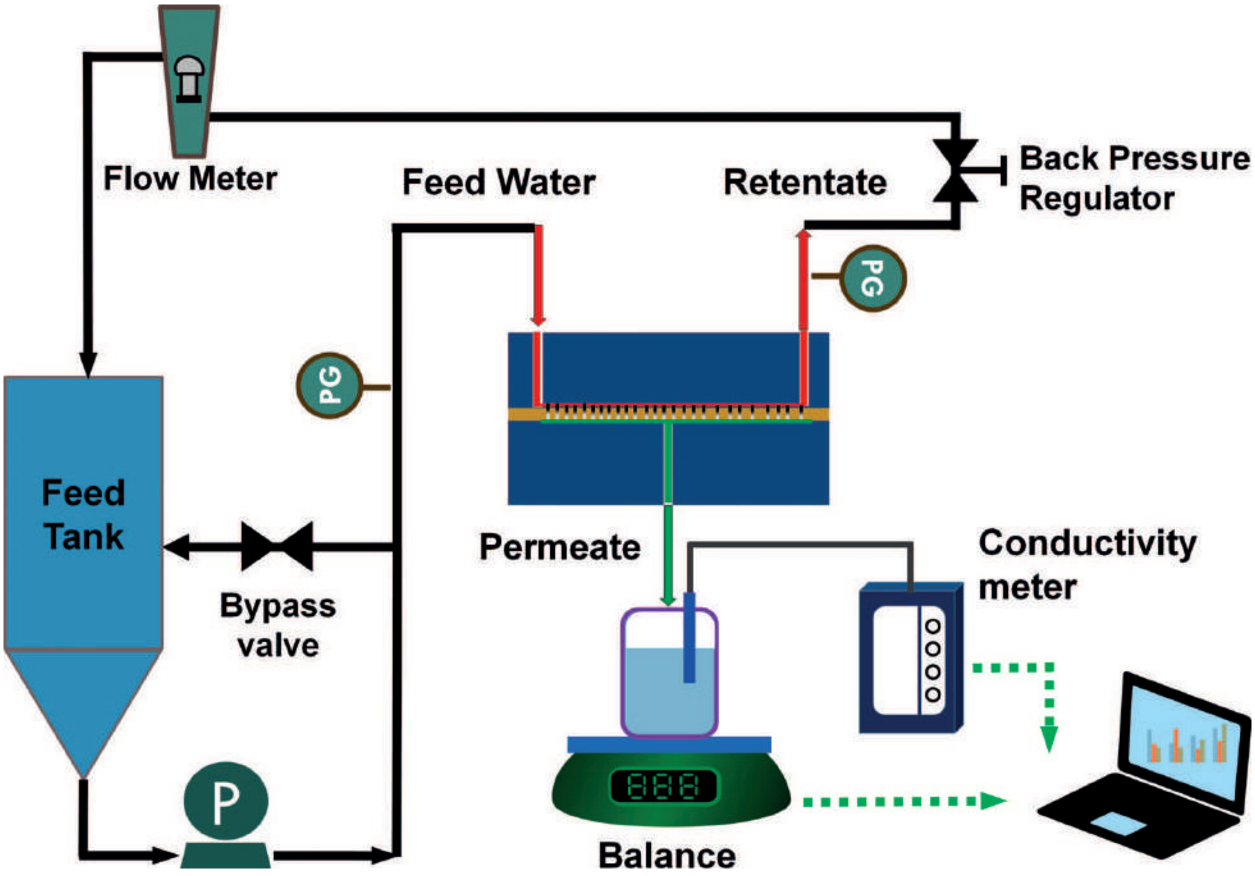

Figure 2. Schematic of a bench scale cross-flow NF setup.

Water flux (J_W) at steady state is obtained by measuring the mass or volume of water (ΔV) passed through the membrane with active surface area A during a certain period Δt:

$$J_W = \frac{\Delta V}{A\,\Delta t} \tag{1}$$

The rejection of contaminants (TDS, TOC, silica, and divalent ions) is calculated by measuring their concentration in the permeate solution as follows:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p and C_f are the constituent concentration in the permeate and feed solutions, respectively.

5. Results and discussion

Membrane performance was evaluated based on permeation flux and removal of the target constituents. The fouling propensity of a membrane is typically evaluated by measuring the rate of flux decline over time. Fouling decreases the performance of a membrane by reducing the water permeation flux and ultimately shortening membrane life (complete replacement or increased cleaning interval) [36]. Therefore, fouling mitigation is a major challenge for sustainable application of membrane processes. A facile method to mitigate fouling during filtration is an abrupt change of operating conditions such as solution pH, temperature, and ionic strength [42]. The impact of changing pH on water flux and rejection of contaminants during SAGD water treatment has, therefore, been investigated [5, 25, 29].

5.1. Treatment of WLS inlet water by various NF membranes

Water flux through NF270, ESNA, and NF90 membranes and TDS/TOC rejection over 360 min at 50°C and pH of 9.0 are shown in **Figure 3(a)**. The initial water flux of 35 LMH was adjusted for all membranes at transmembrane pressures of 276, 552, and 552 kPa for NF270, ESNA, and NF90, respectively. Water flux was found to decline gradually due to combined silica/organic matter/divalent ion fouling. Based on the data presented in **Table 2**, the concentration of divalent ions in the WLS inlet water is negligible compared to the total concentration of silica and organic matter (~500 mg/L). Hence, combined colloidal and organic fouling was the principal fouling mechanism in this study. The adsorption of silica and DOM onto the membrane surface reduced the permeate flux due to pore blocking, formation of silica/DOM gel, and induced hydrophobic properties [25].

The bar chart in **Figure 3(a)** shows that the initial flux decline for the NF270 membrane was lower than the other NF membranes. Fouling is mainly affected by the feed properties (e.g., pH, ionic strength, and concentration) [43], operating conditions (e.g., pressure and cross-flow velocity) [44], and the physicochemical properties of the membrane (e.g., hydrophilicity and charge) [25].

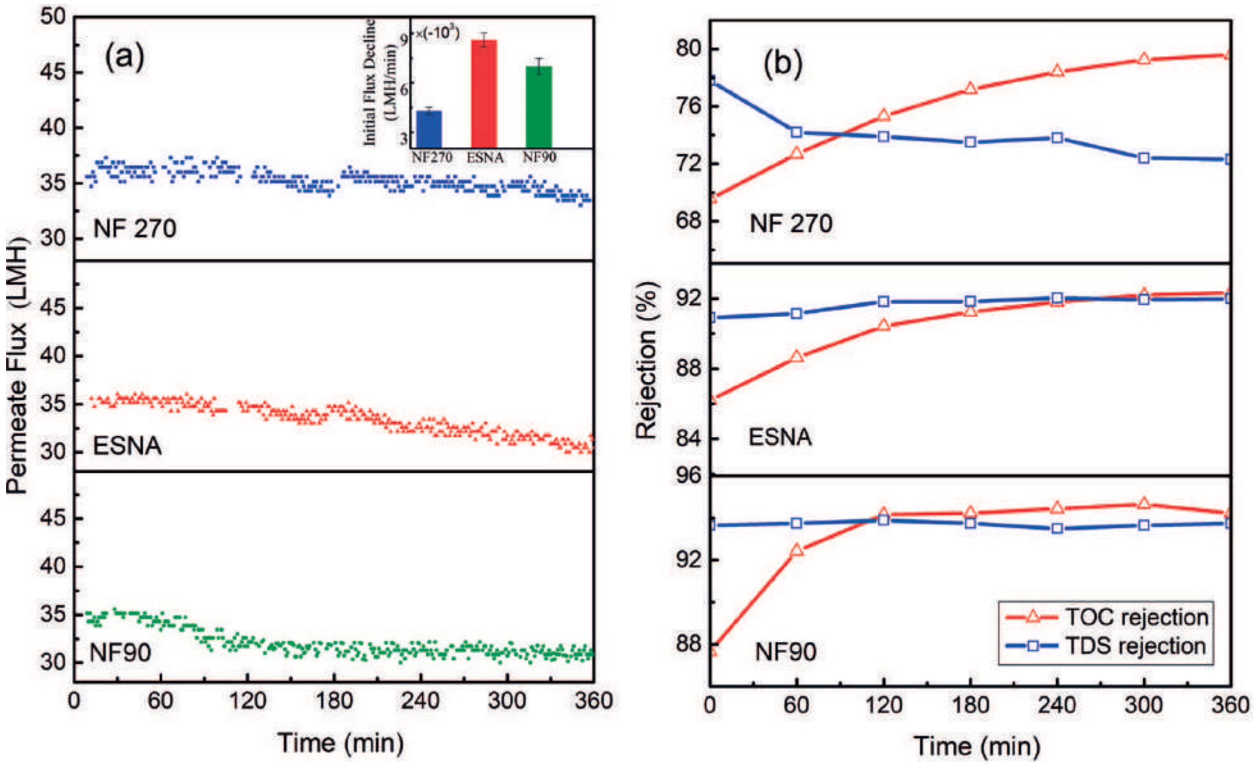

Figure 3. (a) Water flux over time and (b) TOC/TDS rejection for WLS inlet water filtration using NF270, ESNA, and NF90 membranes at pH 9.0 and 50°C [25]. Copyright 2016, Reproduced with permission from Balaban Desalination Publications, Rome, Italy.

Hence, at a constant initial permeate flux, feed flow rate, and feed solution chemistry, the rate of flux decline strongly relates to the surface properties of the membrane. The surface roughness and contact angle data in **Table 3** shows that NF270 is smoother and more hydrophilic than ESNA and NF90. The zeta potential of NF270 is similar to NF90 and is more negative than that of ESNA [25]. It is widely accepted that membranes with higher hydrophilicity and more negatively charged surfaces are less prone to fouling by DOM and silica due to the lower hydrophobic interaction and higher electrostatic repulsion between the foulants and the membrane surface [45].

Figure 3(b) displays the variation of TOC/TDS rejection with time. For all NF membranes tested, TOC rejection increased over time. Earlier studies revealed that the adsorption of DOM on the membrane surface increases its hydrophobicity [45, 46]. This phenomenon enhances the layering attachment of DOM on previously deposited organic matter through hydrophobic interactions that subsequently increase TOC rejection. Rejection of TDS, however, remained constant for the tighter NF90 and ESNA membranes, and decreased for the looser NF270 membrane. Based on the cake-enhanced concentration polarization (CECP) mechanism, both flux and salt rejection should decrease as fouling progresses [47]. Deposited foulants on the membrane surface prevent back diffusion of salt from the surface to the bulk solution and thus increases the salt concentration at the membrane surface significantly. The enhanced concentration-gradient across the membrane increases the passage of salt ions toward the permeate side. In this study, however, TDS rejection remained constant for the denser NF membranes [25]. A possible explanation is that there was clogging of membrane hot spots (the valleys on the surface of membranes with the lowest thickness and the highest local water flux) by the DOM, which restricted the transport of salt [48, 49].

The effect of pH on the performance of the NF90 membrane was studied. The pH of WLS inlet water was progressively decreased from 9 to 7 after 120 min, then increased to 10 after 240 min. As can be seen in **Figure 4(a)**, by reducing the pH from 9 to 7 the water flux declined sharply, then recovered by increasing the pH from 7 to 10. The variation of flux with pH can be attributed to a change in the surface properties of the membrane and by changes to the solution chemistry [25]. At lower pH values, the protonation of the functional groups of DOM, as the major constituent in the WLS inlet water (**Table 2**), decreases the negative charge and ultimately reduces the electrostatic repulsion between DOM molecules [50–52]. Changing the pH also affects the DOM/membrane interaction. In general, the zeta potential of membranes becomes less negative as pH decreases. The foulant/foulant and foulant/membrane attraction causes more deposition of foulants, and increases the thickness of the cake layer. These phenomena can explain the lower permeation flux observed at lower pH values [53]. It was also reported that pH varies the macromolecular conformation of DOM so that a smaller structure forms at a lower pH [50]. This leads to the formation of a denser cake layer and decreases the water flux accordingly.

The effect of pH on TOC/TDS rejection is shown in **Figure 4(b)**. As can be seen, TDS rejection increased after the pH was decreased from 9 to 7. The precipitation of silica and DOM at lower pH values has led to the formation of a closely-packed fouling layer that improved the TDS rejection. The effect of pH on TOC rejection was, however, insignificant. At pH 9, TOC rejection enhanced over time due to the cake filtration, then decreased marginally as pH decreased to 7. This rather contradictory result of TOC and TDS rejection is still unknown and calls for further investigation.

To select an appropriate membrane for the treatment of SAGD WLS inlet water, the trade-off relation between energy consumption and permeate water quality should be considered. Energy consumption in pressure-driven membrane processes is directly linked to the applied pressure. Therefore, a loose NF270 membrane is likely to be less energy-intensive than a tight NF90 or ESNA membrane. In this study, employing all NF membranes adequate Ca/Mg/Si removal is achieved to replace the current water treatment scheme. In addition, the NF270

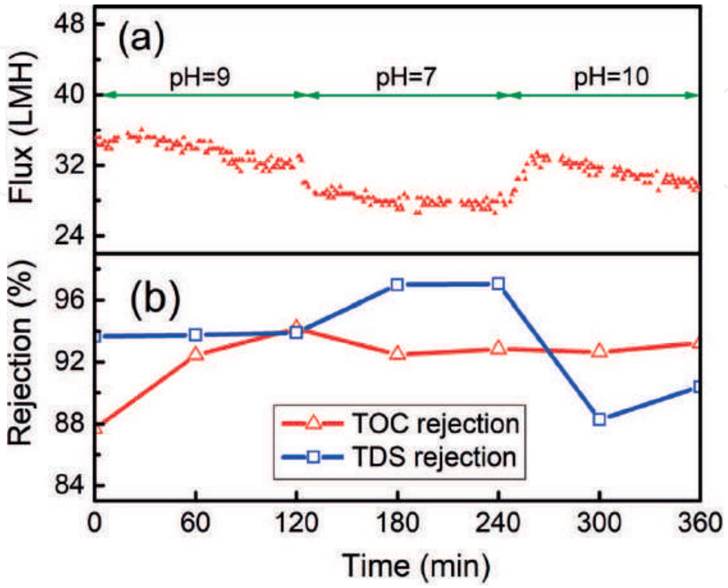

Figure 4. Effect of pH on performance of NF90 membrane for the filtration of WLS inlet water at 50°C [25]. Copyright 2016, Reproduced with permission from Balaban Desalination Publications, Rome, Italy.

membrane provided TOC/TDS rejection of more than 70% at pressures as low as 276 kPa. As a result, when highly purified water is not required, the NF270 membrane would be an excellent energy-efficient candidate. The ESNA and NF90 membranes provided 35 LMH water flux at the same transmembrane pressure of 552 kPa. The TOC/TDS rejection of the NF90, however, is slightly better than the ESNA (**Figure 3b**). Therefore, the NF90 membrane is proposed as the best candidate when a high water quality with reasonable energy efficiency is desired. In summary, replacing the current water treatment scheme with a properly designed cross-flow NF process (**Figure 1**) yields a higher quality of recycled water and consumes a lower amount of chemicals and energy. In addition, pH pulsation was found to be an efficient technique for the mitigation of membrane fouling and water flux recovery.

5.2. Treatment of model BFW by a tight NF membrane

Water flux and TOC/TDS rejection of the NF90 membrane at 50°C and pH 10.5 (raw BFW pH) are shown in **Figure 5(a)**. The normalized flux declined due to the combined fouling of silica and DOM in the model BFW (**Table 2**). In the treatment of model BFW, TDS rejection increased over time (from 80–95%), while TOC rejection remained constant (~98%), which is contrary to that observed for filtration of WLS inlet water [5]. This discrepancy demonstrates the effect of solution chemistry, primarily pH and ionic strength, on the rejection of salt and organic matter. Taking a closer look at **Table 2** reveals that the model BFW has a significantly higher pH and slightly higher salt concentration as compared to the WLS inlet water. Higher pH leads to the increased solubility of organic matter in the feed solution and less tendency to precipitation on the membrane surface. On the other hand, high salt concentration reduces the thickness of electric double layer around silica particles and thus facilitates the precipitation of silica and co-precipitation of DOM [54]. The latter effect seems to be dominant and results in the formation of selective fouling layer, which increases the TDS rejection over time. Also, an increase of TDS rejection again confirms the significance of organic fouling (plugging of hot spots by DOM) in the treatment of SAGD-produced water.

Figure 5(b) shows the effect of a step change in pH on flux and rejection at 50°C. Decreasing the pH from 10.5 to 8.5 reduced the flux by 20%, but enhanced the TDS rejection. Returning the pH back to 10.5 has quickly returned the water flux and TDS rejection to the previous trend. For all pH values, >98% of the organic matter was removed by NF90. Dynamic pH experiments showed that a more stable flux with higher TDS rejection can be obtained at lower pH values. However, higher overall water flux at higher pH values was achieved. The rapid change of flux and salt rejection by injecting acid or basic solutions into the feed stream demonstrates the significant impact of pH on fouling, particularly, in the presence of both silica and organic matter [5]. This behavior can be explained by a rapid change in foulant/foulant and foulant/membrane interactions by altering the pH as described earlier.

The results of scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) on NF90 membranes before and after filtration are shown in **Figure 6**. After NF, a layer of rejected solutes was formed on the membrane surface. More foulants were clearly deposited on the membrane when the pH of the solution was decreased to 8.5 (**Figure 6c**, **d**). Decreasing the pH resulted in precipitation of silica and co-precipitation of DOM, which were adsorbed on the surface of the membrane. EDX analysis revealed the presence of silica and iron in

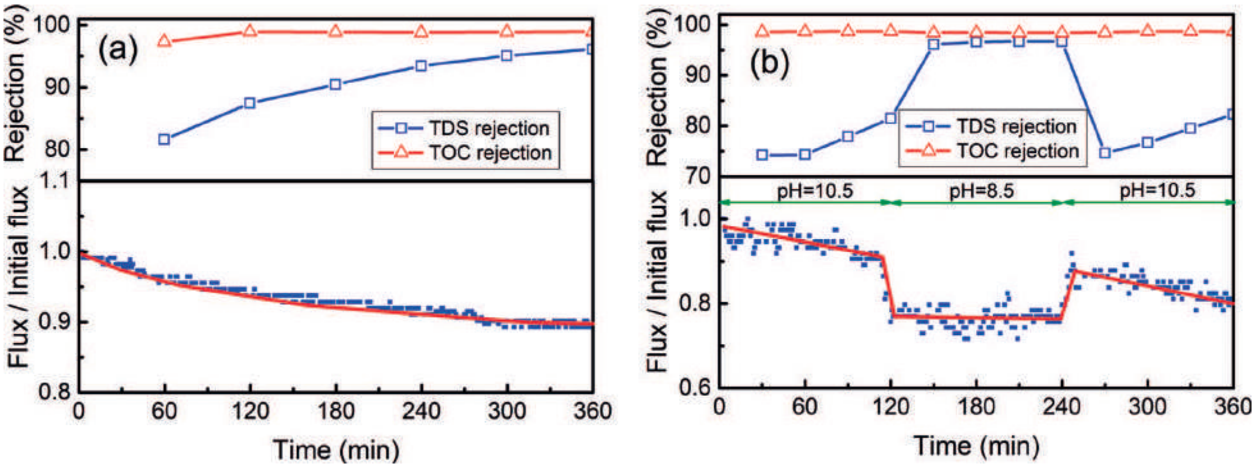

Figure 5. Water flux and TOC/TDS rejection for model BFW filtration using NF90 at (a) constant pH = 10.5, and (b) variable pH 10.5–8.5–10.5 at 50°C [5]. Copyright 2015, Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

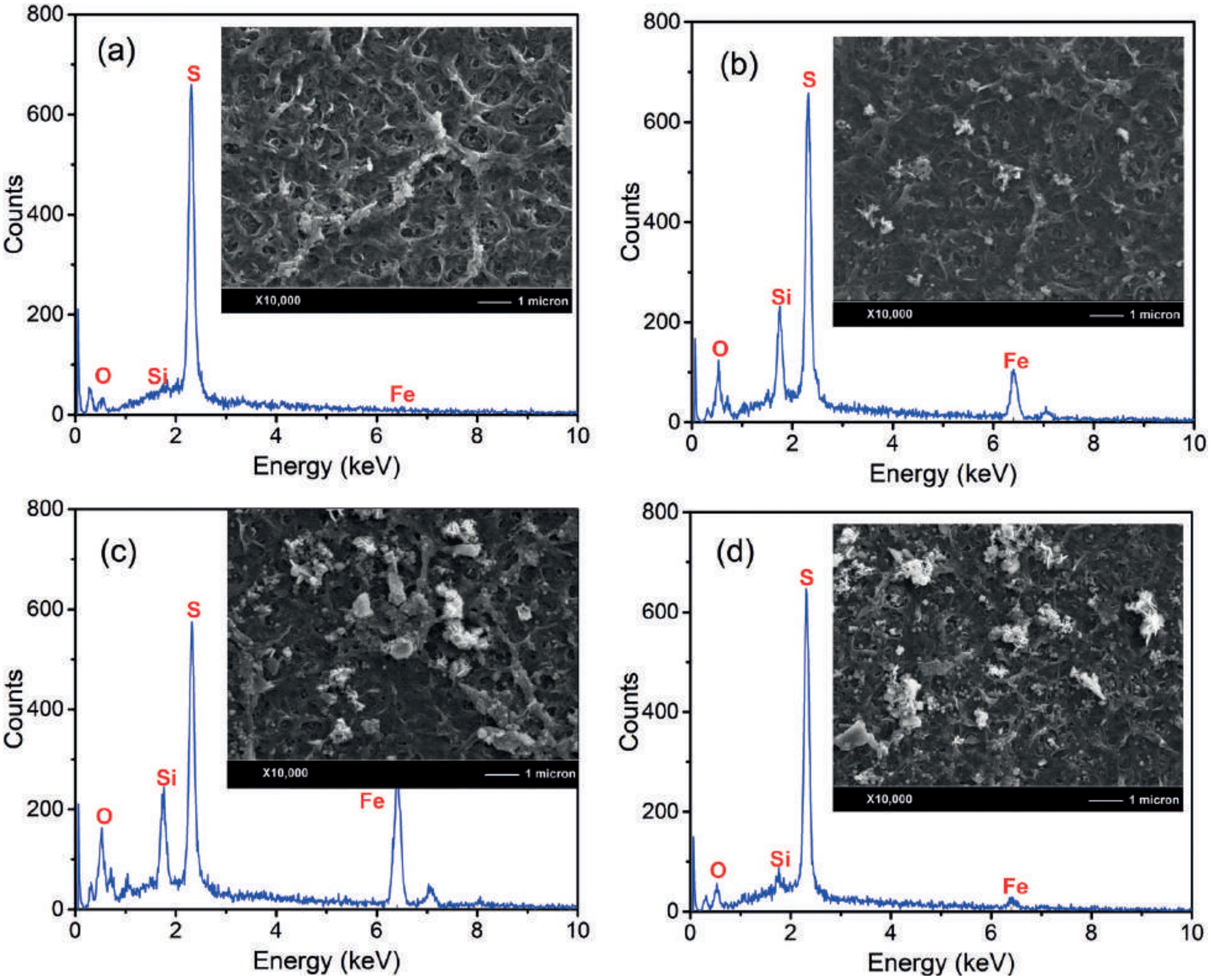

Figure 6. FESEM-EDX of (a) virgin membrane, and fouled membranes at (b) pH = 10.5, (c) pH = 8.5, and (d) pH = 8.5 then 10.5 [5]. Copyright 2015, Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

the fouling material. The iron peak became larger as the pH decreased from 10.5 to 8.5. This indicates precipitation of more solutes on the membrane surface at a lower pH. As expected based on solubility considerations, when the pH of the feed solution increased from 8.5 to 10.5 both silica and iron peaks shortened noticeably which shows re-dissolving of these materials at higher feed pH. This result implies that fouling is reversible by increasing the pH [5]. It is worth noting that the intense sulfur peak in all EDX results is related to the PES support layer of NF90 membrane.

Removal of inorganic elements from model BFW was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis and the results are provided in **Table 4**. Almost 98% of the dissolved silica and more than 99% of divalent ions (Fe^{2+}, Ca^{2+}, and Mg^{2+}) were removed by NF90 [5]. With 98% rejection of silica its content in the BFW becomes more than 90% lower than typical BFW and, therefore, would significantly reduce the fouling propensity in steam generation. Such a low level of DOM, salt, and scale-forming species in the permeate would significantly reduce the fouling/scaling propensity of the BFW if NF was employed as a polishing stage in the current SAGD process train (see **Figure 1**). Production of higher quality BFW may significantly reduce capital and operating costs through reducing the membrane area required for water treatment.

5.3. Treatment of BBD water by chemically and thermally stable NF membranes

A further concern for oil sands producers is minimizing the volume of BBD water requiring disposal [55]. Therefore, a process configuration involving NF of BBD to remove silica, TOC, and TDS in which the permeate would be used for BFW with a reduced volume of concentrate sent to disposal. Hurwitz et al. [29] evaluated NF for this application. Direct NF treatment and NF with coagulation and acidification pre-treatment were evaluated. Direct nanofiltration of chemically unadjusted BBD at its original pH was found to be the optimal treatment option with respect to the flux stability and the removal of TOC and TDS. The high DOM concentration and high pH of the BBD made coagulation of the bulk DOM difficult. Without NF, a maximum DOC removal of 30–40% was possible, but this required either very high coagulant doses (>400 mg/L as Al) and/or very low pH (4–6) [29]. Although upstream removal of DOM can be beneficial in some membrane process configurations, in this case, neither pH reduction nor coagulation significantly improved the rejection of DOM or TDS. Additionally, acidification and/or coagulation consistently resulted in increased membrane surface fouling and flux

Elements (mg/L)	Model BFW	NF90 Permeate	Rejection (%)
Na^+	880	53	94
Cl^-	510	15	97
Mg^{2+}	0.18	<0.02	> 99
Ca^{2+}	0.66	<0.03	> 99
Iron, total	0.48	<0.03	> 99
SiO_2, dissolved	21	0.4	98

Table 4. Rejection of inorganic materials by NF90 obtained by ICP-OES [5]. Copyright 2015, Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

decline. Because of the naturally high pH of the BBD, prolonged operation with at elevated fluxes and recoveries was possible, while maintaining solute removal as high as 80 and 45% for DOC and TDS, respectively.

A specially formulated sulfonated PES TFC membrane (HYDRACoRe) was used to treat the BBD. The high thermal and chemical stability of these membranes as well as their high negative surface charge (see **Table 3**) make them well suited to the treatment of BBD water. The HYDRACoRe membrane with a MWCO of 720 Da (the tightest membrane in this series of commercial membranes) was utilized for filtration studies. Dead-end NF tests were conducted to determine the effect of coagulation and BBD pH on the performance of the membrane. Stable operation was observed for water flux and DOC/TDS rejection across the range of initial fluxes tested (**Figure 7**). No flux decline was observed for the high, middle, and low initial fluxes (**Figure 7b**). A slight increase in the water permeability over time for low and intermediate initial fluxes was attributed to the swelling of membrane caused by electrostatic repulsion between the charged solutes (ions and charged DOM) and the membrane itself [29]. Likewise, neither elevated temperature nor initial flux had a significant effect on solute rejection (**Figure 7b**). Between 60 and 85%, DOC rejection was obtained over the range of initial fluxes. Interestingly, no loss in rejection was detected over the 60 min test period. This might be attributed to the very low total suspended solids (TSS) of BBD water (2 ppm) which mitigates the effect of cake enhanced concentration polarization and thus diffusion of organic matter toward permeate side. Applying a moderate initial flux of 60 LMH resulted in 80% DOC removal from BBD sample. Very high pH of BBD water minimizes the deposition of silica and DOM that reduces the effect of cake filtration on DOC rejection. In fact, NF membrane just strains out a certain molecular weight of organics without any deposition of foulants. Similarly, the TDS rejection was not significantly affected by the initial flux and feed solution temperature. Optimal TDS rejection was 40–50%, which obtained at a moderate initial flux. Operation at the middle initial flux, 60 LMH, was reported to provide the most sustainable combination of minimal fouling and maximum DOC/TDS rejection.

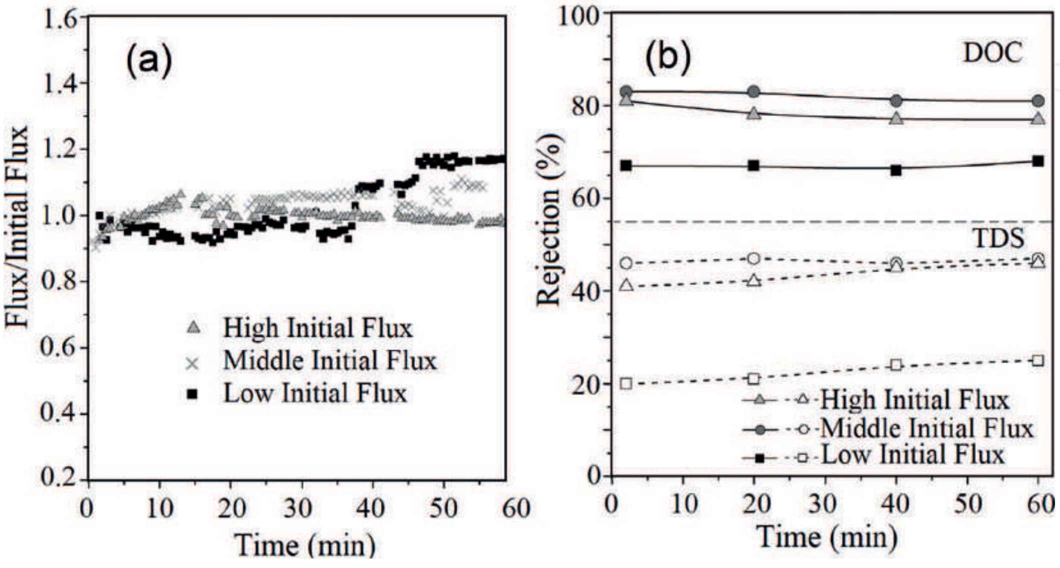

Figure 7. Effect of the initial flux on (a) the flux decline and (b) DOC/TDS rejection using 720 Da MWCO HYDRACoRe NF membrane at 70°C [29]. Copyright 2015, Reproduced with permission from ACS Publications, Washington, DC, USA.

6. Conclusion

The Alberta oil sands industry is actively developing and deploying technologies that reduce operating costs per barrel of product, as well as the amount of energy and fresh water consumed during resource extraction. Development of tailored NF membranes has created new interest in the application of membrane separation processes for the treatment of oil sands-produced water. In this chapter, several studies of NF membranes being tested for oil sands-produced water treatment were presented. Based on these studies, three scenarios for the application of NF membranes in the SAGD-produced water treatment train are suggested: (i) replacing the current WLS-IX process scheme with a cross-flow NF membrane softening process that gives higher-quality boiler feed water with lower energy consumption, (ii) integrating a NF process as a polishing stage downstream of the current WLS-IX processes to produce higher-quality BFW and thus increase the reliability of the boilers, and (iii) using NF to treat OTSG BBD water in the current WLS-IX scheme to increase the reuse of produced water and reduce BBD disposal rates. The major challenge for NF membrane processes in SAGD-produced water applications was found to be fouling by high concentrations of organic matter. pH pulsation was suggested as an effective method for the fouling reduction and water flux recovery. Treatment with loose NF membranes was found to remove more than 70% of the TDS and DOM. Tight NF membranes rejected more than 86% of the TDS and TOC. NF membranes for the treatment of SAGD-produced water should be selected based on the required trade-off between energy consumption and permeate water quality required for steam generation.

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Chapter 3

Zeolites-Mixed-Matrix Nanofiltration Membranes for the Next Generation of Water Purification

Mahboobeh Maghami and Amira Abdelrasoul

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.75083

Abstract

Designing high performance and antifouling membranes are in a great need to remove water contaminations and to regulate the quality of drinking water. Mixed-matrix membranes (MMMs) could offer a solution to the permeability and selectivity trade-off in nanofiltration (NF) membranes. MMM could offer the physicochemical stability of a ceramic material while ensuring the desired morphology with higher nanofiltration permeability, selectivity, hydrophilicity, fouling resistance, as well as greater thermal, mechanical, and chemical strength over a wider temperature and pH range. Zeolites are fascinating and versatile materials, vital for a wide range of industries due to their unique structure, greater mechanical strength, and chemical properties. This chapter focused on zeolite-MMM for nanofiltration. Several key rules in the synthesis procedures have been comprehensively discussed for the optimum interfacial morphology between the zeolites and polymers. Furthermore, the influence of the zeolite filler incorporation has been discussed and explored for water purification. This chapter provided a broad overview of the MMM's challenges and future improvement investigative directions.

Keywords: mixed-matrix membrane, filler, zeolites, hydrophilicity, interfacial, morphology

1. Introduction

Both polymeric and ceramic membranes have been the center of interest for their tremendous contribution in the water treatment industry. Despite their advantages, these synthetic membranes have limitations in terms of operation and strength. Over the years, researchers have been attempting to combine the effective features of both, polymeric and ceramic, materials in one new material called mixed-matrix membrane (MMM) or hybrid membrane. The sole purpose of developing new materials has been to associate the advantageous characteristics of the two types of membranes boosting the overall process efficacy. Conventionally, objectives such as enhancements in permeability or selectivity, reduction in fouling, and removal of specific contaminants have been attained either by combining two or more processes or by developing an integrated filtration process. Nevertheless, material advancement in membrane technology and nanotechnology has made it possible to fine-tune the process efficiency and has successfully paved the path for the synthesis of MMMs for different applications. Aside from the water purification applications, the advent of MMMs has revolutionized other areas also where separation or purification is of big import. Some of these potential applications reported in literature include water purification, medical industry, catalytic, and gas separation. Nevertheless, MMMs have not even crossed the laboratory-scale barrier because the MMM technology is nevertheless in a developmental phase and only a few lab-scale developments have been described thus far.

2. Types of MMMs

MMMs can be defined as incorporating of dispersed nanomaterials such as zeolite, carbon molecular sieve, and carbon nanotubes incorporated in a continuous polymer phase. **Figure 1** presented a schematic of an ideal MMM structure including the dispersed phase and the polymer matrix [1].

MMM could offer the physicochemical stability of a ceramic material with promising the desired morphology with higher permeability; selectivity; higher hydrophilicity; high fouling resistance; high thermal, mechanical, and chemical strength over a wider temperature; and pH range [2–7]. These types of MMMs are named as inorganic filler-based MMMs, organic filler-based MMMs, biofiller-based MMMs, and hybrid filler-based MMMs, depending on the type

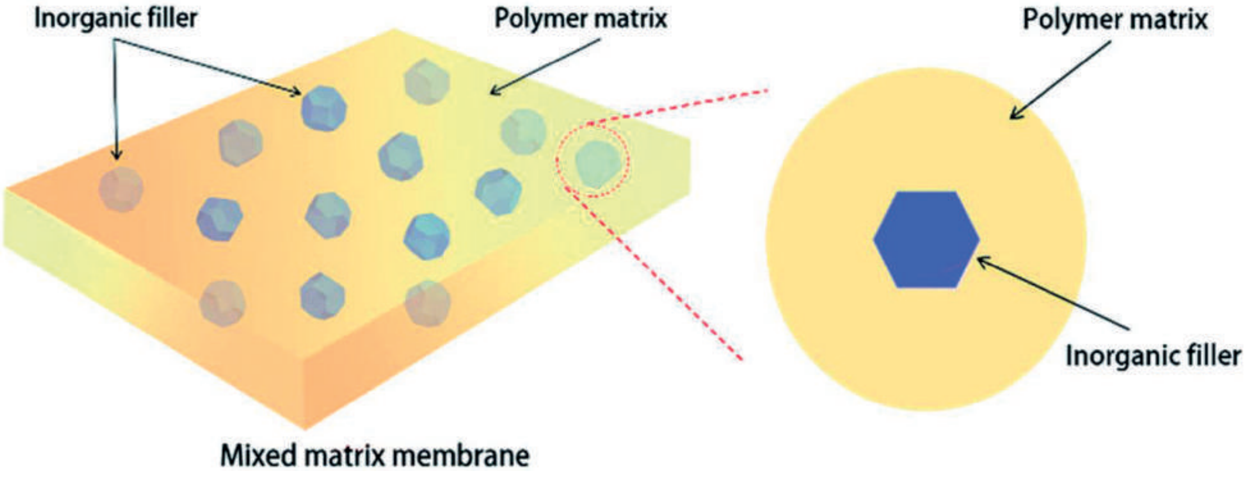

Figure 1. Schematic diagram of an ideal MMM structure [1].

of the dispersed fillers in the polymer matrix, as presented in **Figure 1** [1]. This chapter will focus on inorganic filler-based MMM, especially zeolite-MMM.

2.1. Inorganic filler-based MMMs

The field of inorganic filler-based membrane is a promising type of membranes, which has been explored extensively over the recent years. In the polymeric matrix, the inorganic fillers attach themselves to support materials by covalent bonds, van der Waals forces, or hydrogen bonds. These inorganic fillers are prepared through processes such as solgel, inert gas condensation, pulsed laser ablation, spark discharge generation, ion sputtering, spray pyrolysis, photothermal synthesis, thermal plasma synthesis, flame synthesis, low-temperature reactive synthesis, flame spray pyrolysis, mechanical alloying/milling, mechanochemical synthesis, and electrodeposition. Currently, different types of inorganic fillers have been added to the polymeric phases. Some of these fillers are zeolite [8], silica [9], TiO_2 [10], carbon nanotubes [11], and silver [12]. There are two methods to incorporate inorganic fillers into membrane structure by blending with the solution or by attaching the fillers to the surface through different techniques [4]. Inorganic-based filler MMMs have been employed in water industry for the adsorptive removal of pollutants, disinfection and/or microbial control, catalytic degradation, and desalination [13]. They also have potentials to provide both high superior selectivity and the desirable mechanical and economical properties. Researchers believe that a suitable combination of polymers and inorganic fillers should offer superior permeability and selectivity compared to simple materials. In this review, zeolite-MMM will be comprehensively studied, as a promising membrane for several applications.

2.1.1. Zeolites-MMMs

Zeolites are microporous crystalline aluminosilicate materials with uniform pore and channel size; thus, they are used in various fields such as catalysts in the petrochemical industry, ion exchangers, and absorbents for softening and purification of water [14–16]. Incorporation of zeolites into a polymer matrix has attracted great attention in membrane technology, due to several excellent advantages such as permeability improvement of the selective component, in addition to the enhancement of the thermal stability, the mechanical strength of a polymeric membrane [17], thermal resistance and chemical stability [18–20]. On the other hand, zeolites are expensive. Limitation in both polymeric and zeolite offers the need to synthesize the novel polymer-zeolite-MMM. The interaction of zeolites in the membrane matrix and its shape-selective catalytic properties could improve permeability and selectivity separations [21]. There have been numerous attempts to incorporate zeolite particles in polymer matrices for gas separation due to its superior separation and size exclusion and in water purification applications [22, 23].

Rezakazemi et al. [24] studied the gas transport properties of zeolite-reinforced polydimethylsiloxane (PDMS) MMM. The filler was dispersed homogenously in the matrix without any voids at the zeolite-polymer interface. It was confirmed that the homogenous incorporation of filler in the matrix resulted in higher permeability for the MMM compared with the polymeric membranes.

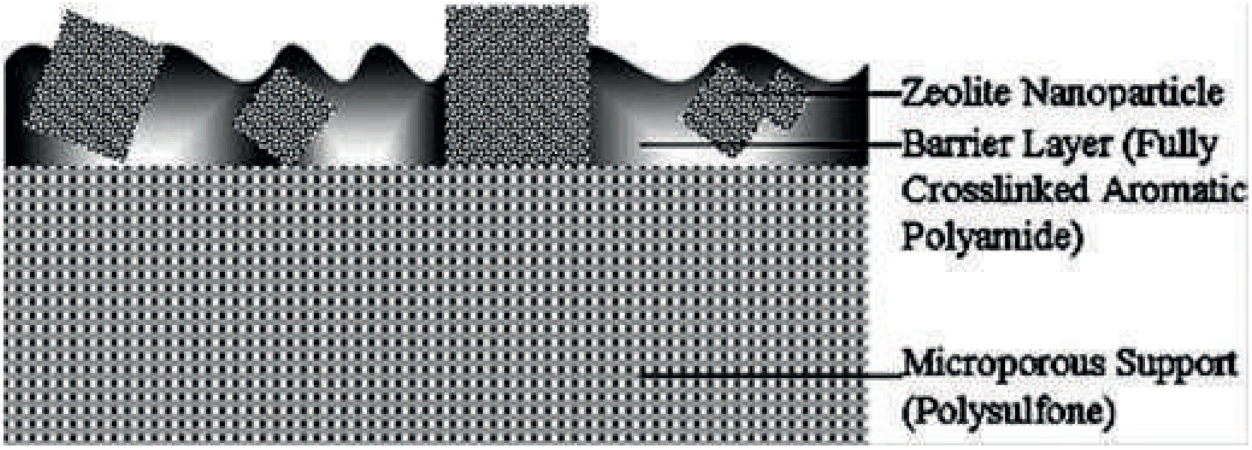

Figure 2. Schematic cross section of zeolite nanocomposite membrane (zeolite-MMM) [26].

Ciobanu et al. [25] reported that zeolite-polyurethane membranes demonstrated improved properties. The good interaction between the polymer and the zeolite at the interface was confirmed, and the membrane swelling was reduced. Consequently, the water flux through membrane increased with increasing zeolite concentration.

Hoek et al. [26] studied the formation of mixed-matrix reverse osmosis membranes by the interfacial polymerization of thin-film nanocomposite polysulfone supports impregnated with zeolites. **Figure 2** represents the cross-sectional image of zeolite nanocomposite reverse osmosis membrane, which is utilized for water purification through desalination process. It was found that increasing the zeolite nano-filler concentrations resulted in smoother, more hydrophilic, and more negatively charged MMM. As a consequence, the MMM membrane demonstrated high flux and a slight improvement in salt rejection compared to thin-film composite (TFC) membrane without zeolite nanoparticles due to changes of membrane morphology.

3. Interfacial morphology of zeolites-MMMs

To obtain the optimum interfacial morphology between the zeolite and polymer, several key roles should be considered. The first one is to promote the adhesion between polymer matrix and molecular sieve phases by modifying the zeolite surface with silane coupling agents [27–29]. The second one is to introduce low molecular weight materials (LMWMs) to fill the voids between polymer and molecular sieve phases [30, 31]. The third one is to apply high processing temperatures close to glass transition temperature (Tg) of polymeric materials to maintain the polymer chain flexibility during the membrane formation [32]. The fourth one is to prime the surface of zeolites by polymer [33].

.The polymer matrix plays an important role for permeability, and the inorganic filler has a controlling factor for the selectivity of the separation process. As a result, interfacial compatibility between the two phases has a profound impact on the separation performance for such membranes. The addition of inorganic fillers has key impacts on the interfacial void formation, aggregation, pore blockage of the morphology, and the transport phenomenon. Consequently, the impregnation of zeolites has a significant influence on the overall performance of the newly developed MMMs. The formation of these interfacial voids is attributed to two main phenomena, the interaction between the polymer phase and the filler and the stress exerted during preparation [1, 32]. The presence of interfacial voids creates additional channels that allow for the solvent to pass through the membrane [34]. However, mechanical strength and rejection rate are also concerned by the channel density [35].

Figure 3 represents various structures at the polymer-zeolite interface region, and S represents the sieve in the polymer [36]. **Figure 3A** demonstrates a homogenous blend of polymer and sieve, indicating an ideal interphase morphology. **Figure 3B** shows polymer chain rigidification due to the shrinkage stresses generated during solvent removal. **Figure 3C** confirmed poor compatibility between zeolite and polymer matrix morphologies, due to the formation of voids at the interfacial region. **Figure 3D** indicates sealing surface pores of zeolites by the rigidified polymer chains. Overall, the interaction between polymer and zeolite is related to chemical nature of the polymer and sieve surfaces, and the stress encountered during material preparation, which are critical factors to form the interphase.

These features are a challenge and should be controlled or avoided for the synthesis of the targeted zeolite-MMM for several applications. The formation of relatively nonselective defects at the interface between the zeolite particles and the polymer medium will result in MMMs, which fail to demonstrate their performance [37]. Therefore, despite the good properties of the polymer-zeolite-MMMs, they still face some challenges to overcome.

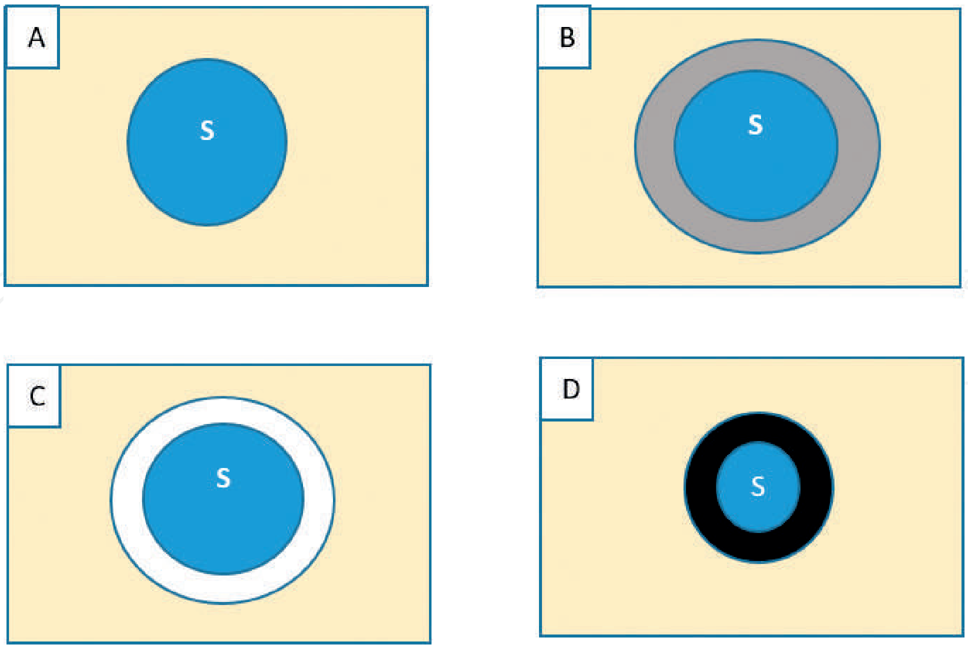

Figure 3. Illustration of various structures at the polymer-zeolite interface region [36]. (A) Homogenous blend of polymer and sieve (B) Rigidified polymer layer around the sieve. (C) Interfacial void around the sieve. (D) Sieve partial pore blockage.

4. Interfacial modification of zeolite-MMMs

Several strategies have been offered to improve the polymer-zeolite interaction and, hence, to avoid nonselective voids. These methods are included in incorporation of a plasticizer into the polymer solution that can decrease the polymer glass transition temperature (Tg) [32]. Consequently, polymer chain flexibility maintains during membrane preparation either by annealing the membranes above glass transition temperature of polymer [38, 39], or external surface of zeolites can be modified by coupling agents. The surface-initiated polymerization is the most frequent technique to improve the polymer-filler adhesion in polymer-zeolite-MMMs [40]. Furthermore, adding the low molecular weight additives (LMWAs) to the membrane formulation can act as a compatibilizer or the third component to prepare glassy polymer/LMWA blend membranes [31, 41]. Priming method can be also used to reduce the stress at the polymer-particle interface and to minimize agglomeration of the particles. Consequently, the interfacial interaction between the two components will be improved through coating the surface of the filler particles with a dilute polymer dope [31]; and eventually, minimizing of zeolite-solvent/zeolite-nonsolvent interaction, especially asymmetric MMM [42]. Therefore, the obtained hydrophobic surface can suppress the zeolite particles from acting as nucleating agents. As a result, it will minimize the voids induced by the unfavorable interaction between polymer and zeolite particles.

4.1. Interfacial modification with silane agents

Silane coupling agents were commonly proposed to modify the zeolite surface in order to improve compatibility of the inorganic filler with the polymeric matrix [43, 44]. It is known from literatures related to the silanation of zeolites that silane coupling agents have two types of reactive groups: the first type is the hydroxyl groups of zeolites, which could make hydrogen bonds with the amino silane agent [43], and the second one is the organo-functional group, such as amino and epoxy, which could be used to bond polymer chains to the zeolite. Therefore, improving adhesion between the zeolite and the bulk polymer phases in the membrane was achieved [45]. **Figure 4** shows a schematic silanation of zeolite surface with 3-aminopropyldimethylethoxysilane (APDMES) coupling agent [45].

Junaidi et al. [46] indicated that the glass transition temperature of MMMs is influenced by silane modification. In other words, the Tg of the zeolite-MMMs increased with the increasing of silane concentration on the surface of the zeolite particles. As a result, the silane modification of zeolite affects the mechanical properties of continuous phase due to the formation of the hydrogen bonding between the zeolite particles and polymer matrix and the movement reduction of the polymer chains [47, 41].

Pechar et al. [48] investigate the effects of silane grafting on the separation performance of MMM for permeation. The 3-aminopropyl trimethoxy silane (APMS) was added to modify SAPO-34 zeolite before the impregnation into the asymmetric polysulfone (PSf) MMMs through dry-wet phase inversion method. Both PSf and modified SAPO-34 membranes showed great enhancement in terms of selectivity and permeability compared to the original PSf membrane.

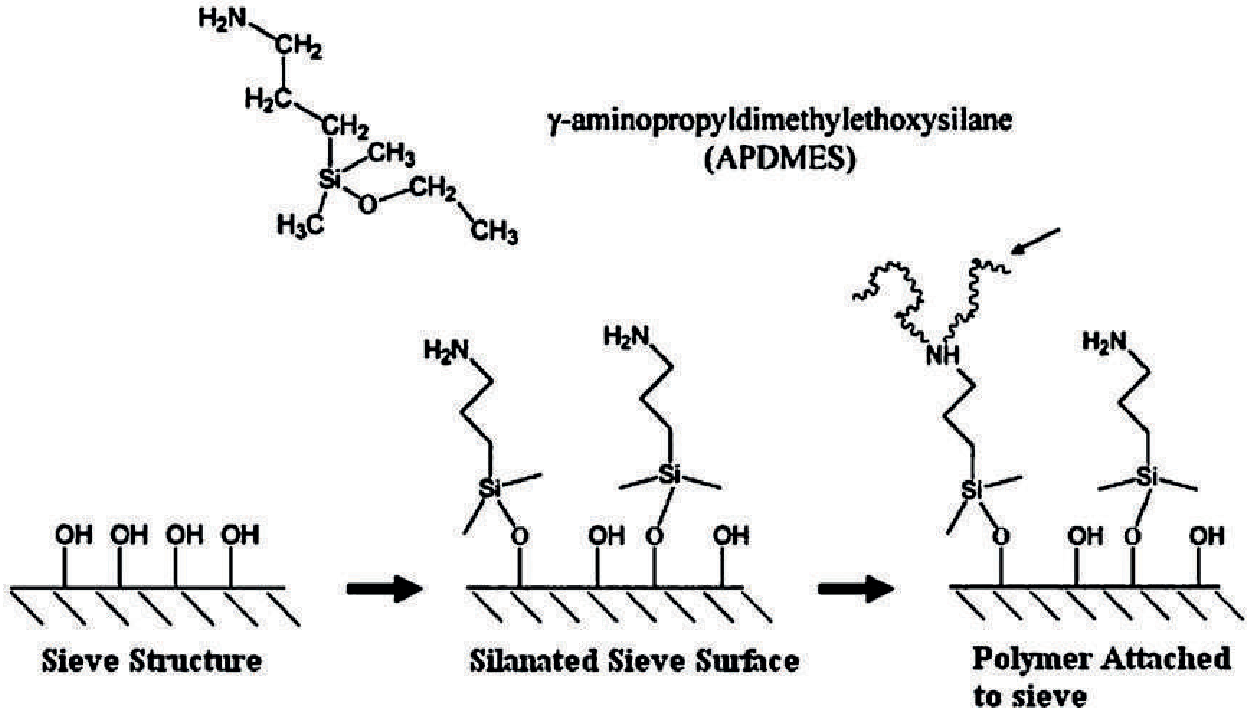

Figure 4. Schematic of the envisioned coupling reaction [45].

The increment of CO_2 selectivity and permeability was correlated to the diminishing of the interfacial voids, when SAPO-34 zeolite was modified using APMS in ethanol.

Sen et al. [49] studied the use of 3-aminopropyltrimethoxysilane (APTMS) influence to modify ZSM-2 zeolite to synthesize polyimide MMMs. Although micrographs showed the absence of voids, however, the modified ZSM-2-MMM performance for CO_2 selectivity and permeability was dropped relatively, similarly, to the performance of pure polymeric membrane, due to the pore blockage of the ZSM-2 zeolite [50].

In order to overcome this problem, other researchers such as Li et al. [28] modified zeolite 3A, 4A, and 5A using 3-aminopropylmethyldiethoxy silane (APMDES) in toluene solvent. Hence, rigidification of polymer chain and partial pore blockage reduced through this modification process. As a result, they showed high improvement for both of the selectivity and permeability of CO_2 than those MMMs containing zeolite without the modification and without major blockage the zeolite pores. Therefore, in some cases, surface modification by the silane coupling agents was recommended to enhance interfacial adhesion but hardly improved permselectivity.

4.2. Addition of low molecular weight materials (LMWMs)

Adding low molecular weight additives (LMWAs) to the membrane formulation acts as a compatibilizer or the third component to improve the compatibility between zeolite and polymer matrices. The low molecular weight materials induce a hydrogen bond with hydroxyl and carbonyl moiety. In addition, the formation of hydrogen bond confirms its solubility in the solvent used to make the polymer dope solution. It should be noted that LMWMs should be solid at room temperature, in order to prevent their evaporation during membrane fabrication, consequently losing their ability of forming interfacial voids [31]. Once hydrogen bonds are formed between polymer chains and LMWMs, the free volume of polymers decreases, which results in a decrease in their permeability, whereas increase in their permselectivity.

kulprathipanja et al. [51] reported mixed-matrix membranes for the use in gas separation by blending polycarbonates (PC) with an additive p-nitroaniline (pNA) and incorporating zeolite 4A particles as filler. The permeability of all gases was measured using differential scanning calorimetry (DSC) analysis through PC/(pNA)/zeolite 4A membranes, which were lower than those through pure PC membrane. The incorporation of pNA was essential, since pNA acts as a facilitator for provision of better interaction between rigid, glassy polymer PC, and zeolite 4A particles. Therefore, the incorporation of a molecular weight additive with functional groups into zeolite-MMMs can be used as a tool to improve the structure and performance properties of the membranes.

One of examples of LMWMs is 2,4,6-triaminopyrimidine (TAP) containing three primary amine groups, which are able to form hydrogen bonds with both hydroxyl and carbonyl groups [31]. Furthermore, it had been reported that the carbonyl groups of polyimides (PI) could interact with amine groups of urethanes through the hydrogen bond formation.

Park et al. [31] used TAP to obtain the interfacial void-free PI membranes filled with zeolites. TAP enhanced the contact of zeolite particles with polyimide chains presumably by forming the hydrogen bonding. As a consequence, the void-free PI/zeolite 13X/TAP membrane showed the higher gas permeability for He, N_2, O_2, CO_2, and CH_4 with little expense of selectivity compared to the PI/TAP membrane having the same PI/TAP ratio, while the PI/zeolite 4A/TAP membrane showed lower permeability but higher permselectivity. The difference between both membranes was influenced by the pore size of zeolites. In addition, the molecular sieving effect of zeolites seemed to take place when the kinetic diameter of penetrants approached the pore size of zeolites.

4.3. Annealing

One of the largest challenges in designing zeolite-MMMs is poor contact between polymer and zeolite defects. Many efforts made to overcome to this problem associated with the zeolite-MMMs through the annealing of zeolite-MMMs above the glass transition temperature (Tg) [32]. In other words, Tg is considered as a qualitative estimation to compare the polymer chain rigidity of mixed-matrix membranes at different zeolite types with simple polymer membrane, and it also leads to a better contact between zeolite and polymer chains [52]. Annealing process at temperature above the Tg results into the formation of stronger bond between polymer matrix and zeolite. Despite advantages of annealing in relaxing the stress imposed to the hollow fiber membrane, it results in higher packing density of polymer chains. Therefore, there are drawbacks associated with annealing. In addition, it did not lead to significant improvement in the morphology of the membranes. Annealing at high Tg formed sieve-in-a-cage morphology, which will be difficult to create a good contact between the polymer and the sieve [32]. In order to overcome to this disadvantage of annealing, incorporation of a plasticizer into the polymer solution can decrease the polymer Tg and thus maintain polymer chain mobility and flexibility during membrane fabrication [53]. Therefore, to develop membrane fabrication technology, a quench method after annealing membranes above Tg can be effective in gas separation process by forming frozen polymer chains quickly [54]. Therefore, it will have a higher free volume in the polymer matrix and subsequently higher permeability without the loss of selectivity.

4.4. Priming method

The dilute polymers are the same as the bulk polymers used for the preparation of MMMs. Coating the surface of the filler particles with a dilute polymer dope is known as the priming method [55]. The agglomeration is considered responsible for the defects between the polymer matrix and zeolite particle phases [56]. Since more agglomeration occurs in the polymer matrix when smaller particles are used, especially at high particle loadings, therefore, large zeolite particles are used to form practical mixed-matrix membranes. Therefore, zeolite particles were primed by increasing the amount of polymer. It should be considered that polymer effectively coats the zeolite particles before adding remaining bulk polymer and mixing with the priming polymer [57]. The purpose of priming is to reduce stress at the polymer-particle interface, to increase the compatibility between zeolite and polymer in MMMs, and to minimize agglomeration of zeolite particles [58, 59].

5. Zeolite nanofiltration MMM for water purification

Water treatment is increasingly important to remove water pollutants and solve water problems. Drinking water may compose of hazardous substances such as toxins and endocrine disrupting compound. Therefore, it would be urgent to invent more sustainable and reliable treatment process to remove water contaminations and to regulate the quality of drinking water. Development of cost-effective membranes is in a great need to effectively replace the conventional water treatment technologies to produce water that meet or exceed stringent standards. Nanofiltration (NF) membranes with pore size of 0.001 μm are among the potential alternatives which can filter wastewater from low organic content up to high organic content.

Recent studies have demonstrated that the zeolite-MMMs were applied to design nanofiltration membranes to enhance permeability, selectivity, stability, surface area, or catalytic activity in water purification and separation processes [60, 61]. Nevertheless, there are only few studies performed on zeolite-MMMs for water treatment; it is determined that the size of zeolite was designed to match the expected polyimide active film thickness, thereby providing a preferential flow path through the nanochannels of zeolites [62, 63]. Thin-film nanocomposite (TFN) membranes have been used by incorporating zeolite particles into the PA rejection layer. It has shown that the incorporation of zeolite in a PA layer could improve its water permeability without significant loss of salt rejection under high pressure during water purification process [64]. The main reason for that is nanochannels of zeolites with great sub-nanometer pores in zeolite nanoparticles that behave as preferential flow channels for water molecules. The zeolite-PA-based TFN membranes are considered as superior separation performance for RO applications due to their enhanced water permeability of active layer [65].

Nanofiltration (NF) is widely used in many treatment processes, such as water softening, seawater and brackish water desalination, and removal of micro-pollutants such as sewage treatment and wastewater [66, 67].

Natural zeolite is considered as a suitable and desired material in the fabrication of NF membrane due to its strength against inflation in water. Furthermore, it can readily form a suspension to coat the membrane as a support [68]. In another research by Damayanti and coworkers, zeolite-based nanofiltration membranes demonstrated an excellent performance and high efficiency for removal of micro-pollutants for laundry wastewater treatment [69]. Membrane performance is measured based on the flux and rejection values. They studied the superior ability of zeolite nanofiltration to treat laundry wastewater as determined by turbidity measurements and phosphate removal as the two significant parameters. More importantly, another advantage of zeolite-based nano-membranes is that such membranes show an enhanced hydrophilicity when zeolites are used since they are hydrophilic in nature, which in turn contributes to enhanced removal of pollutants from wastewater.

In addition, the zeolite nanofiltration membranes showed improved separation performance and antifouling properties. In addition, a number of nanomaterials can be applied as potential

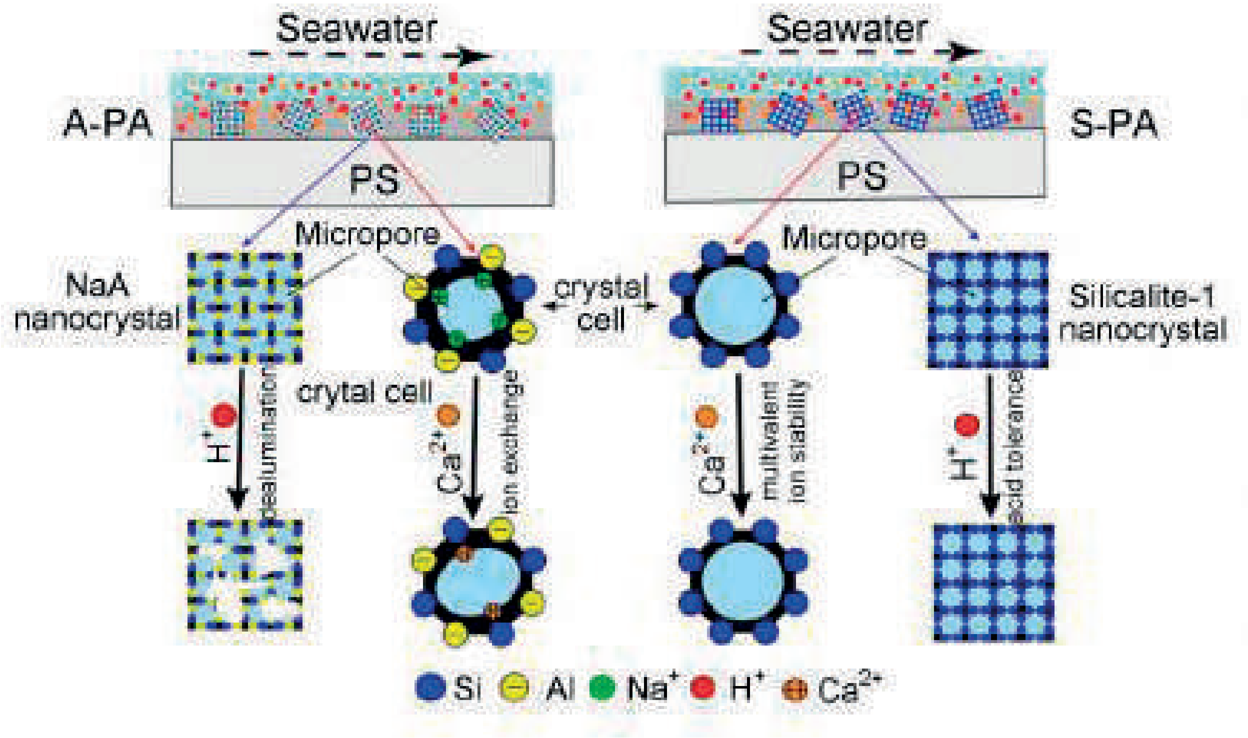

Figure 5. Schematic illustration of acid and multivalent ion resistance in thin-film nanocomposite membranes incorporated with NaA and silicate-1 zeolites [70].

water transport channels and modify the structure and surface properties of the membrane thin-film layers [70, 71].

In a systematic study by Zhang et al., it was shown that when silicalite-1 nanozeolites incorporated into polyamide (PA) thin-film composite membranes, they observed a higher membrane permeability as well as enhanced acid and multivalent cation resistance compared to NaA nanozeolite-incorporated membranes, as presented in **Figure 5** [70]. The effect of the silicalite-1 nanocrystals on the membrane properties was investigated. Contact angle measurements indicated that the silicate-1-PA (S-PA) membrane exhibited a more hydrophilic surface than the PA membrane by itself, in comparison with the PA and NaA-PA (A-PA) membranes. S-PA membranes evaluated by cross flow reverse osmosis tests showed greatly enhanced water permeability and improved acid stability. All of these results confirm that silicalite-1zeolites are superior compared to NaA zeolites in fabrication of thin-film nanocomposite membranes.

Furthermore, Yurekli showed filtration and adsorption processes by impregnation of zeolite nanoparticles in polysulfone (PSf) membranes for the removal of nickel and lead cations from synthetically prepared solutions [71]. The results also revealed that the sorption capacity and the water hydraulic permeability of the membranes could both be improved by simply tuning the membrane fabricating conditions. The coupling process suggested that the membrane architecture could be efficiently used for treating metal solutions with low concentrations and transmembrane pressures.

6. Future development

Recently, novel zeolite-MMMs have attracted great attention in membrane technology, due to the excellent advantages such as improvement in the permeability, selectivity, thermal stability, and mechanical strength of a polymeric membrane. However, the comprehensive understanding of organic-inorganic interfaces is in a great need. Zeolite-MMM performance suffers from defects caused by poor contact at the molecular sieve/polymer interface, the complexity of the synthesis process, high cost, identification of compatible inorganic particles, agglomeration, inorganic particle concentration, phase separation, control of morphology, and structural defects. Moreover, some zeolite-MMMs for water purification application are considered potential hazards to humans and the environment, which also needs more study to determine the hazardous character of these nanoparticles and mechanism of nanoparticles embedded membrane fouling in industrial water purification in the future.

One of most difficulties associated with membrane technology is fouling for a long time. Although several strategies such as incorporation of antifouling nanoparticles and surface modification have been used to overcome this problem, intensive investigations are needed to stop regeneration of microbial colonies on membrane surface and to reduce the leaching of filler. The next-generation MMM should be developed with producing nano-size fillers without aggregation to improve their separation properties for membrane industry especially MMMs. There are several reasons to produce nano-size fillers, especially zeolite fillers such as more polymer-particle interfacial area and enhanced polymer-filler interface contact by smaller particles. The potential of incorporating fillers such as zeolite particles has not been attained up to the expectation of zeolite-MMM performance, due to the smaller sizes, homogeneous distribution, agglomeration, price, availability, compatibility with polymer interface, their relation with water chemistry, better interfacial contact, and stability.

Despite many novel MMMs, fillers are being investigated, so far but their performances are restricted due to limited synthesis processes. Previously, the process fails to demonstrate their performance due to formation of relatively nonselective defects at the interface between the zeolite particles and the polymer medium on laboratory scale. Therefore, other major issues related to MMM is the interface defects that can lead to isolating zeolite fillers from the transport processes. Therefore, new techniques to achieve a perfect interface between inorganic fillers and polymers in membranes without compromising performance and scaling up these novel membranes under industrially relevant conditions are greatly needed.

In addition, many of these novel MMMs reported so far have been only tested on a laboratory scale and need further research to be used commercially in the industry. It is required to produce novel materials that can have high selectivity as well as nano-size fillers with incredibly small sizes. There are limitations on developing novel materials due to high prices or expensive synthesis processes. The molecular dynamic (MD) simulations of mixed-matrix materials could be an effective approach to predict diffusive performance of MMM, especially zeolite-MMMs, and to provide experimental guidelines for tuning the membrane permeability at the molecular level without high costs. Although there are many developed models for predicting the membrane performance, however, these models could not include the influence of inserting zeolite on membrane performance. Therefore, MD will be essential and effective to predict the morphology and intrinsic properties of these fillers and its interaction of the polymeric matrix.

Last but not least, factor is changing, and membrane morphology could change properties of membranes and subsequently will influence the membrane performance. Therefore, improving membrane performance in real conditions such as high temperature and high pressure and incorporating a plasticizer into the polymer solution would be possible and essential in order to provide better thermally and chemically zeolite-MMMs at different operating conditions.

Although development success of the synthesis and the application of MMMs impregnated with zeolites for water purification, however, the mechanisms behind these phenomena require intensive investigations for more advanced MMM technology.

7. Conclusion

Mixed-matrix membranes with zeolite fillers have attracted a lot of attention in membrane technology research due to its excellent advantages, such as high permeability and improved selectivity. Zeolite-MMMs could be considered an ideal candidate for purification industry since it combines the properties of polymeric matric and zeolite inorganic fillers. Application and fabrication techniques of zeolite-reinforced polymeric membranes have been comprehensively reviewed in this chapter with the aim of optimizing interfacial interaction between the zeolite and the polymeric matrices. Compatibility between zeolite and polymer matrices can be improved with a number of methods, such as by applying high processing temperature during membrane formation, the silane modification and priming on the particle's surface, annealing that can relax the stress imposed to hollow fiber and result in higher packing density of polymer chains, and the introduction of a LMWA agent between the polymer matrix and inorganic particles.

There have been numerous attempts to incorporate zeolite particles in polymer matrices in water purification applications. The silicalite-1 zeolites are superior compared to NaA zeolites in fabrication of thin-film nanocomposite nanofiltration membranes. However, despite its advantages there are still issues and difficulties associated with zeolite-MMMs that have restricted their wider applications. Therefore, the advancements in the application and fabrication of zeolite-MMM need further intensive investigations. Future research should be conducted with the aim of developing new techniques that provide better understanding of zeolite incorporation into polymer structures. New materials should also be considered as a way of reducing the fouling concerns. Additional study is necessary for an improved understanding of the basic transport mechanism occurring through the MMMs. The next-generation MMMs must be developed with nano-size fillers and without aggregation so as to improve their separation properties severely needed in the membrane industry. Some results indicate that the nano-size zeolite particles incorporated in MMMs offer better performance in comparison with micro-size particles. New additives and modification agents should be produced to improve adhesion between polymer and inorganic fillers. In conclusion, despite of all the identified problems, MMM technology with zeolites could be considered a strong candidate for modern purification industry due to the remarkable properties of polymeric and inorganic zeolite materials.

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Chapter 4

The Use and Performance of Nanofiltration Membranes for Agro-Industrial Effluents Purification

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Additional information is available at the end of the chapter

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Abstract

Nanofiltration (NF) technology offers several advantages over classic separation processes. NF membranes have been increasingly implemented in water treatment processes (e.g., desalination of brackish water and seawater) and for wastewater (e.g., textile, pulp and paper, pharmaceutical, and agro-industrial). The specific selectivity toward small solutes and the lower energy consumption of NF membranes have enhanced their use. However, some drawbacks need to be faced when NF is applied on an industrial scale. The main drawback is fouling that reduces the production capacity of the plant and shortens the membrane service lifetime if of irreversible nature, thus increasing the operating and capital costs. Moreover, fouling alters the selectivity of the membrane and thus the rejection efficiency. This chapter focuses the use of NF for the treatment of different agro-industrial effluents (such as dairy, tomato, and olive oil) and addresses membrane fouling as the main drawback against NF competitiveness.

Keywords: dairy wastewater, olive mill wastewater, tomato wastewater, artichoke wastewater, nanofiltration, wastewater treatment

1. Introduction

In the last decades, new advanced separation technologies, less intensive in terms of specific energy consumption than conventional separation ones and “greener” regarding the minor use of chemicals and reagents to achieve the desired separation, have been developed. Concretely, membrane technology can take the lead for these purposes.

In the current scenario, scarcity of water particularly concerns agricultural irrigation, which demands more than 70% of worldwide water consumption [1]. Nevertheless, wastewater regeneration for several purposes such as irrigation stands as a solution to reduce environmental and economic impacts.

Besides, due to population increase, food production has become a major concern worldwide. Food industries are quickly multiplying all over the world because of globalization of markets and the lifting of trade barriers, thus contributing to the large-scale manufacture of a vast range of food and beverage products. Consequently, the high volumes produced, environmental impact, and nutritional value of its by-products/wastes are an enormous challenge that the food industry is facing, with the goal of valorization.

Membrane technology is modular and scalable, is environmentally friendly, requires low maintenance, and can provide high purifying standards [2–4]. In the last years, there has been a significant trend in the use of membranes for a wide range of applications, and particularly in the field of water and wastewater treatments to replace classic separation unit operations, as well as for the reclamation of effluents of different origins, especially those by-produced in agro-industries. This impulse has been a result of the new membrane materials, module designs, and the optimization of the operating conditions, in specific those for minimization of fouling [2–12].

Concretely, nanofiltration (NF) provides a series of advantages over classic separation processes. For example, for clean water production, NF technology has been replacing or working alongside reverse osmosis in water treatment processes for clean water production (e.g., desalination of brackish water and seawater) and for wastewater treatment (e.g., textile, pulp and paper, pharmaceutical, and agro-industrial) due to the cost-benefit analysis of lower-pressure operations. The specific selectivity toward small solutes and the lower energy consumption of NF membranes have enhanced their use. By contrast, in the food industry, the use of nanofiltration is too low, despite this sector has been the first one to introduce membrane technology in dairies, especially to recover cheese whey. Membrane processes that have been predominantly used are microfiltration and ultrafiltration, e.g., for removal of bacteria or to produce whey protein concentrates from ultrafiltration [13]. So, while research about using nanofiltration for by-products recovery from agro-food industry is increasing, real applications are still very low [14]. Some drawbacks must be inevitably faced when NF is applied on an industrial scale. The main drawback is fouling that reduces the production capacity of the plant and shortens the membrane service lifetime if of irreversible nature, thus increasing the operating and capital costs. Moreover, fouling alters the selectivity of the membrane and thus the rejection efficiency.

This chapter focuses the use of NF for the treatment/valorization of different agro-industrial effluents or by-products, mainly dairy, tomato, artichoke, and olive oil, and addresses membrane fouling as the main drawback against NF competitiveness.

Among agro-industrial effluents, olive mill wastewater (OMW), generated during the production of olive oil in factories commonly known as “mills,” is one of the most heavily polluted wastewater, depending on the procedure used, reaching chemical oxygen demand (COD) values up to 100,000 mg O_2 L^{-1}. The volumes of these effluents have increased in the last decades due to the marked increment of olive oil consumption worldwide given its well-proven health-promoting properties (nutritional, antioxidant, anti-inflammatory, cosmetic). This fact led to the change in the extraction technology from batch to continuous production procedures as a response to cope with this higher demand. Currently, average-sized modern olive oil mills generate several tens of cubic meters of OMW daily, which sums up several millions of cubic meters a year.

The same applies to other agro-industrial effluents like tomato and artichoke ones. Moreover, one critical aspect in the treatment management of these types of agro-industrial effluents relies on the high variability in volume and organic load, as well as on the seasonality of by-production. This poses an additional handicap to find efficient treatments focused on this type of effluents.

Otherwise, in dairies, NF has been mostly used for the demineralization of salted and acid whey, substituting reverse osmosis, or to produce desalted lactose-containing whey in a single process. The performance of NF is mainly affected by concentration polarization due to an accumulation of solutes at the membrane surface and, simultaneously, to the increase of osmotic pressure, which reduces the effective transmembrane pressure. The resulting boundary layer is usually the reversible part of NF fouling, in which its characteristics are related to the wall shear stress and the driving force (average transmembrane pressure). Besides, that boundary layer can give rise to irreversible adsorption or precipitation of foulants, namely, calcium phosphates, at the membrane surface [15]. The mineral fouling depends on environmental conditions, such as pH and temperature, and should be controlled during NF process. The prevention and control of fouling in NF of dairy or other products can be done through selection of an adequate feed pretreatment, choice of membrane and module design, and optimizing operating conditions.

2. Membrane processes for tomato manufacturing and artichoke wastewaters

Wastewater by-produced during tomato manufacturing is characterized by a dark color and bad odor and presents a considerable concentration in organic compounds, suspended solids, and ground particles [16, 17]. This process water, generated during cleaning, sorting, and moving of tomatoes, constitutes the main tomato industry wastewater and deteriorates very quickly. An additional difficulty for the treatment of these effluents, as previously said, relies on the variability in time and space of composition and pollutant concentration, as it is very seasonal, and depends on the geographical zone, type of fruit, composition, as well as changes in the production, among others. The typical composition of this wastewater, reported by Iaquinta and co-workers [18], is pH around 6.6, high electrical conductivity (2.56 mS cm^{-1}), relatively high COD (1200–1700 mg O_2 L^{-1}), and total organic carbon (TOC; 340 mg L^{-1}).

Because of this, tomato manufacturing wastewater cannot be discharged straight in municipal sewage systems, as the high organic content exceeds legal limit standards. Thereby, the treatment of these effluents is needed beforehand. In this framework, Iaquinta and co-workers proposed a combined treatment process comprising a biological treatment followed by NF, at a pilot scale [16, 17]. The used NF membrane was a commercial spiral-wound module (Desal-5 membrane, model DK2540, produced and supplied by Osmonics). NF process optimization was carried out relying on critical flux methods, in order to avoid operating at fouling conditions. Within critical flux conditions, short-term fouling phenomena are drastically reduced, and, consequently, the productivity and the longevity of the membranes are significantly increased. Critical fluxes were measured at different recovery levels. The authors reported purification of the wastewater up to a water compatible with municipal sewer system requirements, with a recovery rate of 90%. A permeate stream with EC of 1778 μS cm^{-1}, COD of 465 mg O_2 L^{-1}, and TOC of 168 mg L^{-1} was attained, and short-term fouling issues could be avoided by operating the system at permeate fluxes about or below 8.2 L hm^{-2}. Moreover, the process was modeled, which permitted the prediction of a final critical flux value equal to 10.1 L hm^{-2}. On the other hand, the authors also prepared a synthetic effluent, by adding mature tomatoes to tap water in a ratio equal to 1:20 and 1:1000, respectively. An analysis performed on the synthetic wastewater confirmed similar chemical characteristics, in line with the real ones. Furthermore, a similar fouling behavior was found for the NF membrane.

Artichoke is cultivated for its immature inflorescence, in which the head flower composes the edible portion. The main producers are Egypt, Italy, and Spain. It is widely consumed as fresh, frozen, or conserved vegetable [18]. Given that just a small part of this vegetable (around 30%) is used in the food industry, artichoke processing generates a huge amount of solid waste (mainly leaves, stems, bracts of the artichoke plant) that is used as animal feedstuff or manure [19] and wastewaters, such as blanching waters, that need to be managed. Nowadays, attempts have been made to reuse waste solid material as a source of health-promoting compounds, leading to improved management of industrial residues and economic benefits for the agricultural and food sector [20, 21].

Artichoke wastewater is the extract from artichoke solid waste. This material contains suspended solids, macromolecules, and prebiotic sugars [18], and it is considered a cheap source of fructo-oligosaccharides. Machado et al. [18] examined the clarification, purification, and concentration of artichoke extract by sequential microfiltration (MF)—aimed to clarify the artichoke extract—followed by NF, to purify and concentrate the prebiotic sugars. The study was performed on a laboratory scale and tested different MF and NF membranes as well as different operation pressures. MF pretreatment achieved total clarification of the extract; that is, 100% prebiotic sugars were reported to be recovered in permeate stream. However, MF membranes presented a certain flux decline (20–40% with respect to the initial values) that the authors attributed to cake layer formation as observed by surface analysis.

Subsequent NF was performed with the permeate of the less fouled MF membrane (polyethersulfone (PES), 50 μm pore size). Three NF membranes were tested for this purpose, that is, NP010 (Microdyn-Nadir, PES, 1 kDa molecular weight cutoff (MWCO)), NP030 (Microdyn-Nadir, PES, 400 Da MWCO), and NF270 (Dow, polyamide, 150–300 Da MWCO). Total retention of prebiotic sugar was achieved with the latter membrane, allowing the obtention of a concentrate pool rich in these compounds, with functional prebiotic properties, which according to the authors could be used as ingredient on foodstuff applications. Nevertheless, the authors pointed that for obtaining a high degree of purification other techniques should be further or alternatively employed.

Moreover, this NF membrane (NF270) was reported to yield a high flux (up to 120 L h^{-1} m^{-2}), as well as the highest retention toward the target species. As reported by the authors, even though NP010 and NP030 membranes present higher MWCO, their filtration fluxes under the given operational conditions were below those yielded by NF270. The former membranes are made of polyethersulfone, which has lower affinity with water than polyamide, the material of which NF270 membrane is made of, and thus lower permeate fluxes were observed.

Another proposal for artichoke wastewater treatment and fractionation was examined recently by Conidi and co-workers [22]. They reported the results of an integrated ultrafiltration (UF) and NF membrane process, at a lab scale. An evaluation of the used membranes was made based on the permeate flux, fouling index and water permeability recovery. Typical chemical composition of artichoke wastewaters reported by these authors is here presented: suspended solids 2.5 ± 0.10 (%), glucose 960 ± 1(mg L^{-1}), fructose 837 ± 1.07 (mg L^{-1}), sucrose 1050 ± 0.41 (mg L^{-1}), total antioxidant activity 8 ± 0.042 (TAA, mM Trolox), chlorogenic acid 251 ± 2.64 (mg L^{-1}), cynarine 164.7 ± 1.41 (mg L^{-1}), and apigenin-7-O-glucoside 101 ± 2 (mg L^{-1}). On the one hand, the used UF membranes were hollow fiber ones and aimed to remove suspended solids from the artichoke extract, to submit the clarified liquor to the NF step. This preliminary UF clarification step permitted the rejection of most suspended solids in the raw water stream. The initial permeate flux was reported to decrease during the UF process by increasing the volume recovery factor (VRF) due to concentration polarization, fouling phenomena, and increased concentration of solutes in the retentate, such that a steady-state permeate flux of 10 kg hm^{-2} was obtained at VRF of 3. Moreover, it is important to highlight that the initial water permeability of the UF membrane could not be completely recovered after the applied cleaning protocol, which comprised two cleaning steps with alkaline (NaOH) and enzymatic solutions: the NaOH solution cleaning recovered just 65% of the initial water permeability, whereas the subsequent enzymatic cleaning step permitted the recovery of up to 88% of the initial water permeability of the UF membrane.

Regarding the NF step, two different spiral-wound membranes (Microdyn-Nadir Desal DL and GE Water & Process Technologies NP030) with different properties were examined. These membranes were noted to present different selectivity toward phenolic compounds and sugars. Both membranes were observed to provide high rejection toward phenolic compounds (chlorogenic acid, cynarine, and apigenin-7-O-glucoside) and, consequently, toward the total antioxidant activity (TAA). On the other hand, the Desal DL NF membrane was capable to provide high rejection (100%) toward sugar compounds (glucose, fructose, and sucrose) in contrast with NP030 membrane (4%).

Furthermore, the Desal DL membrane yielded higher permeate fluxes than NP030 membrane, despite its minor nominal MWCO: the initial permeate flux was around 21 kg h^{-1} m^{-2}, which decreased to 18 kg h^{-1} m^{-2} at a steady state upon VRF of 3, whereas for NP030, a lower steady-state permeate flux was measured (5 kg h^{-1} m^{-2}). The fouling index values measured for both selected membranes on the base of their water permeability before and after the treatment of clarified artichoke wastewaters also supported this: the NP030 membrane showed a higher fouling index (41%) in comparison with the Desal DL (1.7%).

As stated by the authors, the proposed process enabled significant advantages in terms of reduction of environmental impact, recovery of high-added-value compounds, saving of water, and energy requirements. It permitted obtaining different valuable products: a retentate fraction (from NP030 membrane) enriched in phenolic compounds suitable for nutraceutical, cosmeceutical, or food application; a retentate fraction (from Desal DL membrane), enriched in sugar compounds, of interest for food applications; and a clear permeate (from Desal DL membrane) which can be reused as process water or for membrane cleaning.

Fouling mechanisms are very important to fully understand what is taking place between the membrane and the effluent, in view of the adoption and implementation of adequate decisions for the successful design of the membrane plant. This comprises the setup of specifically tailored pretreatment process and optimized operating conditions. Irreversible fouling arises quickly on the membranes due to the high concentration of pollutants when wastewater is purified without any pretreatment [2–12]. Therefore, adequate and optimally designed pretreatment processes on each particular feedstock, in other words, pretreatment tailoring of membrane processes, must be developed in order to maximize productivity and minimize fouling.

3. Membrane processes for olive mill wastewater purification

OMW is characterized by strong odor, violet-dark color, acid pH, high organic matter content, and high saline toxicity, as confirmed by its high EC values [23]. Uncontrolled disposal of these effluents constitutes an environmental hazard, causing contamination of soil and aquifers, underground leaks, water body pollution, strong odor nuisance, plants growth inhibition, hindrance of self-purification processes, as well as negative effects on the aquatic fauna and the ecological status. Due to the presence of high COD load including recalcitrant compounds, as well as fats and lipids, direct discharge of these wastewaters to the municipal sewage treatment plants is not allowed. In fact, as the majority of municipal wastewater treatment plants include biological treatment processes, legal limits for wastewater discharge into sewer system are set to prevent the inhibition of the microbiological activity. Moreover, discharge of OMW to the ground fields and superficial water bodies is currently prohibited in Spain, whereas in Italy as well as in other European countries, only partial discharge on suitable terrains is allowed; otherwise, in Portugal OMW can be stored and used for irrigation of arbustive cultures under controlled manner (Despacho Conjunto 626/2000) [23–28].

Several wastewater streams can be produced in an olive oil mill, wastewater from the washing of the olives (OWW), olive mill wastewater (OMW-3, only for three-phase mills), wastewater from olive oil washing (OMW-2), and wastewater from cleaning processes. OWW has a high concentration of suspended solids (mainly peel, pulp, ground, branches, and leaf debris) dragged during the olive fruit washing process, but low concentration of dissolved organic matter—which varies in function of the water flow exchange rate in the washing machines and ripeness state—usually below standard limits for discharge on suitable superficial land.

Currently, not only the Mediterranean countries, where this industry is ancestral and represents an important sector of the industrial economy (Spain, Italy, Portugal, Greece, and Northern African countries—Syria, Algeria, Turkey, Morocco, Tunisia, Libya, Lebanon, and Egypt), are affected by this problem but also France, Serbia and Montenegro, Macedonia, Cyprus, Turkey, Israel, and Jordan, as well as the USA, the Middle East, and China, where this industry is growing each year.

The two-phase extraction process appeared in the 1990s as a more ecological system, has been strongly promoted in Spain, and is now being implemented in Portugal and Greece.

Nevertheless, the three-phase system is still surviving in other countries where scarcity of financial support has not favored the change of technology. In the two-phase extraction, water injection is only performed in the final vertical centrifugation step (olive oil washing). The effluent volume derived from the decanting process (OMW-2) is thus reduced on average more than 30%, if compared to the three-phase system (OMW-3). On the other hand, OMW-2 contains lower organic load because part of the organic matter remains in the solid waste, which presents higher moisture than the pomace from the three-phase system (60–70 vs. 30–45%). The measured COD in OWW is commonly in the range 4–16 g O_2 L^{-1} in contrast with up to 30–200 g O_2 L^{-1} for OMW-3. Inorganic compounds including chloride, sulfate, and phosphoric salts of potassium, calcium, iron, magnesium, sodium, copper, and traces of other elements are also common traits of OMW and OWW [28]. The average physicochemical composition of the different types of olive mill effluents is briefly reported in **Table 1**.

The major problem in the treatment of OMW relies on the large volumes produced with high concentration of organic matter (polysaccharides, sugars, polyalcohols, proteins, organic acids, tannins, fatty acids, oil, and organohalogenated pollutants) including a wide variety of phenolic compounds [23–28]. Among them, phenolic compounds represent one of the major factors related to the environmental problems caused by this effluent and its low biodegradability. They are highly concentrated and carry different negative effects such as phytotoxicity, toxicity against aquatic organisms, suppression of soil microorganisms, and difficulty to decompose. Despite that fact, phenolic compounds possess high antioxidant activity that makes them interesting for the food, pharmaceutical, and cosmetic industry. Because of that, the recovery of these compounds by different physicochemical methodologies should represent an important objective for the olive oil industry, obtaining added-value extracts of one of the main olive oil industry by-products.

Furthermore, geographical dispersion and the small size of olive oil mills, as well as the previously mentioned seasonality of production, are drawbacks for establishing a cost-efficient

Parameter	OMW-3	OMET-2	OMW-2	OWW
pH	5.4	7.2	4.9	6.3
Moisture (%)	93.4	99.4	99.3	99.7
Total solids (%)	6.6	0.59	0.6	0.27
Organic matter (%)	5.8	0.39	0.49	0.10
Ashes (%)	0.9	0.21	0.11	0.17
BOD_5 (g O_2 L^{-1})	42.0	0.29	0.79	0.50
COD (g O_2 L^{-1})	151.4	7.1	7.8	0.8
Total phenols (mg L^{-1})	921.0	86.0	157.0	4.0
EC (mS cm^{-1})	7.9	1.9	1.3	0.9

OWW: olive washing wastewater; OMW-3 and OMW-2: olive mill wastewater from three-phase and two-phase continuous extraction procedures; OMET-2: mixture of all effluents produced in the olive mill, including OWW, OMW, and from other activities in the facility (e.g., cleaning and sanitation); COD: chemical oxygen demand; BOD_5: biological oxygen demand; EC, electrical conductivity.

Table 1. Average physicochemical composition of the different types of olive mill effluents [23–28].

treatment/management for the produced effluents. Additionally, the physicochemical composition of these effluents is very variable as it depends on the edaphoclimatic conditions of the region and cultivation practices, the processed olives (type, quality, and maturity), as well as the oil extraction process.

Regarding the use of membranes for agro-industrial wastewater stream treatment, characterized by high concentration in colloids and suspended solids, the major technical drawback for implementation is the high fouling potential (**Figure 1**). Membrane fouling is mainly caused by colloids, soluble organic compounds, and microorganisms and, thus, can be of biological, organic, or scaling source. In any case, fouling increases the feed pressure and obliges to frequent plant shutdown for membrane cleaning procedures. In this regard, as this kind of effluents contain not only high concentrations of organic pollutants but also inorganic matter deleterious scaling problems may happen.

Specifically tailored pretreatment processes can be set upstream the membrane module to avoid high fouling rates, especially in cases in which the feed stream would rapidly lead to zero flux conditions if no pretreatment is conducted. Among recent literature on the topic, Stoller and Chianese [11] reported the purification of OWW by batch-sequenced spiral-wound UF and NF polymeric membranes preceded by solid/liquid (S/L) separation by coagulation-flocculation. OWW contains moderate organic pollutant load but is rich in suspended solids. To this end, the authors tested two different polyelectrolytes: aluminum sulfate (AS) or aluminum hydroxide (AH). Despite similar COD and BOD_5 removal efficiencies, the former provided enhanced flux (7.7 L h^{-1} m^{-2} at 10 bar) of the NF membrane, which yielded a treated permeate dischargeable in municipal sewers. Similar results were obtained by using

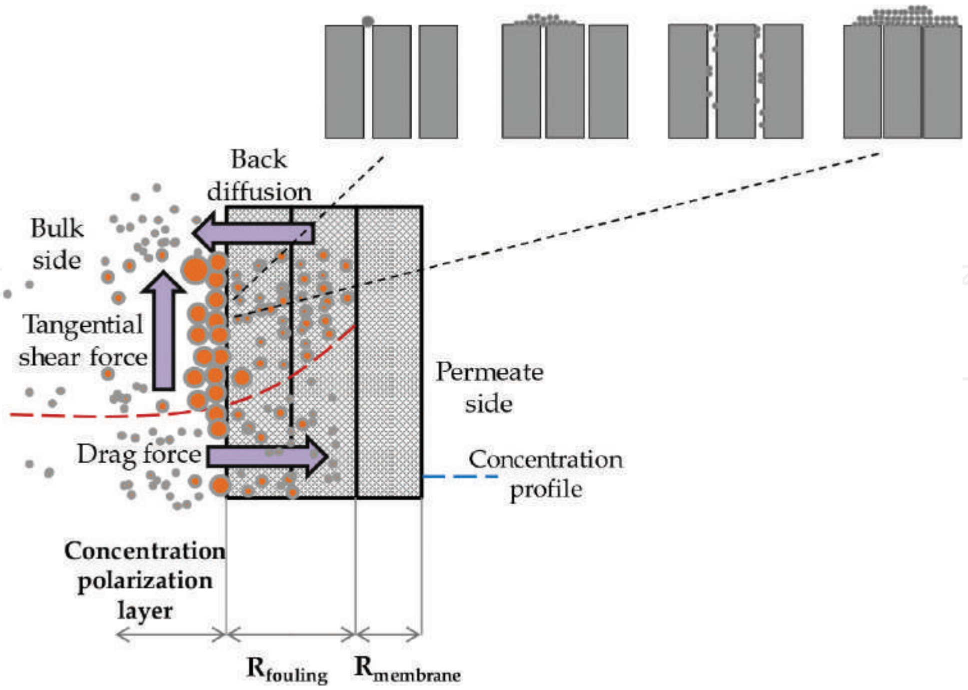

Figure 1. Concentration polarization and membrane fouling mechanisms during membrane filtration: from left to right, (i) pore sealing or complete pore blocking, (ii) intermediate pore blocking, (iii) standard blocking or pore filling/constriction, and (iv) cake or gel layer (adapted from Ochando-Pulido and Martínez-Férez [29]).

the same coagulants-flocculants on OMW-3 [12], much more polluted than the former OWW, up to 55,000 mg O_2 L^{-1} COD, in an integrated process comprising MF, UF, NF, and RO in batch sequence, from which a final stream complying with irrigation standards was attained. Moreover, UV photocatalysis (PC) with titanium dioxide anatase nano-powders and aerobic digestion (AD) was compared with the former pretreatment, also yielding an equivalent outlet stream. PC was more efficient upon the lowest residence time (24 for AS vs. 72 h for PC vs. 7 days for AD) and enabled the highest membrane productivity (13.5 L h^{-1} m^{-2} at 13 bar).

Results obtained by Stoller and co-workers highlight the importance of adequate pretreatment processes, underlining the fact that higher pollutant abatement is not sufficient to ensure the suitability of the pretreatment. It is necessary to confirm that the shift carried by the pretreatment process on the particle size (dp) distribution of the effluent does not lead to a stream with particles of similar size of the membrane's pores (Dp) that would cause deleterious fouling problems by pore plugging and clogging [30–38].

Centrifugation integrated with NF was also tested for OMW-3 [39], permitting to achieve fluxes of up to 21.2–28.3 L h^{-1} m^{-2} and COD removal efficiencies of 59.4–79.2% (at 10 bar). For OMW-3, Zirehpour and co-workers applied MF (50, 5, and 0.2 μm) and UF prior to NF [40]. However, MF membrane showed significant fouling problems, common in MF membranes. On the other hand, the commercial UF membrane examined provided higher permeate flux than the lab-made polyethersulfone (PES) one, but the antifouling properties and rejection efficiency of the latter were reported to be superior. Regarding the use of NF membranes, commercial NF-90 and NF-270, as well as NF-(self-made) one, NF-270 yielded higher permeate flux than NF-90 and NF-(self-made), but major rejection efficiency was found for NF-90. NF-90 and NF-(self-made) membranes are fully aromatic polyamide membranes prepared from interfacial polymerization of m-PDA and TMC. These membranes have relatively rough membrane surfaces. Otherwise, NF-270 is a semi-aromatic piperazine-based membrane with considerably smoother surface, significantly higher water permeability, and lower salt rejection than the former ones, as well as higher hydrophilic and negative charge. COD removals from NF-90 at VRF = 1 and VRF = 2.5 were about 93.4% (COD = 690 ± 10 mg O_2 L^{-1}) and 79% (COD = 2200 ± 10 mg O_2 L^{-1}), respectively. When NF-270 permeation was used as feed to NF-90, the permeate flux of NF-90 was 22.4 L h^{-1} m^{-2} at the beginning of VRF filtration, while permeate flux of NF-90 without NF-270 was 15.1 L h^{-1} m^{-2}, which means that this arrangement with NF-270 followed by NF-90 enhanced the permeate flux (5 L h^{-1} m^{-2} at 5 bar) up to 48%.

Another study by Ochando-Pulido and co-workers [41–43] presented a batch membrane-in-series processes, UF followed by NF, both polymeric in spiral-wound configuration, for the reclamation of OMW-2. Previously, flocculation (pH-T) and UV photocatalysis with ferromagnetic titanium dioxide nanoparticles were performed. The whole pretreatment sequence led to minor membrane area requirements (104.6 and 81.4 m^2, respectively) and enhanced productivity supported by minimized fouling rates. A final treated permeate compatible with irrigation use was obtained. On the other hand, the mix (1:1 v/v) of OMW-2 with OWW enhanced significantly the fluxes observed on both UF and NF membranes, 15.5 and 22.2 L h^{-1} m^{-2}, respectively, which were stable in time [43].

Some authors have also tried to extract added-value compounds contained in these effluents (polyphenols, sugars, pectin) by concentration with membranes. For example, Paraskeva and co-workers fractionated and recovered the phenolic fraction from OMW-3 (Greece) with UF + NF + RO membranes, including 80 μm polypropylene filtration pretreatment [28]. NF spiral-wound polymeric membranes (with 200 Da MWCO) were tested to further purify the UF permeate. In NF tests, a pressure value (TMP) of 20 bar led to satisfactory permeate flow (100–120 L h^{-1}) and 95% rejection of the phenolic concentration. Otherwise, 78% phenolic fraction recovery from OMW-3 (Italy) was achieved by Garcia-Castello et al. [44] with a process comprising ceramic tubular MF (Al_2O_3, 200 nm average pore size) followed by a hydrophobic polyethersulfone spiral-wound NF (Nadir N30F cutoff 578 Da). The NF polyphenol-enriched permeate, with valuable antioxidant properties, could be used in formulations in food, cosmetic, and pharmaceutical industries after the final vacuum membrane distillation (VMD) or osmotic distillation (OD). However, fouling on the membranes was evidenced throughout the whole proposed treatment process: the initial permeability could not be restored after the cleaning procedure and decayed progressively after each working cycle noticing irreversible fouling phenomena on the membrane.

On the other hand, Di Lecce et al. [45] proposed the fractionation of OMW-3 by a two-step MF and NF membrane process, at a pilot scale. The MF membranes were tubular made of polypropylene, whereas the NF membrane was in spiral-wound configuration and consisted of a polyamide thin-film composite. Filtration through cotton fabric filters was performed as pretreatment. In these conditions, the NF membrane achieved 98% rejection of COD, dry matter, and phenols. The quality of the obtained purified NF permeate was close to the standards established for its discharge in surface water bodies, but the dynamic performance of the membranes was not reported.

Recently, Ochando-Pulido and co-workers [46] reported the simultaneous phenol recovery and treatment of OMW-2 by NF. In their work, a polymeric TFC NF membrane was studied. Primarily, different pretreatments (sedimentation, centrifugation, and coagulation-flocculation) upstream the membrane unit were examined, adequating the effluent characteristics, that is, reducing the organic and inorganic concentration without compromising the phenolic content for its ulterior recovery. Among them, centrifugation was the most effective pretreatment in terms of TSS abatement, providing 85.7% recovery of supernatant (only 14.3% sludge), no phenolic compounds loss, and subsequently the highest EC and COD NF rejection. The fact that centrifuges are already available in the olive mills, implying minimization of fixed costs and needless of chemicals (flocculants), reinforces the proposed process. Moreover, this pretreatment enhanced the downstream stable membrane flux, up to 64.52 L h^{-1} m^{-2}, concentrating the feed up to 8.4 times. The obtention of a permeate stream with very good saline quality, 86.8% reduced COD, and practically free of phenolic content, thus minimized in its recalcitrant and phytotoxic potential, and a concentrate pool enriched in high-added-value antioxidant compounds (up to 1315.7 mg L^{-1}) would contribute to the economic feasibility of the reclamation process.

As it can be seen (**Table 2**), interesting added-value compounds contained in OMW may be recovered, concentrated, and fractionated with the aid of the adequate membranes, to counterbalance the treatment process costs of these agro-industrial effluents. Further investigation is still to be done to comprehend, model, control, and minimize associated fouling problems and the selection of optimal membrane materials.

Author/s	Raw OME source	Tretment process target	Scale	Process flow-scheme	Used membranes characteristics	Dynamic fouling-flux behaviour	Achieved standards	Results
Stoller et al. [37]	Continuous 3-phase olive oil extraction	OVW and OVW for sewers discharge or irrigation + fouling inhibition and prediction	Pilot (batch)	(1) Pretreatment among flocculation/ UV-TiO_2 photocatalysis/ aerobic digestion/ MF, followed by (2) UF + NF + RO	Composite SW MF (300 nm), UF (2 nm), NF (0.5 nm) and RO (<0.1 nm); operating below critical pressure	Lowest flux drops MF 17.3–18.9%, UF 23.1%, NF 18.5%, RO 22.9–23.7%; reversible fouling removed after cleaning	Overall COD abatement 98.8–99.4%	Italian standards for municipal sewer system discharge (COD values below 500 mg L^{-1}) achieved
Paraskeva et al. [28]	Continuous 3-phase olive oil extraction	Fractionation of value by-products to and effluent reclamation	Pilot (batch)	(1) 80 μm polypropylene filter, (2) UF, (3) NF and (4) RO	Multichannel UF (zirconia, 100 nm, 1–2.25 bar); polymeric SW NF (200 Da, 20 bar) and SW RO (100 Da, 40 bar)	Fouling data not reported; 100–120 L h^{-1} within NF, 30–32 L h^{-1} with RO	90% lipids and 50% phenols separated by UF; 95% phenols removal	Effluent suitable for irrigation or aquatic receptors
Coskun et al. [39]	Continuous 3-phase olive oil extraction	OMW reclamation for sewers discharge or reuse in process	Pilot (continuous)	(1) Centrifugation, (2) UF, (3) NF and (4) RO	UF cellulose and polyehtersulfone, NF polyamide and RO polyamide	Permeate fluxes up to 21.2–28.3 L m^{-2} h for NF membranes and 12.6–15.5 L m^{-2} h for RO membranes	COD removal 59.4 –79.2% for NF membranes, whereas 96.2–96.3% for RO membranes	Even though these values of conductivities were within acceptable standards for drinking waters, higher effluent COD values were observed, due to fermentation products during storage of the raw effluent
Garcia-Castello et al. [44]	Continuous 3-phase olive oil extraction	OVW reclamation + selective separation of added-value products	Pilot (batch)	(1) MF, (2) NF and (3) OD or VMD	MF ceramic (Al_2O_3, 200 nm, 0.72 ± 1 bar); SW NF (hydrophobic PES, 578 Da, 8 bar)	35% MF initial flux drop and incomplete restore after cleaning (106 L h^{-1} m^{-2} bar); 35% NF initial flux (4.68 L h^{-1} m^{-2}) drop above VRF = 3	MF achieved 91 and 26% TSS and TOC reduction; NF removed 63% TOC and TC reduction in MF permeate	NF permeate stream containing polyphenolic compounds for food, cosmetic or pharmaceutical sectors; 0.5 g L^{-1} free LMW polyphenols, with 56% hydroxytyrosol, obtained by treating the NF permeate by OD

Author/s	Raw OME source	Tretment process target	Scale	Process flow-scheme	Used membranes characteristics	Dynamic fouling-flux behaviour	Achieved standards	Results
Zirehpour et al. [40]	Continuous 3-phase olive oil extraction	OMW reclamation for irrigation reuse purposes	Pilot (continuous)	MF-UF-NF membrane system	MF (50, 5 and 0.2 μm), UF (100–35 kDa) and NF (450–150 Da)	34.1 L h^{-1} m^{-2} for UF and 9.4 L h^{-1} m^{-2} for NF	51.2% UF COD rejection and 64% NF salt rejection (VRF = 4)	98.8% COD removal in whole integrated system, with applied pressure for NF lower (5 bar) in comparison with other studies
Ochando et al. [41–43]	Continuous 2-phase olive oil extraction	OMW reclamation for sewers discharge or reuse in process	Pilot (semi-continuous)	(1) UF followed by (2) NF and (3) RO	Composite PA/PS SW	13.2 L h^{-1} m^{-2} for UF 10.5 L h^{-1} m^{-2} for NF steady-state performances	90.5% UF and 82.8% NF COD removal	Final treated effluent compliant with standards for reuse in olives washing machines

SW: spiral-wound; LMW: low molecular weight; OD: osmotic distillation; VMD: vacuum membrane distillation; CA: cellulose acetate; PES: polyethersulfone; PS: polysulfone; PA: polyamide; PVDF: polyvinylidenefluoride ; ZO: zirconium oxide; VRF: volume recovery factor.

Table 2. Main research works on olive mill wastewaters treatment by nanofiltration membrane technology.

4. Membrane processes for recovering and purifying dairy by-products

The largest by-product from the milk processing industry is cheese whey [47]. Worldwide, whey production is estimated at 180–190 million tons per year, which is one of the most challenging and demanding environmental aspects of this activity since only 50% is currently processed into products, such as whey protein concentrates and isolates [48]. Cheese whey contains about 55% of the nutrients of milk, namely, soluble proteins (20% of the milk proteins), lactose, minerals, and vitamins, which give it a high nutritional value [49]. On the other hand, this composition is also responsible by its high environmental impact, with values of BOD_5 and COD in the range 27–60 and 50–102 g L^{-1}, respectively [50].

Due to the physical-chemical composition of ultrafiltration permeates, where lactose is the major compound of the dry matter and several ions are present (sodium, potassium, calcium, magnesium, chloride, phosphate, citrate), nanofiltration can play an important role in separation/valorization of this fraction.

One of the most important uses of nanofiltration is the production of whey-demineralized lactose concentrates for the food industry, or even, if enough purification is achieved, for pharmaceutical purposes. During nanofiltration of these permeates, some problems can occur. The accumulation of solutes of lower molecular weight on the membrane surface leads to an increased osmotic pressure and polarization concentration phenomena, giving rise to a lower performance, with a decrease of permeate fluxes and altering its selectivity. However, the major drawback of this process is the fouling caused by mineral precipitation of calcium phosphates.

Rice and co-workers [51] carried out nanofiltration of ultrafiltration permeates using polyamide membranes NF270. They observed a severe flux decline during filtration at high temperatures and pH, due to calcium phosphate precipitation, because of its lower solubility in these operating conditions. However, washing with an acid solution allowed to recover water flux. Those authors suggested that by changing the pH of the feed, fouling could be avoided, despite changing the separation properties of the membrane.

Cuartas-Uribe and co-workers [52] also studied the concentration of lactose from whey ultrafiltration permeates, combining concentration by nanofiltration with continuous diafiltration modes, and found that the best operating conditions were a transmembrane pressure of 2.0 MPa and a volume dilution factor of around 2.0, because a good removal of chloride was possible with the lowest lactose loss for the permeate. Authors claimed that no fouling problems were detected during NF tests, but experiments at a larger scale to evaluate the economic feasibility of the process are essential.

Dairy wastewaters, generated during production of dairy products (milk, cheese, butter, yogurt), usually contain remains of milk, casein fines, protein, lipids, lactose, starters, enzymes, detergents, and chemicals from the cleaning and disinfection processes used in the plant. Similar to what happens with the recovery of cheese whey nutrients, where membrane technologies have a very prominent place, also in the treatment of wastewater from dairy products, their use has been growing a lot. The most used membrane processes are mainly ultrafiltration, nanofiltration, and reverse osmosis. When nanofiltration or reverse osmosis are directly used to recover the nutrients (proteins, lactose) contained in dairy wastewaters, also chemicals are retained by the membrane, whereby the use of retentates is a major problem. Besides, during this process, the increase of concentration polarization and osmotic pressure phenomena, due to accumulation of small organic molecules and salts near the membrane surface, leads to a sharp decrease of permeate fluxes and change membrane selectivity.

Luo and co-workers [53], based on the knowledge about recovery of nutrients from cheese whey, proposed a two-stage UF/NF process for the treatment of a model dairy wastewater, being in mind that at the first stage (UF) protein was recovered, and at the second one (NF), a retentate rich in lactose and a permeate free of organics was produced. The authors suggested that both UF and NF retentates of UF could be used for bioenergy production. To control the performance of the membranes used in both stages, the authors calculated the membrane hydraulic permeability before and after the trials, the recovery of solutes, the apparent rejections of solutes, and the irreversible fouling. Based on their experimental results, they concluded that a sequence of UF/NF to treat model dairy wastewaters can be a good proposal to solve the problem of the large volumes of these effluents that are produced worldwide. However, it should be emphasized that experiments with real solutions are needed, due to the complex composition of these types of samples, where other compounds, such as casein fines, lipids, microorganisms, detergents, and other cleaning chemicals, are also present, thus affecting membrane performance.

In order to improve the process proposed by previous researchers, Chen and co-workers [54] proposed an integrated process for reclamation of dairy wastewaters using a model solution. This process includes isoelectric precipitation of caseins—ultrafiltration-nanofiltration of the permeates of UF, producing a lactose concentrate which was used for acid lactic production through fermentation by *B. coagulans* IPE22 and a final reusable permeate. The experiments were performed in a dead-end filtration cell and in a pilot-scale plant. For UF, the most hydrophilic membranes were selected for experiments, due to its lower fouling potential by whey proteins, as was also observed by other authors during ultrafiltration of cheese whey [55]. Regarding NF, the results obtained allowed to conclude that the previous separation of casein, before UF, enhanced the performance of subsequent NF process, because irreversible fouling decreased from 44.4 to 11.1%, in the pilot plant test. While this work presents an improvement in relation to the previous work [53], it is important to stress that, with real dairy wastewaters, the major problem in what concerns nanofiltration of the permeates of UF is the concentration of salts, namely, calcium phosphates. In milk, the concentration of calcium and phosphate ions is very close to its solubility constant, and so since during the process of NF, both lactose and calcium phosphates are concentrated, this can lead to mineral precipitation on membranes, thus sharply decreasing the permeate fluxes.

Bertoluzzi and co-workers [55] compared the performance of two double-stage membrane processes for treatment of dairy wastewaters: (i) microfiltration (MF) plus NF and (ii) MF plus OI. For MF, a hollow fiber module was used, being membranes made of poly(ether sulfonate)/ poly(vinyl pyrrolidone) (PES/ PVP) mixture with a 0.20 μm pore size. In the NF and RO experiments, polymeric flat-type membranes were used, being these membranes made of polyamide composites. For the NF experiments, they used two different membranes (NF90 and NF), which are made of the same material but have different rejection properties, since NF90 is a tighter membrane, while the other one is a looser membrane, as can also be confirmed by their

Author/s	Byproducts/ dairy wastewaters	Module	Pretreatment	Membrane characterisitics	Achieved standards	Results
Cuartas-Uribe et al. [52]	Cheese whey	Spiral wounded module with an active surface of 2.51 m^2 (batch and continuous)	Pre-concentration by ultrafiltration	Thin film composite (TFC), DS-5DL, with polyamide active surface (cut-off of 150–300 Da)	Both lactose and whey demineralization were achieved with the combined process concentration/continuous diafiltration	NF permeate should be further treated in order to discharge into sewers, due to this COD values
Luo et al. [53]	Model and real dairy wastewaters	Rotating disk module (RDM)	Real effluents pretreated by two sieves with pore sizes of 0.25 and 0.10 mm	NF 270 made of polyamide and with cut-off 150–200 Da	Dairy wastewaters with pH between 7–8 are most suitable to be treated by NF using RDM due to a good compromise between permeate flux, membrane fouling and permeate quality. Membrane fouling is very sensitive to pH in the range 8–10	Similarity between model and real dairy wastewaters can be a valuable tool for process control in industrial applications
Luo et al. [53]	Model dairy wastewater	Dead-end filtration with a stirring cell fitted with a membrane disk	Previous separation of proteins and lipids by ultrafiltration	Several NF membranes were tested: NF270, NF90, Nanomax50, Desal-5 DL and Desal-5 DK, all of them with a surface layer oy polyamide, but with different cut-off´s	A two stage UF/NF for treatment of dairy wastewaters revealed to be a good method to purify dairy wastewaters. The combination of Ultracell for UF followed by NF of permeates with membranes NF270 was the best option, for purification	Retentates of UF were used for production of biofuels; lactose retained in NF was used for biogas production and the final permeate was a reusable water
Chen et al. [54]	Model dairy wastewater	Dead-end filtration cell for UF/NF (lab scale) and pilot plant for NF	Separation between caseins and whey proteins by isoeletric precipitation and centrfugation, followed by UF of supernatants to concentrate whey proteins	Four UF membranes were used: PES5, PES10, PES30 and Ultracell PLGC, made of different surface materials (polyethersulphone and regenerated cellulose) and cut-off´s. Membrane NF270 was used in the pilot scale tests	Both IP pretreatment and membrane surface material contributed to reduce irreversible fouling of UF and NF membranes. The combination of a previous removal of caseins followed by UF with the most hydrophilic membranes (Ultracell PLGC) allowed to drastically reduced the increasing pressure, thus improving the performance of UF and NF	Production of water of a better quality and simultaneous recovery of whey proteins, lactic acid (through lactose fermentation) and cells. Lactic acid and cells can be used for bioplastics production

Table 3. Some research works about the use of nanofiltration for recovery of dairy byproducts and dairy wastewaters purification.

hydraulic permeabilities to pure water. Before the experiments, the dairy wastewater was prefiltrated across a filter of 0.25 μm to remove solids and to avoid a quick fouling of membranes. After that, microfiltration was also used as a pretreatment for the next operation (NF or OI) with the objective of improving their performance. The authors found that the sequence of MF followed by RO allowed a better removal of total solids and organic matter. Besides, the composition of the final permeate was compatible with the discharge on receiving waters according to the Brazilian environmental regulations or could be used in cleaning-in-place processes in the dairy factory. Although the results of this study are a good basis for other similar dairy wastewaters, since the variety of manufacturing processes involved in dairy products used is too large, for each type of sample/desired goal, a previous study is always necessary.

Dairy by-products and wastewaters contain high nutritive, functional, and bioactive compounds, which can be recovered to produce food or other applications (**Table 3**). Nanofiltration, due to its specific characteristics, can play a role in the recovery/valorization of those compounds, allowing at the same time the reuse of its main component, the water. Nevertheless, a deep insight about its separation mechanisms and detailed knowledge on feed composition is necessary to control fouling phenomena.

5. Conclusions

This chapter focused on the use of NF for the treatment of different agro-industrial effluents, dairy, tomato, artichoke, and olive oil. Appropriate pretreatments to avoid membrane fouling have also been addressed as this is the main drawback against NF competitiveness. Among them, other pressure-driven membrane processes, such as microfiltration and ultrafiltration, are used as pretreatment, thus avoiding the use of chemicals. From our review, it was possible to conclude that the implementation of the circular economy vision to the mentioned production chains can be an interesting strategy to balance the investment costs that need to be carried out in order to build treatment plants. In fact, the recovery of added-value molecules (such as lactose and derivatives, polysaccharides, polyphenols, etc.) and of water can be a key aspect for the viability of the treatment processes. As previously said, water scarcity is a growing problem in Mediterranean countries, and therefore alternative sources of water are highly valued. For all of these reasons, it is considered that NF deployment is expected to grow in the forthcoming years.

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