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Nanofiltration

Edited by Muhammad Akhyar Farrukh

NANOFILTRATION

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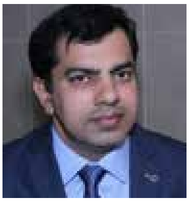
Meet the editor



Dr. Muhammad Akhyar Farrukh is a pioneer in Pakistan who established Nano-Chemistry Lab at GC University Lahore with the research funds won from international and national organizations. He has been duly awarded *three gold medals* for his outstanding academic performance in Chemistry and *four gold medals* for his excellent performance in research service to society. He has been awarded many international and national awards, was selected by the UNESCO as a *representative of Pakistan* in foundation of WAYS in Morocco; was awarded *Young Chemist Award* by IUPAC in Italy; was selected as *Young Scientist* by TWAS in Egypt and IAP/GYA in Germany, *Young Scientist* by IAP/World Economic Forum in China, and *Young Researcher* by the Council for Lindau Nobel Laureate 63rd Meetings; was awarded IUPAC-2015 *Award for Chemists* as an outstanding chemist from developing countries in S. Korea; received *Research Productivity Awards* Category A in 2016 and was *ranked 11th in Pakistan in Chemistry* and was selected as *Productive Scientist of Pakistan* and *ranked 11th in Pakistan* in Chemistry category Young Scientists in 2017 and 2018. He received SATHA *Innovation Award* 2018 and a *gold medal*.

Contents

Preface

The nanofiltration (NF) technique lies between ultrafiltration and reverse osmosis techniques. However, NF is considered a low-cost process and is capable of removing pesticides, organic matter, desalination of sea water, oil process and pollutants from industrial wastewater. The separation mechanism in NF is attributed to dielectric property, and the charged NF membrane attracts opposite charges to pass through it and repels like charges on the basis of difference in dielectric constant. However, membrane fouling is still a critical problem for efficient commercialization of NF. The use of nanoparticles in the manufacturing of membranes allows for a high degree of control over membrane fouling. Nanoparticle-based membranes can be developed by assembling engineered nanoparticles into porous membranes or blending them with polymeric or inorganic membranes.

The main challenge in the implementation of NF membrane is its ability towards fouling and low performance at high temperature. This book covers topics from multiple ranges from manufacturing of NF with their applications in wastewater treatment, drinking water treatment, degradation of pollutants, to fouling.

Removal of high concentrations of organic and inorganic matter from aquatic solution using crossflow spiral wound nanofiltration membranes with semi-industrial pilot plant is discussed, where natural organic matter, ammonia ions and total arsenic removal were examined using concentrates—wastewater obtained from industrial nanofiltration plant. Steam-assisted gravity drainage processes use recycled water that is produced 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. Zeolite-mixed-matrix membranes for nanofiltration are discussed. Zeolites are fascinating and versatile materials, vital for a wide range of industries due to their unique structure, greater mechanical strength and chemical properties, while mixed-matrix membranes offer a solution to the permeability and selectivity trade-off in nanofiltration membranes. The NF is also being used for the treatment of different agro-industrial effluents such as dairy, tomato and olive oil and addresses membrane fouling. Micellar-enhanced ultrafiltration technique is focused on the surfactant micelle-assisted removal of ions and organic solutes from aqueous media.

Membrane fouling is the most critical bottleneck for the widespread application of membrane separation technology. The fouling is an irreversible and time-dependent phenomenon, which is related to the characteristics of the membrane and solute-solute and solute-membrane interactions. Therefore, understanding fouling mechanisms such as fouling characteristics and consequences, fouling mathematical models and physical-chemical and processing factors affecting fouling is very important. Application of electric current to the surface of membrane provides a promising alternative for fouling mitigation, which may involve electrophoresis, electro-osmosis and electro-oxidation. Two separate chapters are dedicated to address these issues.

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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 Φ = 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.

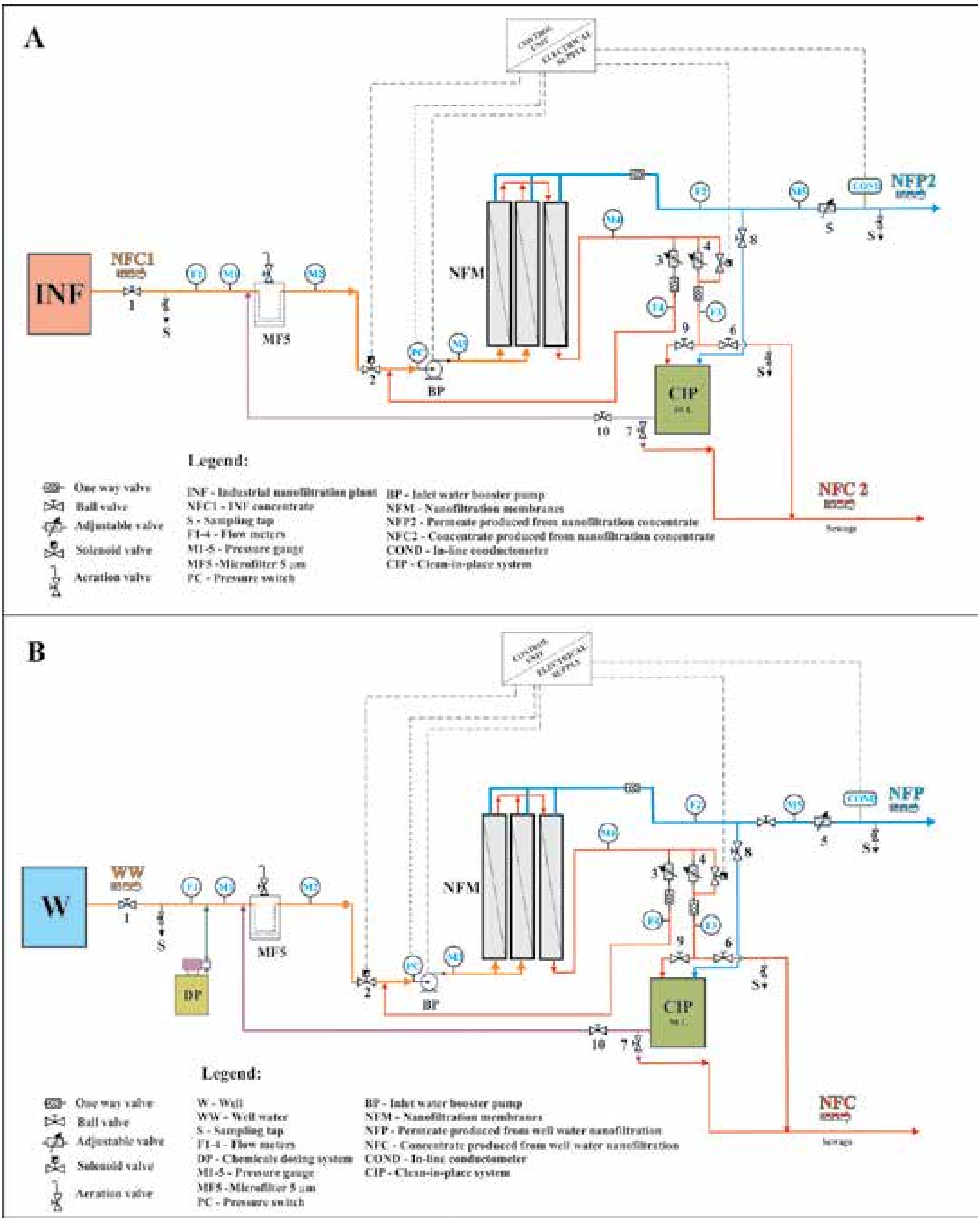

Figure 1. Pilot plant schematic diagram used in NFCP experiment series (A) and NFWP experimental series (B).

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].

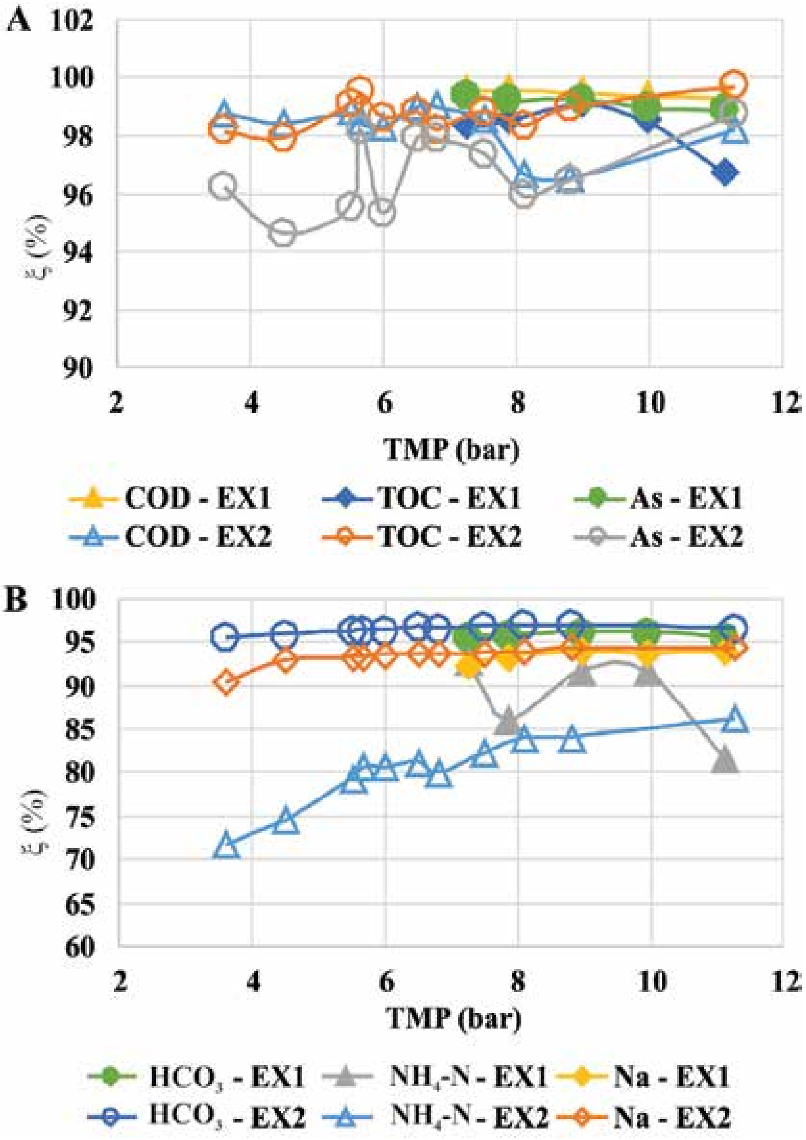

Figure 2. Transmembrane pressure influence on (A) COD, TOC, and total As and (B) bicarbonate ion, ammonium ion, and sodium ion removal efficiency.

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

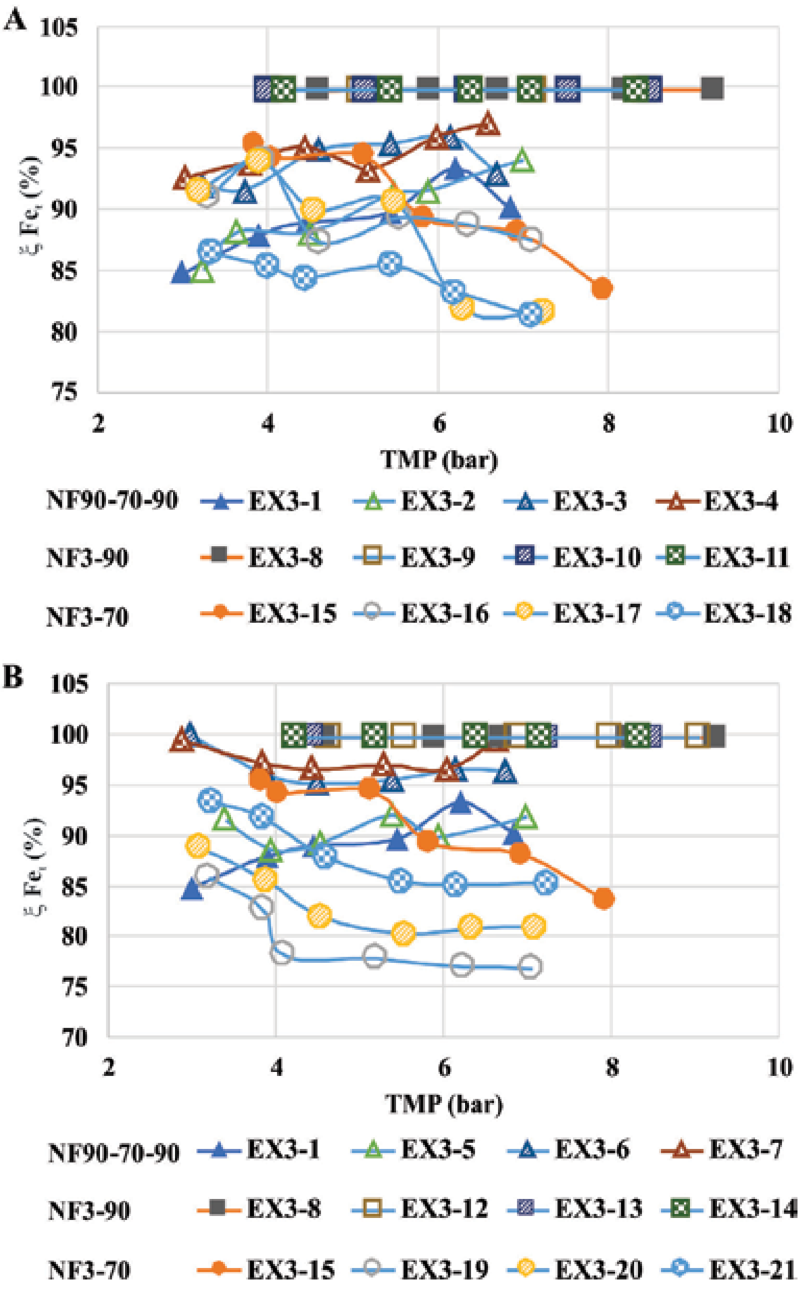

Figure 3. Influence of transmembrane pressure on iron removal from groundwater water (EX3-1, EX3-8, and EX3-15) and from groundwater with addition of CA solution (A) and Na4EDTA (B) with regard to NF membrane configuration.

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 $\xi_{\mathrm{Mn(II)}}$ increase proportional

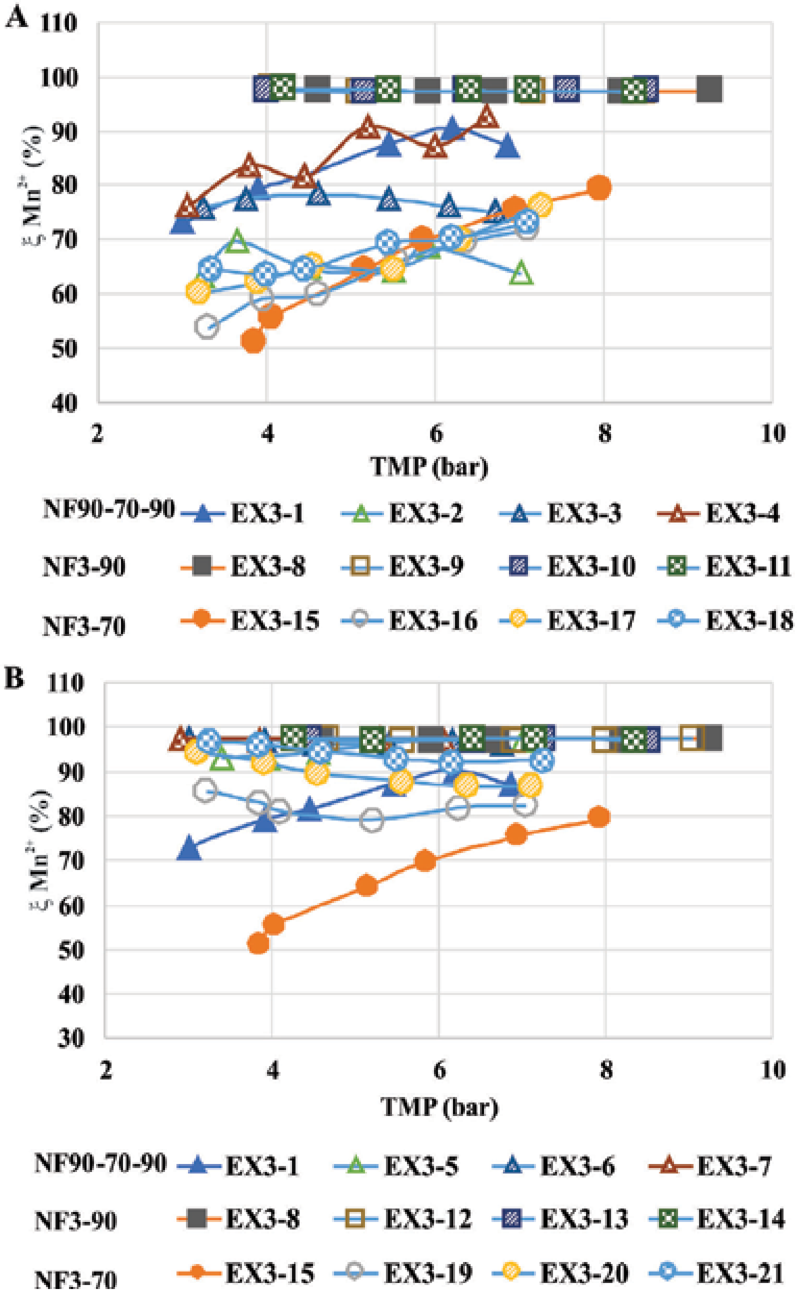

Figure 4. TMP influence on manganese removal from well water (EX3-1, EX3-8, and EX3-15) and well water with addition of CA solution (A) and Na4EDTA solution (B) in all experimental membrane configurations.

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.

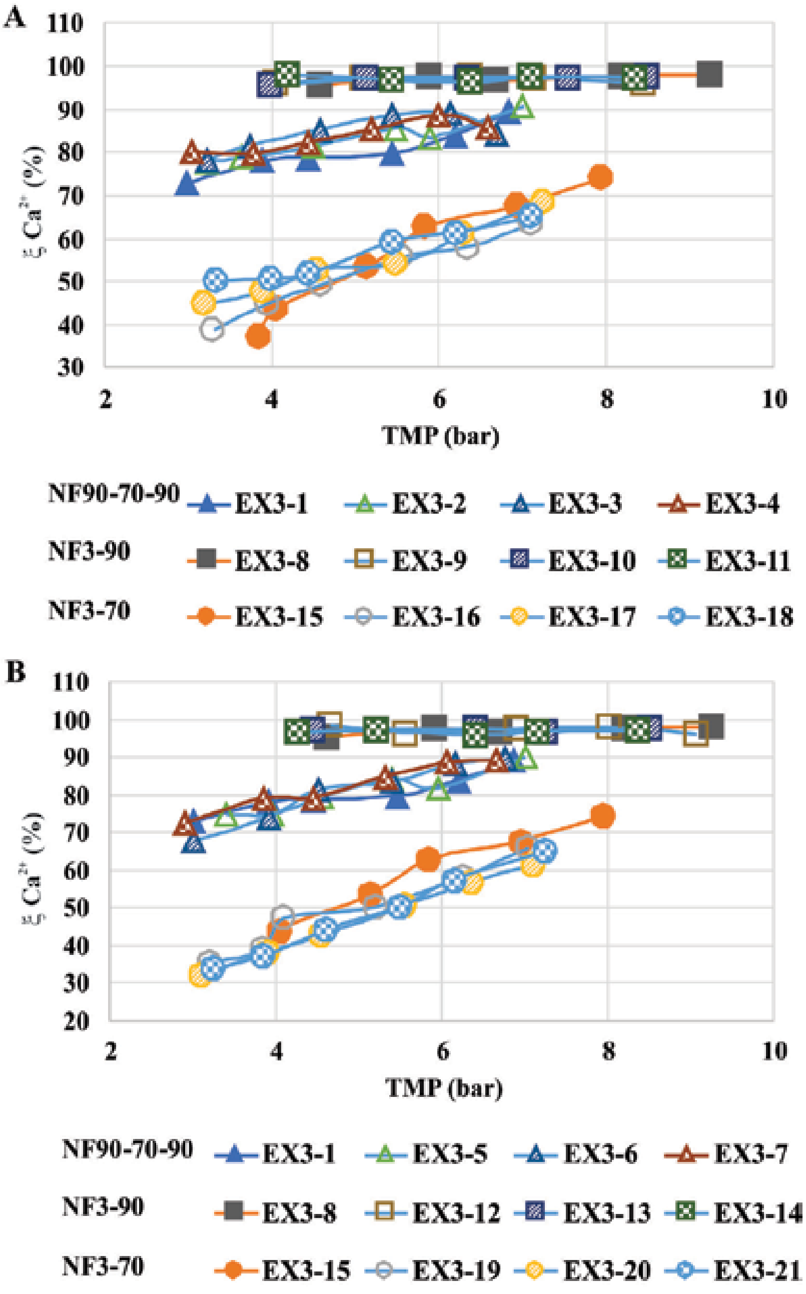

Figure 5. Influence of NF configuration on calcium ion removal efficiency from raw water (EX3-1, EX3-8, and EX3-15) and from raw water with addition of CA solution (A) and Na4EDTA (B) in the dependence of TMP.

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

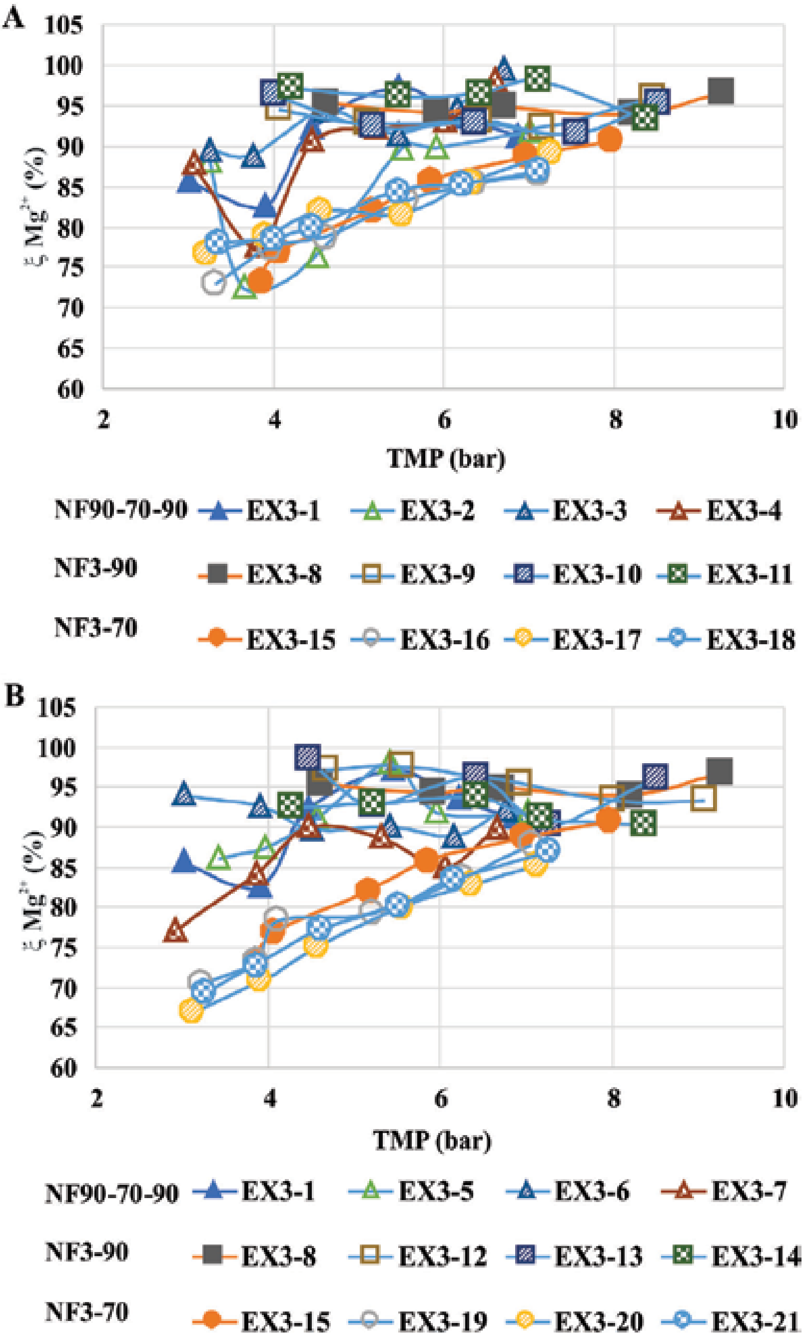

Figure 6. Transmembrane pressure influence on magnesium ξ changes with regard to NF membrane configuration. Experiment with well water: EX3-1, EX3-8, and EX3-15. Experiments with well water + CA solution (A). Experiments with well water + Na4EDTA (B).

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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Mick McGregor

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

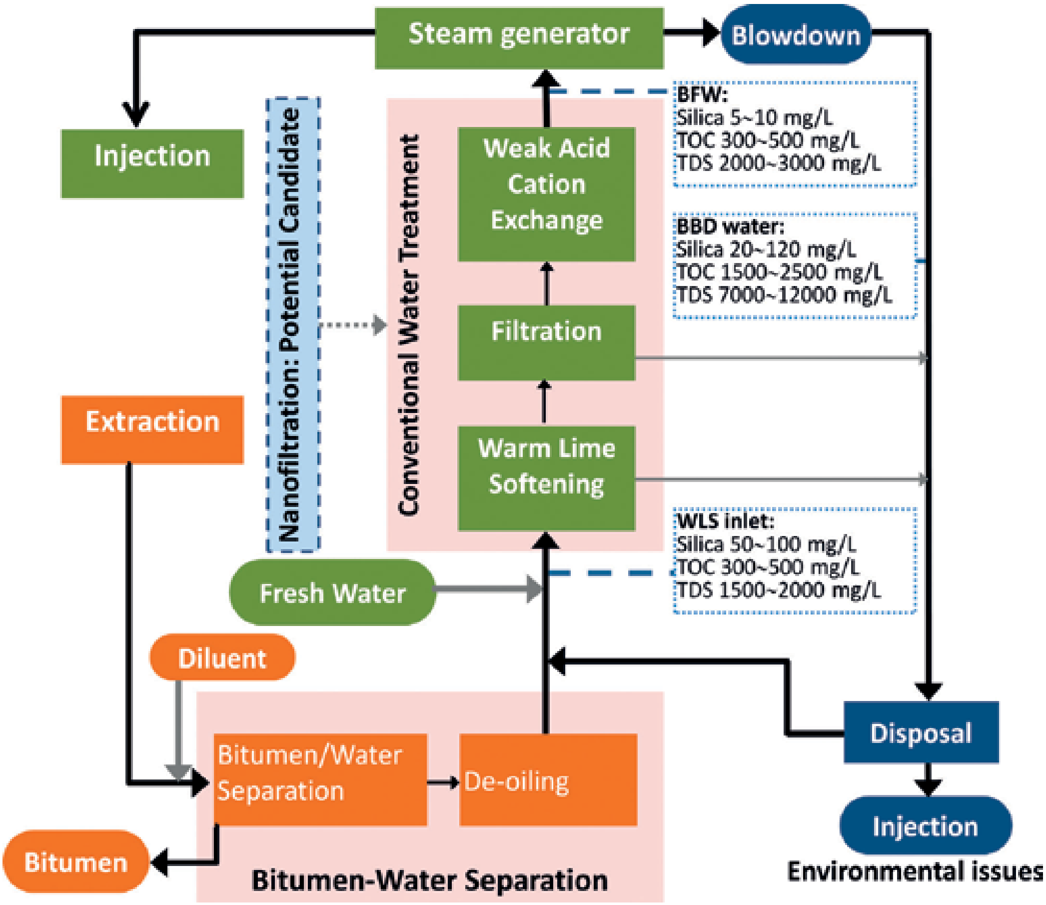

Figure 1. Main steps in SAGD-produced water treatment operations.

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.

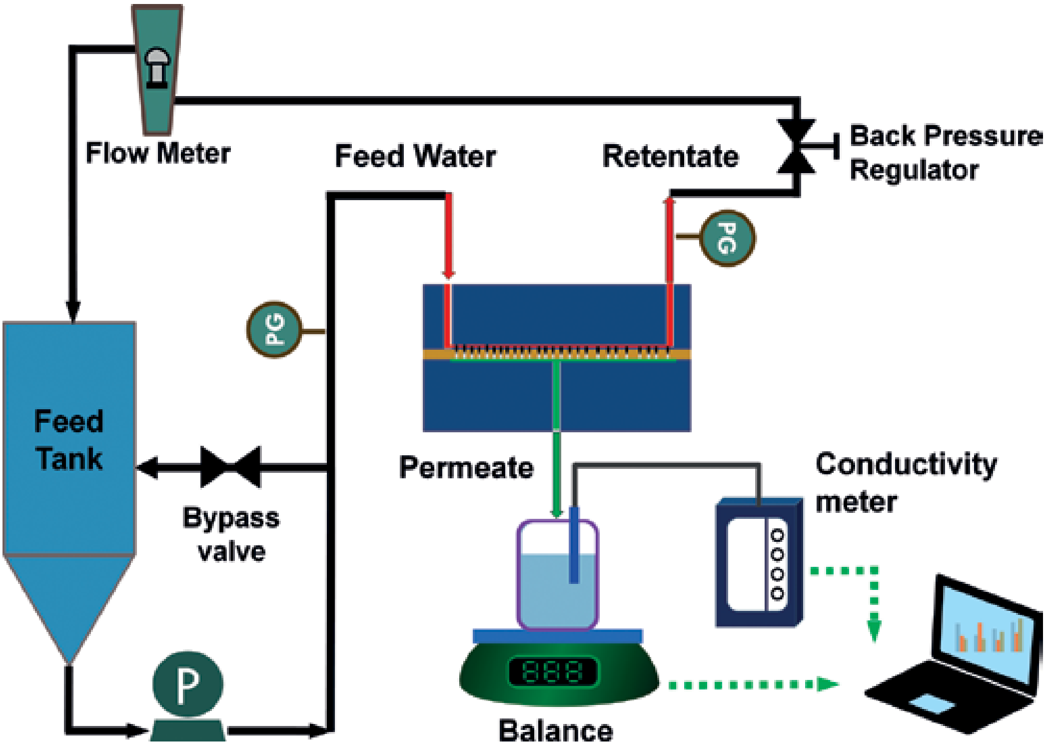

Figure 2. Schematic of a bench scale cross-flow NF setup.

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].

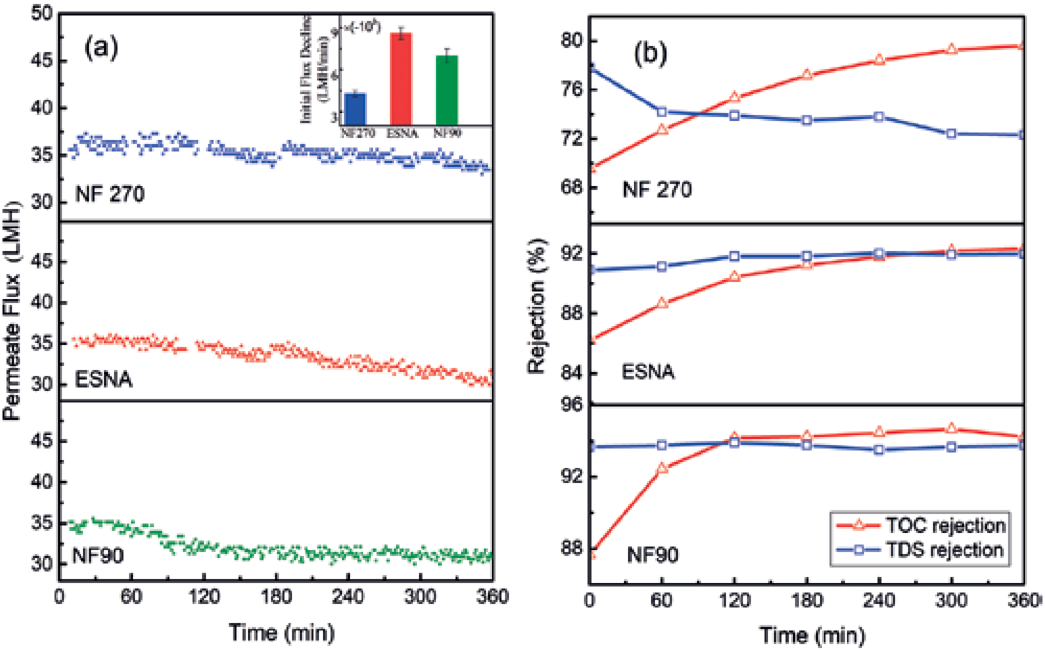

Figure 3. (a) Water flux over time and (b) TOC/TDS rejection for WLS inlet water filtration using NF270, ESNA, and NF90 membranes at pH 9.0 and 50°C [25]. Copyright 2016, Reproduced with permission from Balaban Desalination Publications, Rome, Italy.

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

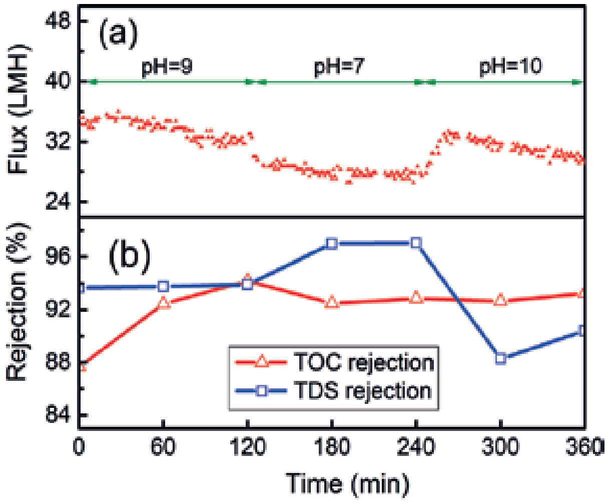

Figure 4. Effect of pH on performance of NF90 membrane for the filtration of WLS inlet water at 50°C [25]. Copyright 2016, Reproduced with permission from Balaban Desalination Publications, Rome, Italy.

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

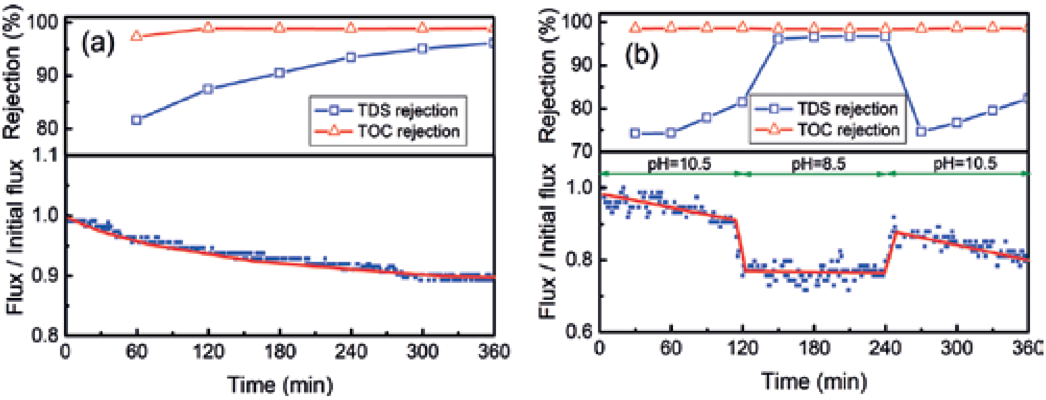

Figure 5. Water flux and TOC/TDS rejection for model BFW filtration using NF90 at (a) constant pH = 10.5, and (b) variable pH 10.5–8.5–10.5 at 50°C [5]. Copyright 2015, Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

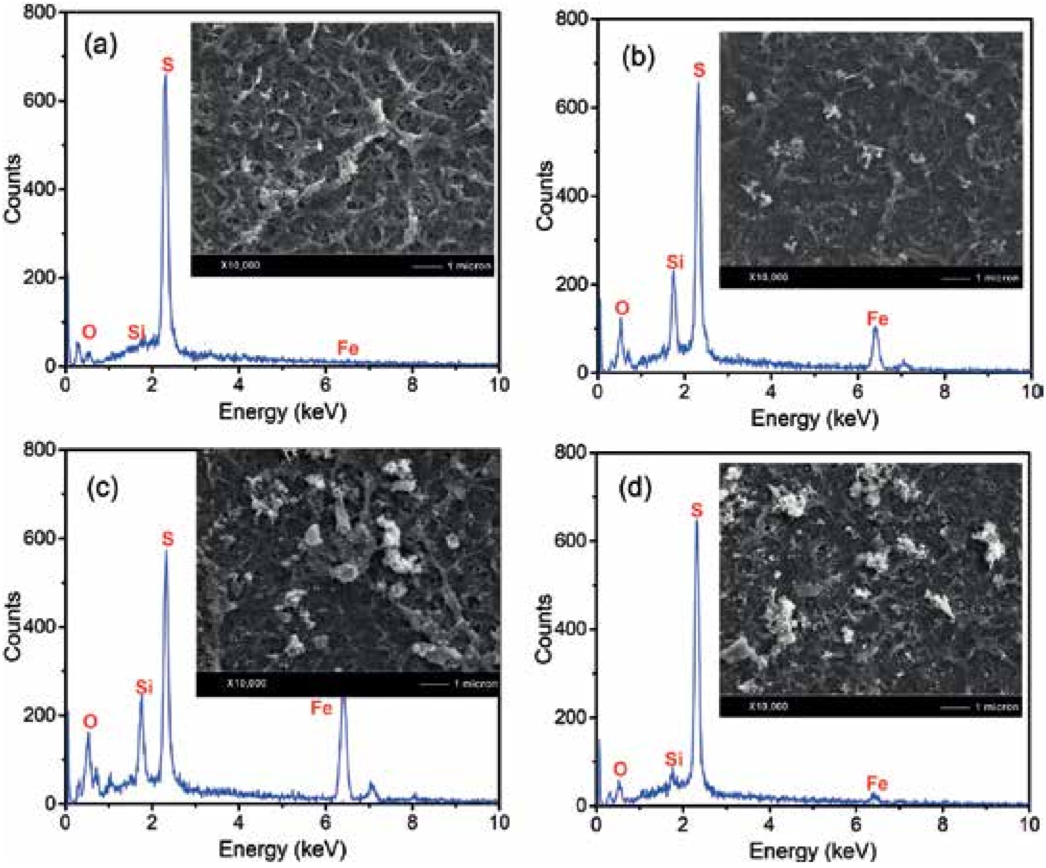

Figure 6. FESEM-EDX of (a) virgin membrane, and fouled membranes at (b) pH = 10.5, (c) pH = 8.5, and (d) pH = 8.5 then 10.5 [5]. Copyright 2015, Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

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.

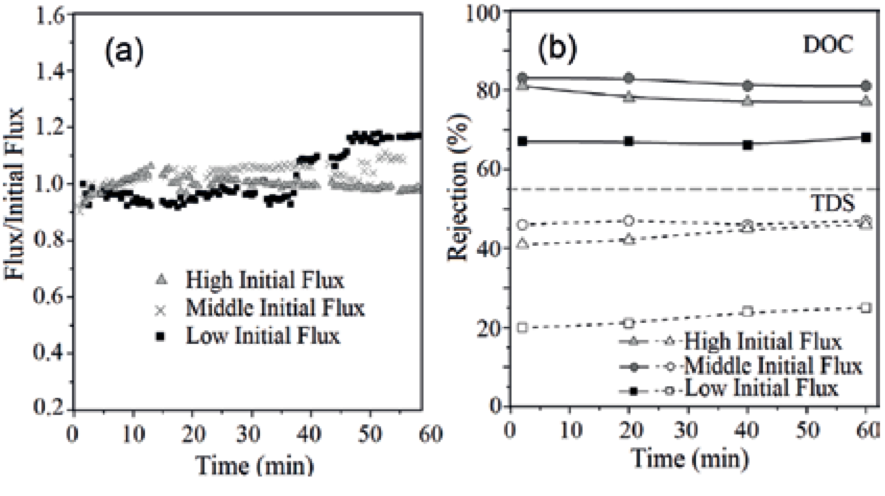

Figure 7. Effect of the initial flux on (a) the flux decline and (b) DOC/TDS rejection using 720 Da MWCO HYDRACoRe NF membrane at 70°C [29]. Copyright 2015, Reproduced with permission from ACS Publications, Washington, DC, USA.

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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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

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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

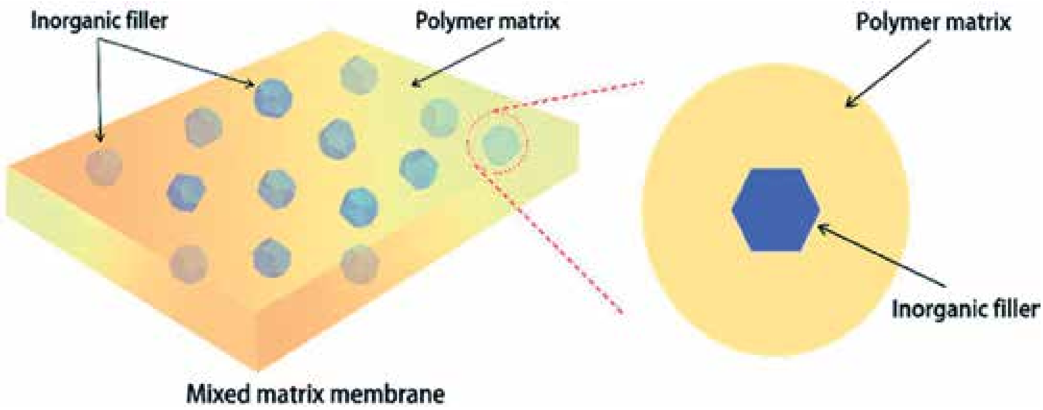

Figure 1. Schematic diagram of an ideal MMM structure [1].

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.

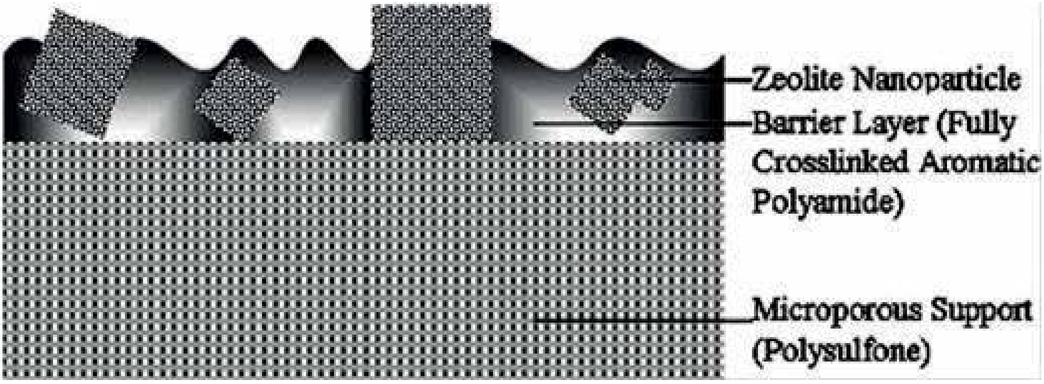

Figure 2. Schematic cross section of zeolite nanocomposite membrane (zeolite-MMM) [26].

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.

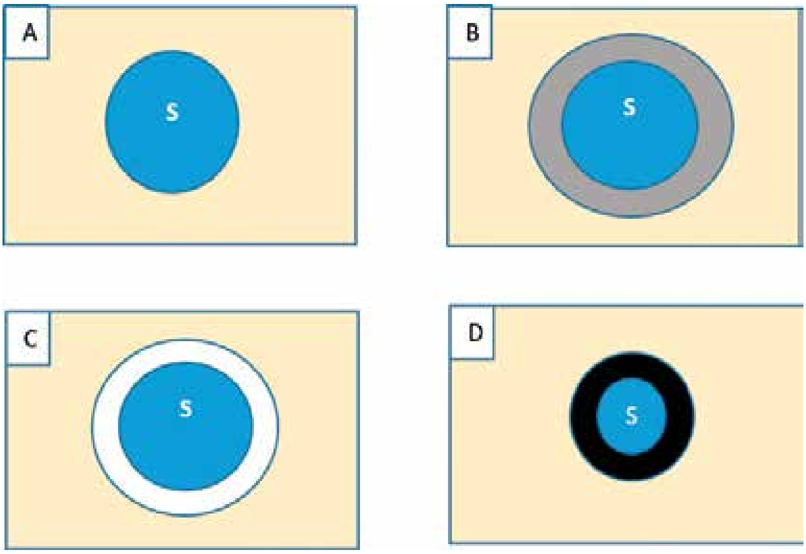

Figure 3. Illustration of various structures at the polymer-zeolite interface region [36]. (A) Homogenous blend of polymer and sieve (B) Rigidified polymer layer around the sieve. (C) Interfacial void around the sieve. (D) Sieve partial pore blockage.

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.

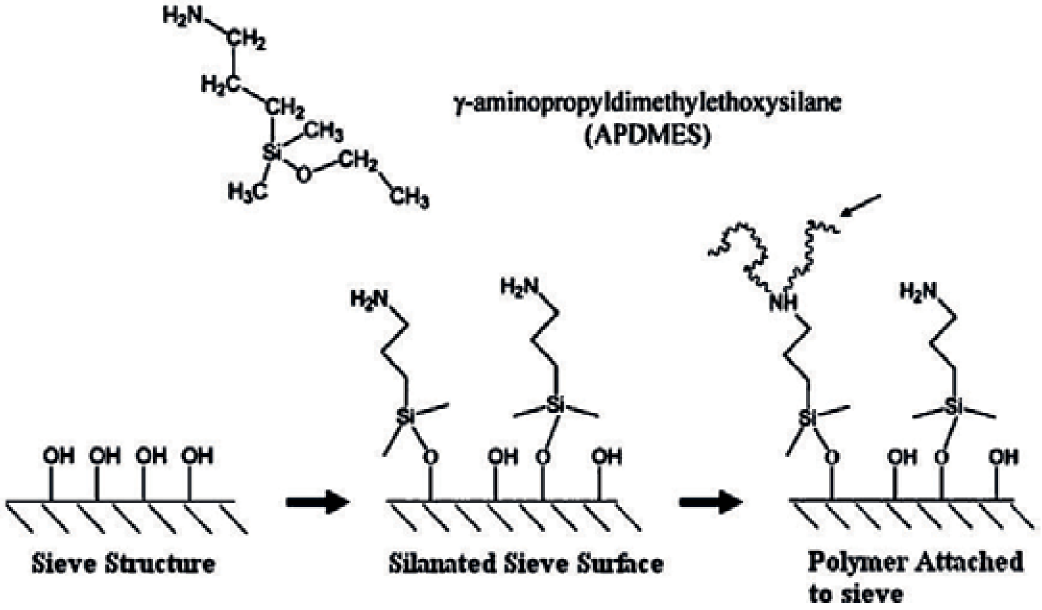

Figure 4. Schematic of the envisioned coupling reaction [45].

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

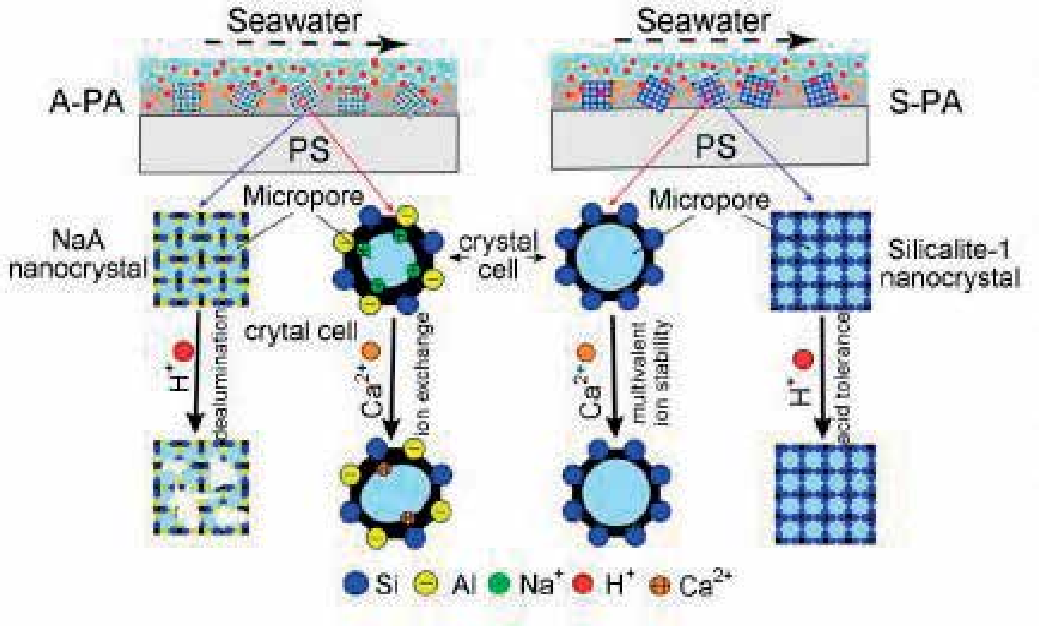

Figure 5. Schematic illustration of acid and multivalent ion resistance in thin-film nanocomposite membranes incorporated with NaA and silicate-1 zeolites [70].

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

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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.

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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

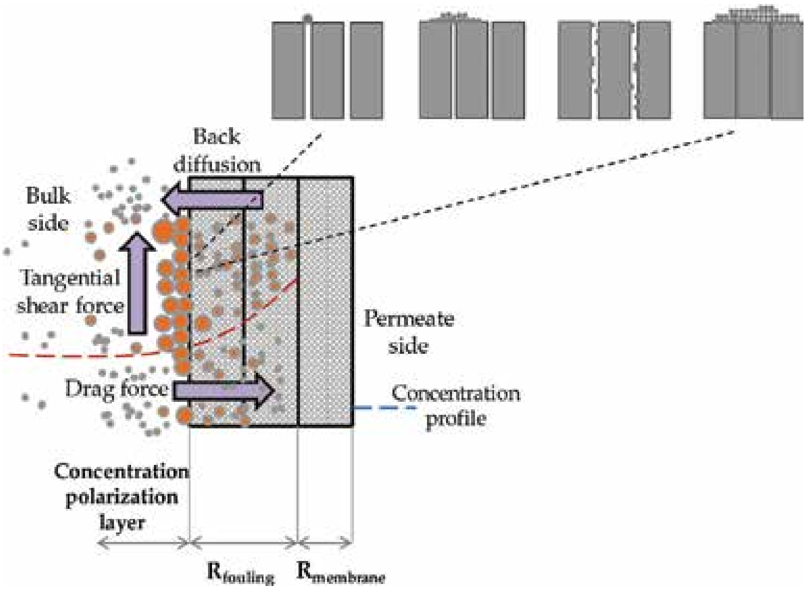

Figure 1. Concentration polarization and membrane fouling mechanisms during membrane filtration: from left to right, (i) pore sealing or complete pore blocking, (ii) intermediate pore blocking, (iii) standard blocking or pore filling/constriction, and (iv) cake or gel layer (adapted from Ochando-Pulido 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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Chapter 5

Nanofiltration Mediated by Surfactant Micelles: Micellar-Enhanced Ultrafiltration

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Additional information is available at the end of the chapter

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Abstract

Surfactant micelle-assisted removal of ions and organic solutes from aqueous media by micellar enhanced ultrafiltration (MEUF), which is a membrane separation technique, is discussed in detail. Following general information about micellar structure, counterion binding, substrate solubilization, and medium effect functions of micelles which enable separation of cationic or anionic ions and organic molecules from aqueous media by MEUF are explained in a comprehensive manner. Some of the recent studies on removing pollutants from wastewater effluents of industrial plants by MEUF, and their results have been summarized to inform about the factors affecting the removal efficiency of this technique. Methods for recovery of surfactant and contaminants from retentate or permeate solutions are also given. Selective separation of metal ions of the same charge from multicomponent solutions is another topic of this chapter. In this context, the last part of the chapter provides an overview on every aspects of ligand modified MEUF (LM-MEUF) process. This report comprises a comprehensive review of MEUF and LM-MEUF studies in the literature.

Keywords: surfactant micelles, micellar-enhanced ultrafiltration, removal of metal ions, removal of organic solutes, selective removal, separation of ions, pre-concentration, recovery, ligand modified micellar-enhanced ultrafiltration

1. Introduction

The topic of this chapter is the function of surfactant micelles in removal of ions and organics from aqueous solutions by membrane filtration. It is necessary to know about the micellar structure and properties to understand the function of micelles in this separation process.

Therefore, this chapter starts with the information about micellar structure and the mechanism of micellar effects.

It is well established that all the features of chemical reactions (rate, mechanism, pathway, product distribution, regio- and stereochemistry) can be altered by performing reactions in micellar media instead of pure bulk solvents. These alterations occur by the virtue of the medium effect of micelles. As a result of the medium effect, micelles can concentrate the reactants within their small volumes and mediate reactions, stabilize and orient substrates, intermediates, or products, so that ionization potentials and oxidation-reduction properties, dissociation constants, physical properties, quantum efficiencies and reactivities are changed. On this basis, micelles are called as "nanoreactors." Micelles act as mediators for reactions such that reactions of polar substances in apolar media or reactions of apolar substances in polar media can be realized in the presence of surfactant micelles [1].

Counterion binding and solubilization functions of micelles play a role in micellar-enhanced ultrafiltration (MEUF). On the other hand, medium effect of micelles is the main factor in ligand modified micellar-enhanced ultrafiltration (LM-MEUF) process. Therefore, two main processes that play the most important roles in removal of ions and organic solutes from aqueous media by MEUF, i.e., substrate solubilization and reactive counterion binding to micelles, as well as the medium effect of micelles which enables selective separation of ions and organics by LM-MEUF have been described in this section.

1.1. Micellar structure

Micelles are dynamic colloidal aggregates formed by surfactant molecules. Such molecules are amphiphilic in character, i.e., there are both hydrophilic and hydrophobic regions in their molecules. They have a long hydrocarbon tail and a small polar head group. Surfactant molecules are called as ionic (cationic and anionic), zwitterionic, or non-ionic, depending on the nature of their head groups. Their micelles are classified in the same way.

Surfactant molecules exist individually in the medium in dilute solutions. Such solutions have completely ideal physical and chemical properties. As surfactant concentration increases, their properties deviate gradually from ideality and at the concentration where aggregation of monomers into micelles occurs, a pronounced change is observed. This concentration is called the critical micellization concentration (CMC) [1].

CMC is experimentally determined by plotting a graph of a physical property of the surfactant solution as a function of concentration. A remarkable change is observed in the slope of the graph around the CMC.

Surfactants have characteristic CMC values under given conditions. However, small differences can be observed between the CMC values determined by different methods. Micellar aggregates have highly dynamic molecular structures. Therefore micelles in solution do not have a certain aggregation number and micellar solutions are polydisperse. Ion pairs or submicellar aggregates of surfactant molecules can form at concentrations below the CMC.

CMC values are affected by some factors such as temperature, the length of the hydrocarbon tail, the nature of the head groups and counterions, and by the existence of salts and organics in the medium.

The substances solubilized in the medium lead to a change in monomer-micelle equilibrium. Thus, CMC of the surfactant to be used in MEUF is changed in the feed solution (solute micellization concentration, SCMC). Therefore, it should be determined in the presence of other solutes in the feed solution such as the target ions, organic solutes, or ligands. But some researchers disregard this fact. They do not determine the SCMC of the surfactant in the presence of the other substances existing in the medium and discuss the results assuming that the CMC of the surfactant in the feed, retentate or permeate solutions is the same as that in deionized water.

Surfactants are used in MEUF and LM-MEUF processes in higher concentrations than their SCMCs, to ensure that the surfactant exists in the medium in concentrations high enough to form micelles.

In polar solvents such as water, surfactant monomers assemble to form a micelle in such a way that their hydrocarbon tails cluster in the core of the micelle such that they are shielded from water and polar head groups project outward into the polar bulk solution. Electrical charge on a micelle is neutralized in a large extent by counterions in the electrical double layer around it.

Micelles are small and spherical, rarely spheroidal, at concentrations close to CMC. As the surfactant concentration increases they increase in size, elongate, and become rod-like micelles when concentration exceeds the second CMC (about 7 CMC). This facilitates the passage of micelles through the membrane during MEUF process and causes to higher surfactant concentrations in permeate.

Aggregates can also form in apolar solvents. In such cases, head groups of surfactant molecules locate inside to form a polar core and hydrocarbon tails are directed toward the bulk solvent. This kind of micelle is called reversed (reverse) or inverted (inverse) micelle.

In this review, the term “micelle” stands for micelles in aqueous solutions (normal micelles) not for reversed micelles.

1.2. Mechanism of micellar effects exerted in MEUF and LM-MEUF

Micellar effects which play a role in MEUF and LM-MEUF processes can be classified as “concentration” and “medium” effects.

1.2.1. Concentration effect

Concentration effect arises from counterion binding and solubilization functions of micelles. As mentioned before, these are the main functions which enable the removal of ions and organic solutes from aqueous media by MEUF. Besides, increments in rates of reactions occurred in micelle nanoreactors are provided by the virtue of this effect. Reactive ions in the bulk solution electrostatically attracted to micelle and micellar solubilized substrate are brought into proximity within small volume of micelle. Thus, reactions occur between the micellar solubilized substrate and the bound counterions in the Stern layer. The frequency of molecular collisions increases as a consequence of close association of two reacting species at the micellar interface. This results in rate enhancement.

Reaction rates in micellar solutions are affected by all the factors affecting the extent of substrate solubilization and reactive counterion binding [1].

1.2.1.1. Counterion binding

One of the most important processes exerting micellar effects in both MEUF and LM-MEUF is the counterion binding to micelles. Micelles can either attract the ions in the medium or repel them depending on the electrical charge of their head groups. Sometimes, even reactive molecules are bound to micelles as their counterions.

Head groups of ionic micelles are generally about 30% ionized, i.e., 70% neutralized by the counterions in the Stem layer, at the CMC. The degree of counterion binding depends on several factors. There are values between 10 and 70% for ionization degree of micelles reported in the literature.

Micelles can bind the other ions in the medium beyond 30%, since there is a competition between the surfactant counterions that already exist in the solution and the other ions added to the medium, for the ionic head groups of micelles. Thus, displacements can occur depending on the nature of counterions and the other ions. The affinity of ions for the head groups increases with increasing ionic charge.

Counterions interact with the head groups not only electrostatically but also hydrophobically. Bulkier ions are preferentially bound by micelles. Some series have been reported for the relative affinities of ions to various micelles [1].

1.2.1.2. Micellar solubilization

Another fundamental process that plays a role in removal of substances from aqueous media by MEUF is their solubilization in micellar interiors. It is possible to solubilize the water-insoluble substances in aqueous micellar solutions.

They penetrate toward the hydrocarbon-like cores of the micelles. Since the solvent molecules penetrate beyond the polar head groups, solute in the solvent phase can interact both with the nonpolar chains of the surfactant molecules and with their polar head groups. Micellar core containing the hydrocarbon tails of surfactant molecules behaves like an organic phase. Therefore, hydrophobic forces play an important role in the solubilization process in micellar interior.

The opposite holds for reverse micelles, i.e., polar substances can be solubilized in reversed micellar media or in microemulsions that contain a water pool surrounded by polar head groups in the central region of reversed micellar aggregates.

One can utilize from solubilization of polar substances in reverse micelles to extract polar substances, even selectively, from their aqueous solutions in contact with an organic phase containing surfactant micelles. Conversely, water insoluble substances can be extracted from organic solvents into aqueous micellar solutions. These processes are called carrier-facilitated transport, where the micelle is the carrier.

Solubilized molecules interact with the polar head groups of a micelle and penetrate toward the core. They reside in the inner core, outer core, and palisade layer or between the polar head groups.

Sometimes micellar effects can also be observed as a result of the stabilization of molecules as counterions, i.e., without solubilization, with the substances not hydrophobic enough to be solubilized in the micellar interior [1].

1.2.1.2.1. Solubilization sites in micelles

Both electrostatic and hydrophobic factors play a role in determining the binding site of solute to the micelle. Therefore, both the structures of the surfactant and the solute are of great importance in determining the extent of solubilization and the penetration of solute into the micelles. If the hydrophobicity of one partner increases, the association constant of the solute increases and the solute penetrates deeper into the micelle.

Micellar-bound polar solutes reside largely in the Stern layer at the micellar surface. If the compound has both a polar and a hydrophobic end, i.e., if it is amphipathic like as the ligands used in LM-MEUF, the polar region orientates itself toward the head groups of the surfactant molecules, while the other end becomes involved with the hydrocarbon tails in the interior of micelle. For example, aromatic anions situate near the micelle/water interface. The aromatic section of the molecule is embedded in the palisade layer, while the charged parts are located near the micellar interface.

1.2.1.2.2. Factors affecting solubilization

The most important factor is the hydrophobicity of the surfactant and the solute. The more hydrophobic the solute, the higher the value of binding constant and deeper the penetration into the micelle occurs. The molecular weight of the solute, chain length and head group structure of the surfactant, temperature, and the existence of added ions in the medium are the other factors. The concentration of the solute and the pH of the bulk phase also affect the quantity solubilized [1–4].

1.2.2. Medium effect

This effect arises from a combination of charge, cage, preorientation, microviscosity and polarity effects. Selective removal of ions with similar properties by LM-MEUF process is provided by the virtue of this effect which can change properties of ligands associated with micelles via hydrophobic or electrostatic forces and so all the features of their complexation reactions.

Charge effect: surfactant micelles attract the ions of opposite charge and repel the ions of the same charge electrostatically. As mentioned above, when micelles attract, oppositely charged reactive ions mediate and catalyze a reaction. Conversely, in cases where micelles solubilize the substrate but repel the reactive ions of the same charge, the reactants are separated and, as a result, the reactions are inhibited. The ions which are attracted by micelles are retained by the membrane, while the ions repelled by micelles permeate through the membrane and pass into permeate during a MEUF process.

Cage effect: micelles can hold two reactive species together for a longer period of time than homogeneous solutions. As a result, the probability of reactions and hence the reactivity are increased.

Preorientational effect: the capability of micelles to solubilize substances in specific orientations is one of the most important factors that facilitates the reactions and provides control over regio- and stereoselectivity. A favorable location and the orientation of the substrate in micelles lead to an increase in its reactivity. Charged substrates reside in micelles with their charged groups directed toward the micellar interface. This location brings the substrate into close proximity with micellar bound reactive ions providing a favorable orientation to react with them.

Microviscosity effect: substrate molecules incorporated in micelles have less translational and rotational freedom, since microviscosity of micellar interior is much higher than the viscosity of homogeneous bulk solvent. This reflects in their reactivity, and in regio-, stereo- and product selectivity.

Polarity effect: for both bimolecular and unimolecular reactions, micellar environment leads to a reduction in the free energy difference between the ground state and transition state and can stabilize intermediates electrostatically, relative to the ground state. Low-polarity environment in a cationic micelle can decrease the free energy of a bulky anionic transition state with more delocalized charge, relative to that of the ground state such that the reactions are catalyzed. An anionic micelle can impose the opposite effect. For some reactions, electrostatic and hydrophobic interactions between the substrate and micelle may contribute to activation energies. Micelles that catalyze a reaction decrease the activation energy and entropy, while the inhibitory ones increase them [1].

2. Micellar-enhanced ultrafiltration

MEUF is such a technique that enables nanofiltration (NF) by use of ultrafiltration (UF) membranes. Drawbacks of NF and reverse osmosis (RO) high-pressure membrane processes which are used for removal of small ions and molecules from aqueous media can be overcome by MEUF. This is because MEUF does not require thick and expensive membranes, frequent replacement of membranes due to irreversible membrane fouling, application of high transmembrane pressure due to low water permeability of membranes, high energy consumption and accordingly high operational cost. Advantages of MEUF compared to NF and RO stems from the use of larger pore-sized UF membranes. Higher permeate flux can be achieved by UF membranes and, therefore, MEUF can be applied under low to moderate transmembrane pressures, membrane fouling is less problematic and can be overcome since fouling is mostly reversible. Pore sizes of UF membranes are too large to filter inorganic ions and small molecules but if they are combined with surfactant micelles, they can be filtered through UF filters with pore sizes small enough to reject micellar aggregates. This is the basic principle of MEUF.

MEUF is mostly applied for removal of heavy metal ion and organic pollutants from industrial wastewater streams, which are hazardous to human health and aquatic biota. Removal of pollutants from industrial wastewaters requires techniques applicable to large volumes of contaminated water. Various methods have been developed for this purpose. Of these, surfactant-based separation (SBS) processes have superiorities in simplicity and low cost compared to the other methods. MEUF is the most preferred SBS technique for removal of heavy metal ions and organics from wastewaters. It enables to treat large amount of wastewater which contains pollutants in considerably low concentrations. MEUF is applied in analytical and environmental science and also as a pre-concentration and recovery method.

This physicochemical technique which is highly effective in removing pollutants was first applied in the early 1980s [5]. It can also be utilized as a recovery method for pollutants since their concentrations in retentate are increased during MEUF process.

MEUF is based on binding of target ions and solubilization of organic pollutants by surfactant micelles. Therefore, a surfactant is added to polluted water in such an amount that it exists in the medium in concentrations higher than its CMC to ensure micelle formation prior to UFs. Micellar bound ions and apolar organics are removed by an ultrafiltration process carried out with membrane filters of low porosity that can retain micelles. Thus, the target ions and organic solutes which can normally permeate through ultrafiltration (UF) membranes are retained in the feed solution (retentate) during MEUF process since micelles with which they are associated cannot pass through the UF membrane pores.

The properties and concentrations of target ions and surfactants, solution pH, ionic strength, surfactant to pollutant mole ratio, filtration pressure, stirring speed, flow rate, and pore size and material of membrane are the factors which affect the removal efficiency of MEUF. The kind of surfactant to be used in MEUF depends on the nature of target ions. Anionic surfactants are used for removing cations, while on the other hand, anions can be removed using cationic surfactants.

The use of binary mixtures of surfactants in MEUF process can improve the retention of pollutants. Functionalities of surfactants can be increased by addition of another surfactant to the medium, i.e., by using a mixed micelle system. When two amphiphiles coexist in the same solution, mixed micelles or comicelles can form as a result of mutual solubilization. Ionic surfactants of like charges and nonionic surfactants form stable mixed micelles over a wide range of ratios. However, reversely charged surfactants can also form mixed micelles but only at certain ratios. Usually mixtures of ionic and nonionic surfactants are used in MEUF experiments. The presence of a nonionic surfactant in the medium leads to a decrease in the CMC of the ionic surfactant and accordingly to an increase in the number of micelles which are to bind the contaminant ions or molecules. Besides, micellar size is increased and micelles have a more rigid structure on mixed micelle formation. Thus, added nonionic surfactants enhance retention of target ions and organics during MEUF and may especially be suitable for use in MEUF studies carried out for simultaneous removal of ions and organics. Use of a nonionic surfactant may also lower the cost of MEUF process since they are cheaper than ionic, especially cationic ones. They also reduce the amount of surfactant monomers leaked through the membrane, by decreasing the surfactant concentration in the feed solution due to CMC lowering, and accordingly reduce secondary pollution by discharged permeates. On the other hand, concomitant use of nonionic surfactants with ionic ones may result in enhanced membrane fouling.

MEUF can be applied as a continuous process in ındustrial scale so as to handle larger volumes of effluents.

The retention factor R is the measure of the filtration efficiency in removing the target ion from the feed solution.

$$R\,(\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100 \qquad (1)$$

C_0 and C_p are the initial concentrations of the target ion in the feed solution and in permeate, respectively.

2.1. Removal of organics by MEUF

MEUF can be utilized in removal of organic pollutants discharged by industrial plants, which are all health hazards for living organisms. This can be provided by the virtue of solubilization function of micelles (Section 1.2.1.2). As mentioned in Section 1.1, hydrocarbon tails of surfactant molecules huddle in the core of a spherical micelle during micelle formation. As a result, micellar core which involves the hydrocarbon tails behaves as a hydrocarbon solvent. This enables solubilization of apolar substances in aqueous media by surfactant micelles via hydrophobic forces. Thus, organics incorporated into micelles in this way are not allowed to permeate through the MEUF membrane which retains micelles. Some examples of recent studies on the removal of organic solutes from industrial effluents by MEUF have been given below.

Phenolic compounds are the most studied organic pollutants in MEUF studies. Their main sources are petrochemical industry plants effluents besides those of many other industries such as petroleum refining, gashouse cooking, drug, plastic, paper and edible oil industry.

Olive mill wastewater (OMW) has a high organic content, mainly polyphenols. The main ingredient in OMW is hydroxytyrosol, it is followed by cinnamic, vanillic and protocatechuic acids and by the others. Polyphenols give phytotoxic, antibacterial, antioxidant, anti-inflammatory, anti-tumor and antiangiogenic properties to OMW. Therefore, besides solving an environmental problem; recovery of phenolic compounds from OMW to be used in food, cosmetics and drug industries has of importance but there appear only very few report in the literature in this field.

El-Abbassi et al. studied the efficiency of MEUF for the removal of polyphenols from OMW using sodium dodecyl sulfate (SDS) as the surfactant and hydrophobic poly(vinylidene fuoride) (PVDF) membrane. The rejection of polyphenols was between 5 and 28% by UF, but it reached 74% in the presence of SDS micelles at pH 2. Permeate from MEUF required 4.33% less chemical oxygen demand (COD) for oxidation than the initial COD and exhibited a color reduced more than 87%. The optimum conditions were 10 CMC SDS concentration, 4 bar transmembrane pressure (TMP) and pH 2 [6].

Huang et al. used polyethersulfone membrane and five kinds of surfactants with different hydrophobic tail length and hydrophilic head groups namely cetyltrimethylammonium bromide (CTAB), p-tert-octyl-phenoxy (9.5) polyethylene ether (TX100), octadecyldimethylammonium bromide (OTAB), cetylpyridinium chloride (CPC) and SDS. Cationic surfactants were found to be more effective than SDS and TX100, with very close efficiencies in the order OTAB > CTAB > CPC. Opposite order was valid for permeate flux.

Rejection of phenol with OTAB, CTAB and CPC micelles were 71.8, 68.9 and 61.5%, respectively, in the presence of 10 mM surfactant. Rejection increased up to 99% in the presence of 30 mM OTAB [7].

Gemini surfactants are also used for phenol removal. Gemini surfactants are a new class of self-assembling molecules. Gemini surfactants contain two hydrophilic head groups and two hydrophobic tails in their structure. The head groups are linked by a spacer. Their polarity depends on the structure of the linker. Spacer can be short (2 methylene groups) or long (12 methylene groups); rigid (stilbene) or flexible (methylene chain); and polar or nonpolar. They are characterized by very low CMC and surface tension values. Thereby they have excellent foaming and wetting properties. CMC values of gemini surfactants are lower up to hundred times than those of corresponding monomeric surfactants. Low CMC values of Gemini surfactants render them more efficient since the number of micelles formed at a certain concentration is higher than those of other surfactants. Thus, they enable to lower the surfactant concentration in the feed and thereby in the filtrate in a MEUF process. Besides, they interact with counterions more effectively compared to conventional ionic surfactants since they bear much more charged moieties in their structure. MEUF carried out using Gemini surfactants are designated as “GMEUF” in the literature.

Zhang et al. investigated the efficiency of cationic Gemini surfactant (CG), N1-dodecyl-N1,N1,N2,N2-tetramethyl-N2-octylethane-1,2-diaminium bromide and nonionic Brij-35 on phenol removal. Phenol retention increased with increasing surfactant concentration and reached a limiting value (90.8%) over 6 mM. They also studied effect of mixtures of CG and Brij-35 with fixed CG concentration (6 mM) and varying concentrations of Brij-35. Brij-35 decreased the CMC of CG and exerted a positive effect on separation performance. Phenol retention increased with increasing Brij-35/CG mole ratio (α). Phenol retention was increased with increasing Brij-35 content to R value of 96 at α value of 1.2. They also reported that the presence of a salt (Na_2CO_3) had a negative effect on phenol retention [8].

El-Abbassi et al. studied MEUF of different phenolic compounds namely p-coumaric acid (PCA), vanillic acid and tyrosol using SDS as the surfactant and polyethersulfone (PES) membranes (20 and 50 kDa molecular weight cut-off (MWCO)). They also studied recovery of SDS by precipitation with salts. R values increased with increasing SDS concentration reaching to the values 67, 66 and 51% for PCA, vanillic acid and tyrosol, respectively, at 10 CMC using a 50 kDa PES membrane. There is no data on R values that could be obtained by using 20 kDa membrane filters in the paper. SDS was recovered from the retentate by precipitating with KCl and $CaCl_2$ in the presence of p-coumaric acid. Effect of the concentration of these salts on the amount of precipitation was investigated by electrical conductivity measurements. Removal of SDS by precipitation did not lead to decreases in amounts of phenolics in the retentate. Not any % value for SDS recovery is given [9].

In another study of Huang et al., removal of p-nitrophenol (PNP), p-chlorophenol (PCP), p-cresol (PC) and phenol (P) was investigated in the presence of cationic, anionic and nonionic surfactants.

As expected, the best result was obtained with cationic CPC. The separation efficiency and distribution coefficient of phenolic compounds in micelles was in the order PNP > PCP > PC > P. Their values increased in the order CPC > sodium dodecylbenzene sulfonate (SDBS) > TX100. In the presence of 4 mM CPC, removal efficiency of PNP was about 75% [10].

Liu et al. studied MEUF of phenolic compounds resorcinol, phenol and 1-naphthol which have high solubility in aqueous media, using a mono-rhamnolipid anionic biosurfactant and a hollow fiber polysulfone membrane with 10 kDa MWCO. Retentate concentration of these compounds increased with increasing pH, transmembrane pressure and surfactant concentration following the order resorcinol > phenol >1-naphthol. Dependence of their permeate concentrations on these parameters followed the reverse order [11].

Biosurfactants are environmentally compatible, biodegradable, non-toxic and economic surfactants effective at very low concentrations. They were shown to absorb metal ions and solubilize organics and can be used over a wide range of pH and temperature. It was also shown that they can be recovered from MEUF retentate. Secondary pollution problem which arises with synthetic surfactants because of the leakage of surfactant molecules into permeate, can be solved with their use in MEUF.

Removal and recovery of phenolic compounds from the effluent of olive oil plants was studied by Víctor-Ortega and his collaborates. They used cationic Esterquat, anionic dodecylbenzenesulfonic acid (DBSS) and nonionic Lutensol AO7. A cationic surfactant was used for the first time in MEUF of OMW and they achieved best retention (>90%) in the presence of Esterquat micelles at 5 CMC and 4 bar TMP. They investigated effect of some other factors on R values for a phenolic mixture composed of 3,4,5-trimethoxybenzoic, 4-hydroxybenzoic, gallic, siringic, vanillic and trans-cinnamic acids; besides the nature of the surfactant; such as transmembrane pressure, pH, surfactant concentration, mole fraction of Lutensol AO7 in its mixtures with ionic surfactants. Addition of nonionic surfactant had no remarkable effect on R value except for a small increase about 4% due to decreasing of CMC of the cationic surfactant [12].

Husein et al. compared the performance of TiO_2 ceramic ultrafiltration membranes with 8, 15 and 50 kDa porosity in removal and recovery of four acyclic naphthenic acids and a mixture of cyclic and acyclic naphthenic acids (NAs) with carbon number ranging from 11 to 18, by MEUF, with that of polymeric PAN membrane using CPC as the surfactant. Ceramic membranes could be preferable in MEUF process due to their stable performance at elevated temperatures and resistance toward the corrosive chemicals. But they observed lower permeate flux and recovery values with ceramic membrane compared to polymeric membrane. On the other hand, ceramic membranes exhibited very good performance in terms of concentration polarization and fouling layer resistances [13].

Tortora et al. studied removal of tetramethylammonium hydroxide from synthetic wastewater of electronic industry.by MEUF. They used two tubular ceramic membranes with different porosity. They achieved 99.75% R value with 1 kDa MWCO membrane [14].

Dyes are also organic pollutants. Removal of dyes is one of the most studied research topic of MEUF. Main source of dyes leading to environmental pollution is textile industry. All the other industries in which dyes are used contribute to environmental pollution. Dyes are not biodegradable because of the complicated aromatic nature of their structures and there are health hazards. Therefore their removal from wastewaters is of vital importance.

There appear a number of MEUF studies in the literature, carried out for removal of cationic dye methylene blue (MB). MB is used in paint production, wool dyeing, microbiology, and as a sensitizer in photo-oxidation of organic pollutants. Khosa et al. studied MB removal using SDS, CTAB, TX100 surfactants and regenerated cellulose membrane filters. They achieved 99% R in the presence of SDS micelles [15]. They reported R values of 98.8, 13 and 53 for anionic alizarin red S (ARS) removal in MEUF processes carried out following a complexation-precipitation process with Cu(II) salt; in the presence of CTAB, SDS and TX100, respectively [16]. Khosa and Shah also investigated the effects of cationic surfactants CTAB and CPC on removal of anionic reactive black 5 (RB-5) using 5,000, 10,000 and 30,000 MWCO membranes under 1 and 1.5 bar TMP. They reported that CTAB was more effective than CPC and provided R value of 98% under 1.5 TMP [17].

Huang et al. carried out several studies to remove MB by MEUF. They used polysulfone hollow fiber membranes in the experiments. They studied the effects of dye and surfactant concentrations, temperature and additional salts. They reported that the addition of NaCl improved the dye and SDS concentrations in the retentate and reduced their concentrations in permeate significantly [18].

Textile plants also discharge heavy metals to the environment. Both heavy metals and dyes are very toxic to living organisms. They are reported even to be carcinogenic. On the other hand, the presence of inorganic ions in the medium enhances the rejection of dyes during MEUF process by lowering the CMC of the surfactant, which results in increased micelle concentration. In addition, metallic ions can form water insoluble complexes with dye molecules. These complexes can be filtered through a filter paper. Thus, a significant amount of dye can be removed by precipitation. Therefore, sometimes, metal ions which form complexes with dye molecules are added to dye solution prior to MEUF process.

Khosa et al. investigated the removal of MB, RB-5 and ARS depending on the nature and concentration of surfactant and membrane MWCO. They reported 99% removal of MB in the presence of SDS micelles, 99% removal of RB-5 and 98.6% removal of ARS in the presence of CTAB. Following addition of Zn(II) ions, they could remove 47% of ARS by the filtration of precipitated ARS-Zn complex. On the other hand, they could remove 98% of ARS by MEUF carried out in the presence of CTAB utilizing from micellar solubilization of ARS-Zn complex [19].

In another research of Huang et al., simultaneous removal of MB and Cd(II) ions were studied with mixed surfactant systems composed of SDS and TX100. They observed that the addition of TX100 enhanced the retentions of both MB and Cd(II) ions and the presence of MB enhanced the Cd(II) rejection [20].

Hussain et al. investigated the removal of reactive blue 19 (RB-19) in the presence of two cationic surfactants (CTAB and ethyl hexadecyl dimethyl ammonium bromide (EHAB)) and with membranes of different MWCOs (5, 10 and 30 kDa). The highest R value was obtained in the presence of CTAB. The higher R values were obtained with the membrane of 5 kDa MWCO because of the retention of large RB-19 molecules by the membrane itself. Micellar effect could be observed with the membranes of larger MWCOs. The role of surfactant micelles in removal could be observed with membranes of 10 and 30 kDa MWCOs. The retention was 39.61 and 96.85% in the absence and presence of surfactant, respectively, with membrane of 30 kDa MWCO. They suggested use of a membrane with MWCO of 10 kDa. İncreasing the membrane MWCO exerted a negative effect on rejection. They achieved the larger R value in the presence of CTAB (99.62%) under 1.5 TMP [21].

Batik wastewater contains reactive dyes such as remazol, indigosol, napthol, benzene, rapid and phenol in high concentrations, sodium salts, wax, chrome, ammonia and solid content. Aryanti et al. investigated decontamination of batik wastewater using CPC as the surfactant. They compared the performances of ultrafiltration (UF) and MEUF and showed the superiority of MEUF in the removal of ammonia and showed that MEUF decreased the chemical oxygen demand indicative of dye-micelle binding. MEUF was found to be superior to UF also in terms of decreasing the total suspended solids [22].

In another study of Hussain et al., the removal of anionic sunset yellow (SY) was investigated in the presence of CTAB and EHAB. They suggested use of a membrane with 10 kDa MWCO and CTAB (R = 99.94) under 1.5 TMP [23].

2.2. Removal of heavy metals

Heavy metals are the elements with high atomic weights which exist at third and higher numbered periods of the periodic table. "Heavy" term stems from their high-specific gravities which are larger than five times of that of water, i.e., larger than 5 g/cm^3. They are environmental pollutants widely distributed to the environment because of their use in many kinds of industrial (fertilizer, paper, pesticide, tannery, etc.), technological, medical, mining, smelting, domestic and agricultural applications. Environmental pollution problems are caused by mainly lead, cadmium, mercury, arsenic, chromium, silver, platinum group elements, iron, zinc, nickel and cobalt. They can reduce the quality of life or even cause death depending on their concentrations in water. When their concentrations exceed the limits, health problems arises. Though some of them are essential for living organisms in very low concentrations, heavy metals are mostly regarded as toxic elements and included in the US EPA (US Environmental Protection Agency) priority pollutant list. They are hazardous to man's health and aquatic biota over concentration limits mainly because they are potent enzyme inhibitors and exert toxic effects on organisms. They compete with essential metals, which are necessary and functional for human health, for binding sites of proteins and thereby for those of enzymes which are of protein structure. Therefore, water which is of vital importance for survival of human beings and for other living organisms should be purged of heavy metals. Arsenic, mercury, cadmium, lead and chromium are the most toxic ones. These cause organ damages even at low exposure. The US EPA and the International Agency for Research on Cancer reports these metals also as carcinogens. Heavy metals are not biodegradable and cannot be discharged from organisms by metabolic route. Therefore, they accumulate in organs, i.e., they are bioaccumulative.

The most preferred technique to remove heavy metals from industrial wastewaters is MEUF. MEUF is carried out by using anionic surfactants, so that counterion binding function provided by the charge effect of micelles can be utilized to bind metal ions to micelles. However, metal cations can be removed also by the use of cationic surfactants, via LM-MEUF process.

Liu and Li studied the removal of Cu(II) ions by MEUF using SDS + TX100 mixed surfactant system and a hydrophilic membrane of 10 kDa porosity. They could remove 94% of Cu(II) content at TX100 concentrations higher than its CMC. TX100 favored micelle formation by decreasing CMC of SDS and lead to increase in micelle size by incorporating into micelle structure. As a result, SDS concentration in permeate was minimized. TX100-enhanced membrane fouling but it was reversible and could be cleaned easily by ultrasonication in water [24].

Rahmanian et al. studied MEUF of zinc(II) using regenerated cellulose spiral-wound membrane with 20 kDa MWCO. Spiral wound membranes are used in various industries because of its compact structure and low cost. The use of spiral wound membranes in MEUF has been shown to be feasible. Spiral wound UF module can be operated in linear continuous and cross-flow modes which have higher flux and membrane effective area compared to batch cell system. They achieved 98% Zn rejection in the presence of SDS in a concentration of 6 mM under 2 bar TMP. Such a high retention can be attributed to the decrement in CMC of SDS in water, caused by the presence of Zn(II) ions. They also carried out MEUF experiments in the presence of SDS-Brij35 mixed surfactant system, and in the presence of EDTA with the consideration that electroplating industry effluents contain ligands, mainly EDTA. They reported an optimum Brij35/SDS mole ratio of 0.5 to achieve maximum Zn(II) rejection to prevent membrane fouling and further decrements in permeate flux. They also reported that ligand imposed a negative effect on Zn(II) rejection [25]. The presence of EDTA could be turned into an advantage by using a cationic surfactant such that MEUF was carried out as LM-MEUF.

El Zefatwy and Mulligan used a rhamnolipid biosurfactant (JBR 425) for simultaneous removal of copper, zinc, nickel, lead and cadmium from six effluents of metal-refining industries using hollow-fiber ultrafiltration cartridges containing polysulfone membrane tubules with MWCO of 10 and 30 kDa. They determined optimum conditions by the response surface methodology and validation experiments as 69 ± 2 kPa TMP, 25 ± 1°C, pH 6.9 ± 0.1, and the surfactant: metal ion mole ratios as 2.5:1 (Cu), 2.6:1 (Zn), 2.3:1 (Ni) and 4.3:1 (Cd). They could achieve >99% rejection under optimum conditions. MWCO of the membranes did not affect the rejections practically indicating that the sizes of rhamnolipid micelles were larger than 30 kDa [26].

Landaburu et al. studied simultaneous removal of Cu(II) and Cd(II) ions from phosphorosus rich synthetic wastewater containing phosphorous, zinc and nickel using 10 kDa regenerated cellulose membranes. Existence of zinc and nickel had no effect but pH and feed concentrations of SDS and phosphorous affected the MEUF results. In the absence of phosphorous, R values over 98% were achieved. Phosphorous affected negatively rejection of both metal ions being more remarkable for Cu due to complex formation at high pHs. Experimental and theoretical results suited quite well [27]. In a similar study which they carried out later, R values of 87.1, 85.1, 84.3 and 75.0 were achieved for Zn(II), Ni(II), Cd(II) and Cu(II), respectively [28].

Simultaneous removal of Cu(II) and Cd(II) ions from phosphorous-containing wastewaters of a fertilizer plant was also studied by Hayrynen et al., in a cross-flow semi-pilot scale equipment using a 10 kDa spiral-wound PES membrane. They achieved rejections around 86 and 80% for Cd(II) and Cu(II) ions, respectively [29].

Oxyethylated fatty acid methyl esters are environmentally safe surfactants obtained from renewable natural sources. The fact that they have low CMC values imposes positive effect on R values. Staszak et al. studied removal of Cr(III) ions by MEUF using anionic SDS and nonionic Rofam 10 which is a product obtained by ethoxylation of methyl esters of rape-seed oil fatty acids, and their mixtures as the surfactants. Cellulose acetate, PES and polyvinylidene fluoride membranes were used. They compared the results of UF and MEUF experiments. R values obtained from UF experiments were below 25 for all three membranes, while R values between 90 and 95 were obtained in MEUF experiments depending on the SDS concentration, regardless of the membrane type. SDS was much more effective than nonionic surfactant. However, higher R values could be obtained by use of SDS-Rofam 10 mixture: they could achieve R values close to 100 [30].

In a study of Abbasi-Garravand and Mulligan, a rhamnolipid (JBR 425) was used as a biosurfactant and a reducing agent, using a polysulfone hollow fiber membrane with 10 kDa MWCO to remove Cr(III) and Cr(VI) ions. Chromium is utilized in many industries such as electroplating, leather tanning, metal finishing, nuclear power and textile plants. From the point of view of environmental pollution, Cr(VI) is more toxic than Cr(III) and it has a high oxidation potential. They reduced Cr(VI) to Cr(III) with rhamnolipid surfactant at different pHs prior to MEUF. They reported pH 6 as the optimum pH for reduction of Cr(VI) both in the presence and absence of rhamnolipid. The highest rejection (96.2%) was achieved at rhamnolipid/Cr(III) molar ratio of 36:1 [31].

Schwarze et al. used nonaoxyethylene oleylether carboxylic acid R090 as the surfactant, which can be anionic or nonionic depending on the pH of the medium and has a lower CMC than that of SDS. It formed larger micelles than SDS, which can be filtered with membranes MWCO of ≥10 kDa. Regenerated cellulose, PES and polysulfone membranes with different MWCO porosities were used. They achieved >95% removal efficiency for six metal ions, R values being in the order $Fe^{2+} \sim Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Mg^{2+}$. They reported the optimum R090 to metal ion molar ratio as 10 ± 1 [32].

Tortora et al. studied removal of nickel, cobalt, chromium, and zinc ions by MEUF using a monotubular ceramic membrane (zirconium oxide) of 210 kDa MWCO and SDS. Ceramic membrane was chosen because of its durable structure. They carried out the MEUF experiments in a tangential flow laboratory pilot plant. They stated that the highest R values (Co(II): 88, Ni(II): 87, Cr(III): 80, Zn(II): 79) was obtained below CMC, but 4 mM is a concentration higher than the CMC of SDS in the presence of metallic ions. One of the reasons for low R values may be high porosity of the membrane [33].

Huang et al. studied pH effect on removal of Pb(II), Cd(II), Zn(II) and Cu(II) by MEUF. They used a hydrophilic polyethersulfone membrane (10 kDa) and SDS (8 mM). The visual MINTEQ ver. 3 was used for theoretical calculations. Higher R values were obtained at pHs between 3 and 12 for Cu (II) and Cd(II), while the optimum range was 3–10 for Zn(II) and Pb(II). At high pHs, hydroxide formation and precipitation contributed to R values while removal efficiency of MEUF was decreased. In the presence of Pb(II), Na^{+} counterions were replaced by Pb^{2+} ions and DS-Pb(II) salt precipitation was also observed. R values for Cu(II), Cd(II) and Zn(II) ions decreased with increasing metal ion concentration. On the other hand, the effect of increments in Pb(II) concentration depended on Pb(II) concentration. They reported optimum Cu(II) and Zn(II) feed concentration to be 150 mg/L while optimum feed concentrations of Cd(II) and Pb(II) were reported to be 300 mg/L [34].

2.3. Simultaneous removal of organics and heavy metals

Wastewaters from chemical and petrochemical industries such as textile, dye, paint, coal refining, fuel processing, battery, metal finishing and electroplating contain both organic and heavy metals. Coexistence of heavy metals and phenolic compounds in industrial effluents is the most encountered case. Heavy metals and organic solutes in the medium affect the removal efficiencies of each others in a MEUF process [35].

Separate and simultaneous removal of MB and Cd(II) ions was studied by Zeng et al. using SDS and hydrophobic polysulfone hollow fiber membrane with MWCO of 10 kDa. They reported R values of 99.2 and 99.9 for Cd(II) and MB, respectively, for single component solutions. Higher R values for Cd(II) was achieved in the presence of MB when SDS concentration was below 1.0 CMC, but removal efficiency of Cd(II) decreased above this SDS concentration. Maximum R value for Cd(II) in the presence of MB was 98.4. R value for MB decreased to 96.5 in the presence of Cd(II) ions. Cd(II) removal from binary solutions increased sharply with increasing pH, but a remarkable effect of pH on MB removal was not observed. R value for MB increased at pHs > 7 [36].

Li et al. studied simultaneous removal of Cd(II) ions and phenol using SDS and its mixtures with TritonX100 as the surfactants. They used polysulfone hollow fiber membrane with MWCO of 10 kDa and a cross-flow ultrafiltration unit. In the presence of 8.0 mM SDS, R values were 97.0 and 40.0 for Cd(II) and phenol, respectively, in simultaneous removal. In the mixed SDS/TX100 systems, R values depended on the mole ratios of surfactants. Maximum R value for Cd(II) was 91.3, while a R value of 42.4 could be achieved for phenol. Permeate surfactant concentration was found to be lower than that observed when SDS was alone in the medium [37].

Tanhanei et al. reported simultaneous removal of aniline and Ni(II) ions which coexist in dying ındustry effluents, by MEUF carried out in the presence of SDS, using polysulfone UFX5 (5 kDa), PES NP010 (1 kDa) and another polysulfone (PS) membrane prepared by the authors. They reported the best R values for aniline and nickel as 97 and 70, respectively, with UFX5-pHt membrane. They studied the effect of membrane size on R values and permeate flux. They observed that coexistence of nickel ions enhanced aniline rejection regardless of SDS concentration while the presence of aniline enhanced nickel rejection in low SDS concentrations but decreased at SDS concentrations over 4.8 mM. They reported that both aniline and nickel caused to increase in micellar dimensions. They could achieve R values of 99 and 64 for nickel and aniline, respectively, in SDS-Brij35 mixed surfactant solution. R values over 90 were achieved using NP010 membrane in the presence of 16 mM SDS. The reason why the highest R values were obtained with NP010 membrane may be its smaller pore size [38].

Verma and Sarkar studied simultaneous removal of Cd(II) and p-Cresol by MEUF using a rhamnolipid biosurfactant and 10 kDa flat sheet PES membrane. The process was optimized using the response surface methodology. Maximum R values were 98.8 and 25 for Cd(II) ions and p-Cresol, respectively, in the presence of 370 mg/L surfactant at pH 7.8. The R value of p-Cresol in single component solution was 23. On the other hand, the presence of p-Cresol did not affect the R values of Cd(II) ions. They compared the results with those obtained in the presence of SDS. The experiments gave slightly higher rejections of both Cd(II) and p-Cresol with R values of 99.4 and 23.9, respectively [39].

2.4. Removal of anions

Cationic surfactants are used for the removal of anions by MEUF so that charge effect of surfactant micelles can be utilized.

Gzara and Dhabbi studied the removal of chromate anions (CrO_4^{2-}) from aqueous streams using CTAB and CPC, and 10 kDa polysulfone membranes in a tangential cell. Rejection was found to depend on ionic strength and pH of the medium besides surfactant concentration and TMP. Increase in ionic strength caused to decrease the retention of CrO_4^{2-} ions and permeate surfactant concentration. They could achieve 99.98% retention in the presence of CTAB at 3 TMP [40].

Baek et al. explored simultaneous removal of ferricyanide and nitrate ions as a function of surfactant to anion mole ratio, using 3 and 10 kDa MWCO regenerated cellulose membranes and CPC under 2 TMP. Cyanides are used in a number of chemical synthesis and metallurgical processes. They readily form ferricyanide or ferrocyanide in the presence of iron. Since they are highly toxic, they must be removed from wastewaters prior to discharge. Nitrate ion is a potential health hazard to human beings since it can convert into nitrite ion. In single solutions, rejections of ferricyanide and nitrate anions increased with increasing CPC concentration to the R values of >99.9 and 93; respectively. CPC concentration imposed a similar effect in binary solutions of these anions. For ferricyanide:nitrate:CPC mole ratio of 1:1:10, rejections of ferricyanide and nitrate were >99.9 and 78%, respectively [41].

Chlorine in gas form (Cl_2), chlorine dioxide (ClO_2), and sodium hypochlorite (NaOCl) are incorporated in the municipal and industrial waters and wastewaters at high concentrations to prevent biological growth of microorganisms. All forms of chlorine are highly corrosive, toxic and carcinogenic to living organisms even at low concentrations. Therefore, the removal of chlorine from wastewaters is crucial. Rahmati et al. studied removal of free active chlorine (FAC) using PES/TiO_2 nanocomposite membranes with different PES/TiO_2 ratios prepared by the authors. Hypochloride rejection decreased with increasing pH and feed chlorine concentration, and increased by increasing TMP and TiO_2 content of the membranes. R value for FAC was found to be around 75 between pHs 2 and 4 [42].

2.5. Use of MEUF as a pre-concentration and recovery technique

Expense for surfactant accounts for a large portion of the operating costs of MEUF. Heavy metals and organics also are of economic value. Therefore, recovery and reuse of surfactants, heavy metals and organics from retentate or permeate, following a MEUF process, is of importance. This also prevents a secondary environmental pollution which will be caused by disposal of retentate and permeate. Retentates contain surfactant, heavy metal ions or organics in high concentrations since surfactants and pollutants are concentrated during MEUF. Therefore, in some cases, MEUF is used as a pre-concentration method for recovery of metals and organics from wastewaters.

Pollutants should be separated from micelles with which they are associated, so that both the surfactant and the pollutant can be recovered. For this purpose, the surfactant can be precipitated as its salts [9] or in its protonated form by addition of salts or strong acids, respectively, or by the addition of their mixtures. Thus metal ions leave micellar surfaces as a result of ionic competition, move to bulk solution and pass from the membrane into permeate during UF.

Another way to separate micelles and metal ions is the addition of a chelating agent to the medium which forms a complex with metal ions of the same charge with micelles. In such a case, metal ions are repelled by micellar surfaces and permeate through UF membrane while micelles are retained.

Metal ions can be recovered from retentate also by electrolysis. Electrolysis process detaches metal ions from micellar surfaces and they are electroplated onto the cathode as solid metal as a result of reduction. Thus, micelles becomes capable of retaining further metal ions entering the reactor and MEUF can be applied as a continuous hybrid process comprising MEUF and electrolysis.

Precipitation of metallic ions as their hydroxides is another method for metal recovery.

Other alternatives are to destroy the micelles such that surfactant undergoes phase separation or precipitation by increasing the temperature above its cloud point or by decreasing the temperature below its Krafft point, respectively.

Removal and recovery of surfactant in permeate can also be provided by foam fractionation carried out in foam fractioners. Surface active and inactive substances in permeate can be separated by this simple and low-cost method. Surface active surfactants are adsorbed onto gas bubbles formed by a strong air flow and migrate to surface with the bubbles rising up to form the foam.

Purkait et al. studied the removal of aromatic alcohols para nitro phenol, meta nitro phenol, beta napthol, and ortho chloro phenol by MEUF. They achieved maximum retention of solutes at surfactant (CPC) to solute ratio of 1:10. Following the MEUF carried out with such a high surfactant content, CPC in the retentate and permeate was recovered by a two-step chemical treatment process. Following precipitation of the surfactant with potassium iodide as its iodide salt (CPI), CPC was recovered from the precipitate by the addition of cupric chloride to convert CPI into soluble CPC [43].

Lui and Li determined optimum conditions to recover Cu(II) ions from the retentate of a MEUF process. Cu(II) ions bound to SDS micelles are accumulated on a cathode by electrolysis such that SDS micelles becomes free from metallic ions and can be reused to bind further ions in the incoming waste stream in a continuous process [44].

Kim et al. compared the efficiencies of three methods for recovery of heavy metals from simulated MEUF retentate. The tested methods were acidification followed by UF (1), use of a chelating agent followed by UF (2) and precipitation by ferricyanide and ferrocyanide followed by centrifugation (3). Copper and cadmium were completely separated from surfactant solution at strong acidic pHs by the method 1. HNO_3 was more effective than H_2SO_4 and HCl. They used EDTA, iminodiacetic acid and citric acid as ligands and provided 100 and 75.5%

separation efficiency by the method 2 for copper and cadmium, respectively. About 84% of SDS was recovered by acidification. 0n the other hand, 100% SDS recovery was achieved by centrifugation after complexation. They pointed out that successive precipitations are required for complete separation of SDS by acidification and that this will increase the ionic strength and acidity of the medium too much. They suggested the use of ferricyanide because of rapid precipitation of metal ions and selectivity [45].

Ghezzi et al. studied removal and recovery of Pd(II) ions from $PdCl_4^{2-}$ solutions by MEUF. They achieved 99% rejection using a cationic surfactant (DTAC) and a regenerated cellulose membrane of 30 kDa MWCO. They could recover 66% of Pd(II) by the addition of 0.8 M $MgCl_2$ salt to the medium [46].

Qu et al. recovered SDS and Cd(II) from MEUF permeate using a continuous foam fractioner. They could recover 52% of SDS and 99.35% of Cd(II) by applying various optimized process parameters such as air and liquid flow rates, the heights of liquid and foam, and the temperature. They could obtain an effluent with Cd(II) concentration lower than 0.1 mg/L, which meets the wastewater discharge standards in China [47].

Ghezzi et al. studied Cd(II) removal and recovery using pyridine-2-azo-*p*-dimethylaniline (PADA) as the ligand and regenerated cellulose 3 kDa MWCO membrane in SDS micellar media. They concluded that 90% of Cd(II) forms complex with PADA, and Cd(II) ions bind to micelles also as free Cd(II) ions providing a rejection of 98%. The retentate containing micelles associated with Cd(II) complex was treated with hydrochloric acid. H^+ ions bound to micellar surface caused to dissociation of the complex and replaced with Cd(II) ions bound to micelles as counterions. Thus, Cd(II) ions were released and separated from micellar surfaces. Protonated ligand remained within the micellar pseudophase. Recovery of Cd(II) ions increased with increasing acidity but since H^+ ions in concentrations higher than 1 M are hazardous for environment and damage the membrane, NaCl was also added to the medium to increase the ionic strength. They achieved more than 80% metal recovery at $3 \geq pH$ in the presence of 0.5 M NaCl (stripping solution). The existence of Mg(II) ions did not affect the Cd(II) recovery since Mg(II) ions did not form a complex with PADA. This result reveals that the presence of Mg(II) ions will not affect heavy metal recovery from sea water. They also studied Cd(II) rejection and recovery in the presence of Zn(II) ions. Both of the metal ions were rejected with R values >95%, but 83 and 76% Cd(II) and Zn(II) could be recovered, respectively, from binary solutions with acidic salt stripping solution [48].

Li et al. determined the optimum conditions for recoveries of SDS and Cd(II) and Zn(II) ions by UF under 0.15 MPa TMP. They used hollow fiber polyethersulfone UF membrane with MWCO of 6 kDa. They applied two methods: chelation followed by UF, and acidification followed by UF. Chelating agents they used were EDTA, citric acid and tartaric acid. They used sulfuric, nitric and hydrochloric acids in 3 mol/L concentration for acidification. The feed metal and SDS concentrations of simulated MEUF retentate solution were 100 mg/L and 3 CMC. Efficiency sequence of the acids in terms of both Cd(II) and Zn(II) separation was $H_2SO_4 > HNO_3 > HCl$ with small differences. They could recover 98.0% Cd(II) and 96.1% Zn(II) by acidification at pH 1, corresponding recoveries obtained using reclaimed SDS were 88.1 and 87.8%, respectively. SDS recoveries were 58.1 for SDS-Cd(II), and 54.3% for SDS—Zn(II) binary solutions at pH 1. EDTA was found to be more efficient compared to citric and tartaric acids. Chelation-UF method provided better results than those from acidification-UF experiments except for Cd(II) recovery. They reported 67.3 and 72.9% SDS recoveries from SDS-Cd(II) and SDS-Zn(II) binary solutions, and 95.8 and 96.8% recoveries for Cd(II) and Zn(II), respectively; by the chelation-UF method at pH 3. Corresponding recoveries obtained using reclaimed SDS for Cd(II) and Zn(II) were 90.3 and 89.6%, respectively [49].

Geanta et al. determined the optimum conditions for the removal of lactic and citric acids from beet molasses previously pretreated with activated charcoal at pH 3 by continuous cross-flow MEUF. Simultaneous recovery of acids and removal of SDS for reuse were achieved by treatment of the retentate with NaOH and subsequent phase separation below the Kraft temperature of SDS. After the phase separation process, 79.34% of lactic acid and 55.6% of citric acid were recovered from the SDS-free supernatant. About 95% of SDS was recovered from the solid phase [50].

Schwarze et al. used a surfactant with a very low CMC (1–20 μmol/L, depending on pH and counterion), which can be nonionic (at low pHs) or ionic (at high pHs) depending on the pH of the medium, namely nonaoxyethylene oleylether carboxylic acid Akypo RO90 VG (R90VG). They used a cellulose membrane of 5 kDa MWCO. They removed Cu(II) ions almost quantitatively at basic pHs and recovered more than 90% Cu(II) ions from the retentate by cloud point extraction. They compared the performance of R090 in copper removal with that of SDS. Copper removal was carried out at pH 6.5 to exclude hydroxide formation. Though the CMC of R090 was quite low from that of SDS, SDS provided the same rejections in lower concentrations. Cloud point extraction was carried out at 50°C and at pH < 2, so that degree of ionization of micelles is almost zero [51].

Aydinoglu et al. could recover 85% of gold from the retentate by a stripping process using a $NaCl/NH_3$ mixture as the stripping agent, followed by UF. NaCl reduced the surface potential of micelles such that electrostatic attraction between DTAC micellar surface and $AuCl_4^-$ ions is reduced. On the other hand, NH_3 converted $AuCl_4^-$ ions into positively charged $Au(NH_3)_4^{3+}$ complex so that it is repelled into the aqueous phase by cationic DTAC micelles [52].

Huang et al. investigated feasibility of repeated recovery and reuse of SDS in MEUF retentate containing Cd(II), by acidification followed by UF. The authors reported that the maximum SDS and Cd(II) recoveries were attained at pH 1 and 0.5, respectively. They did not suggest working at pH 0.5 since the solution became too sticky. 94.38% Cd(II) could be removed by recycled SDS at pH 2. Optimum conditions for SDS recovery and reuse were initial SDS concentration 2 CMC, pH 1, use of sulfuric acid and volume of the acidified concentrated solution 0.2 L. They recovered and reused SDS three times and stated that this does not provide economic profit but solves the problem of secondary environmental pollution substantially caused by concentrated retentate solution [53].

2.6. Selective separation by MEUF

There are some reports on selective separation of heavy metal ions by MEUF in the literature. In these studies, two ions to be separated have quite different chemical and physical properties such as Cu(II) and Ca(II), Cu(II) and Co(II) or Cu(II) and Pb(II).

Das et al. studied feasibility of selective separation of Cu(II) and Ca(II) ions by cross-flow MEUF. They compared experimental and calculated fractional counterion binding constants for these ions and Na^+ ions which are inherent counterions of SDS in both single component and binary solutions. Binding constant of calcium ions to the micelles was larger than that of Cu(II) ions implying that competition of these ions for micellar surfaces will result in an ion exchange between sodium and calcium ions rendering selective separation of these ions feasible in a MEUF process, such that micellar bound calcium ions are retained in the retentate and most of the copper ions, released from micellar surfaces, pass through the membrane into the permeate [54].

Anthati and Marathe investigated the performance of continuous cross-flow MEUF for selective separation of Cu(II) and Co(II) ions using SDS as the surfactant and iminodiacetic acid (IDA) as the chelating agent. They compared the retentions of both metal ions by UF and MEUF. At optimal conditions, 96% selective separation of copper ions was achieved. Cobalt ions remained in the retentate. They also studied recovery of SDS from the retentate. About 75 and 84% of SDS was recovered by acidification followed by UF and addition of a ligand followed by UF methods, respectively. Cobalt ions passed through the membrane into permeate by the second method. If they used a membrane with smaller MWCO than 30 kDa, they could possibly achieve higher recovery results [55].

2.7. Membrane fouling

Membrane fouling is a major problem in membrane separation processes which results in decline of permeate flux [54, 56, 57]. It is an undesirable phenomenon which slows down MEUF process. Membrane fouling may be reversible or irreversible. Reversible fouling occurs as a result of concentration polarization which leads to accumulation of surfactant or any other solute aggregates forming a layer of gel structure over the membrane surface. This layer can be removed from membrane surface by a washing process including backflushing in the UF cell under pressure. In case of irreversible fouling, pores of the membrane are clogged partially or completely in an irreversible manner. Membrane fouling is generally characterized by the results of flux decline experiments.

PES is a thermoresistant polymer with good mechanical strength. These properties make this polymer preferable as a membrane material. But its hydrophobic character makes its fouling by adsorption easy. Pozniak et al. modified PES membrane to decrease its fouling during MEUF. For this purpose, they formed porous asymmetric ion exchange membranes by various methods: phase inversion, sulfonation (cation exchange membrane), and chloromethylation followed by aminolysis (anion exchange membrane) of PES (neutral membrane). Sulfonated PES (SPES) increased the rejection of Cr(III) ions by SDS micelles and aminated PES increased the rejection of Cr(VI) ions by CPC micelles. Charged membranes decreased membrane fouling and thereby increased the flux rate. Reduction of SDS concentration increased the permeate flux [58].

Huang et al. investigated the effects of feed surfactant concentration, recycling of retentate to the feed tank and TMP on membrane fouling; in a continuous cross-flow MEUF process carried out to remove Cd(II) ions. They concluded that fouling becomes a big problem at SDS concentrations over 5 CMC. The effect of TMP was found to depend on the stage of MEUF at which

TMP decreased or increased. They suggested the use of low- and high-concentrated surfactant solutions and different TMPs consecutively to remove the gel layer on the membrane [59].

Effects of SDS feed concentration, TMP and hydraulic flushing on permeate flux were investigated in another research of Huang et al. They carried out both experimental and theoretical studies. SDS rejection increased with increasing SDS concentration, but at 10 CMC, SDS rejection decreased and the biggest fouling resistance and lowest permeate flux were observed. They studied the effects of three kinds of hydraulic flushing methods for membrane cleaning: periodic forward flushing, periodic backwashing and forward flushing followed by backwashing. They stated that backflushing can dislodge the particles in the cake layer blocking the membrane pores but might damage the membrane. Forward flushing could easily remove the layer on membrane by means of cross-flow rinse. They suggested consecutive use of both methods to provide more effective cleaning [60].

Miller compared membrane fouling at constant flux and TMP considering that many industrial UF applications operate at constant permeate flux. They studied emulsified soybean oil fouling of 20 kDa PS ultrafiltration membranes at constant permeate flux and transmembrane pressure. Constant flux fouling was studied at fluxes below and above the threshold flux (the flux at which the rate of fouling begins to increase rapidly, TH flux). Modest increases in TMP were observed below TH flux while fouling, TMP and rejection were increased substantially above TH flux [61].

Zhang et al. studied fouling caused by Gemini micelles in MEUF of phenol containing water. They used two kinds of Gemini surfactant and Brij35 as the surfactants. They recycled retentate and permeate solutions back to the feed tank. They investigated the dependency of TH flux and limiting flux on feed surfactant concentration, TMP and on the nature of surfactants. TH flux decreased with increasing feed concentration due to increased irreversible fouling. They discussed fouling mechanism in MEUF [62].

2.8. Hybrid processes

Some researchers combined MEUF with some other processes to increase removal and/or recovery efficiency. Various auxiliary techniques have been applied prior to or during MEUF to reduce the surfactant and energy consumptions as well as membrane fouling and to shorten the process time.

Liu and Li compared the results of four kinds of processes for Cu(II) removal: UF, electrolysis-UF, MEUF and electrolysis-MEUF using SDS and 10 kDa PS membrane. The best results were obtained with the latter. Before starting, 17 mM SDS was put into the reactor. The copper removal efficiency at the steady-state condition depended on the balance between Cu(II) amount entering the reactor and Cu(II) amount removed by the electrolysis. Copper removal efficiencies were 64.6 and 90% for MEUF and electrolysis-MEUF processes, respectively, for an input SDS concentration of 5.56 mM. Higher R values could be obtained at higher SDS input concentrations. They chose 5.56 mM as the working concentration with the consideration that it was lower than CMC of SDS. But in fact, it is higher than CMC of SDS in the presence of Cu(II) ions (SCMC), which is between 1.5 and 2.2 mM, depending on the purity of SDS and Cu(II) concentration [44].

Sometimes metal salts are added to dye solutions to precipitate vast amount of dye molecules prior to MEUF. Ahmad and Puasa combined coagulation followed by filtration as a pre-treatment method prior to MEUF for the removal of C.I. Reactive Black 5 (RB5) and C.I. Reactive Orange 16 (RO16) dyes. Thus, the dye content of aqueous solution could be reduced substantially before MEUF process. The concentrations of dyes were reduced by pre-treatment from 0.5 to 0.0219 g/L (95.61% removal) and 0.1031 g/L (79.39% removal) for RB5 and RO16, respectively. They could achieve 99.75 and 99.98% R values for RB5 and RO16, respectively, using a commercial cationic coagulant and CPC as the surfactant [63].

Bade et al. combined adsorption of pollutant on activated carbon filter (ACF) and cross-flow MEUF processes for removal of chromate anions using CPC. They also removed CPC in permeate using ACF. Chromate (initial concentration 20 mg/L) removal efficiencies were 98.6 and 99.5% at 1:5 and 1:10 chromate to CPC molar ratios, respectively [64].

Venkataganesh et al. studied the effects of various parameters, including external electric field application, on removal of naphthenic acid (NA) by MEUF, using 10 kDa MWCO PES membrane and SDS. They applied electric field in two modes: in mode 1, a stepwise electric field was applied such that the operating field strength across the membrane increased stepwise; and in mode 2, a fixed electric field was applied throughout the experiment. Application of an external electric field had no effect on NA rejection. R value for NA was 98. On the other hand, electric field accelerated the filtration. Mode 2 increased the flux 24% while step 1 provided 14% increment [65].

Rafique and Lee also used MEUF-ACF hybrid process in the removal of Cd(II) from aqueous solution using SDS and hollow fiber polyacrylonitrile membranes of 100 and 300 kDa MWCO. MEUF was carried out with cross-flow type filtration. The rejected permeate was re-circulated into the feed tank and permeate water was collected at the separation tank. R values for Cd(II) removal (initial concentration 0.065 mM) by MEUF were 68.5 and 36.4 using 100 and 300 kDa membranes, respectively. Corresponding R values were 99.6 and 99.5 with combined ACF-MEUF process [66].

3. Ligand-modified micellar-enhanced ultrafiltration

MEUF has a drawback that it cannot provide high selectivity in removing ions of the same charge. It can be effective in selective separation of metal ions with quite dissimilar properties, such as Cu(II) and Ca(II) or Cu(II) and Pb(II). On the other hand, selective separation of ions can effectively be provided by use of a ligand which undergoes selective complexation with one of the target ions. The complex is solubilized in micelles via hydrophobic forces between the ligand and micellar interior, so it is retained during MEUF providing metal ion rejection. This process is called ligand-modified MEUF (LM-MEUF). The use of a ligand in MEUF process was first applied in the late 1980s [67, 68]. A number of LM-MEUF studies were carried out in 1990s in which LM-MEUF and MEUF techniques were compared and superiority of LM-MEUF to MEUF in terms of removal of metallic ions was shown. It was also shown that cationic surfactants were more effective in metal ion removal by LM-MEUF compared to anionic ones.

The ligands chosen are generally of very low solubility in water, so that leakage of free ligand molecules to permeate is minimized. Therefore, complex formation occurs at the micellar surface mainly between the amphiphilic ligand molecules solubilized in micelles and metal ions in the bulk phase. Thus, micelles behave as nanoreactors and bring close together two reactants in their small volumes (concentration effect of micelles, see Section 1.2.1). Micelles can also solubilize any metal complex molecule formed in the bulk phase (see Section 1.2.1.2). Micellar size is increased and micelles have a more compact structure as a result of complex solubilization. Accordingly, rejection of metal ion-bearing micelles is enhanced.

The efficiency of LM-MEUF process depends on the pH of the sample solution since complex formation is pH-dependent. The other factors are the ligand to metal ion and surfactant to metal ion mole ratios and the natures of the ligand and the surfactant. The working pH is generally between 3 and 7 which can be achieved easily with waste waters.

Ions of similar chemical properties are expected to interact with complexing agents in the same way under the same conditions. Nevertheless, their complexation behaviors can be differentiated in micellar media by the virtue of the “medium effect” of surfactant micelles mentioned in Section 1.2.2. Medium effect arises from the fact that microenvironments in which micellar bound reactants reside have quite different properties from those of the bulk phase. As a consequence, ionization equilibria of ligands interacting with micelles and thereby the stability constants and even the stoichiometry of their complexes to be formed are changed [1, 69, 70]. That the complexation behaviors of two ions with the same complexing agent are differentiated by micelles make selective separation of these ions by MEUF possible.

Superiority of LM-MEUF to MEUF in terms of metal ion removal efficiency has been reported in a number of papers. Pozniak et al. compared the results of MEUF and LM-MEUF experiments in which EDTA was used as the ligand. The presence of ligand in the medium decreased the SDS concentration two times to provide 99% removal of Cr(III) ions with SPES membrane. They attributed this to the fact that EDTA decreased CMC of SDS, and that more rigid structures of ligand-surfactant mixed micelles facilitated the rejection of micelles by the membrane, without referring to increased incorporation of Cr(III) ions to micelles by complex formation [58]. Decrease in SDS feed concentration provided by LM-MEUF enabled higher permeate flux and lower SDS concentration in permeate.

Reuse of a catalyst used in homogeneous catalysis provides economic benefit, but it is not easy to remove and recover it as it is in case of separation of a heterogen catalyst from a reaction system. Schwarze et al. studied the recovery of a catalyzer to enable reuse of rhodium-based homogeneous hydrogenation catalyst precursor, in the absence and presence of triphenylphosphine ligand (TPP) using nonylphenol ethoxylate (Marlopen NP9) nonionic surfactant. They used regenerated cellulose (C) and PES membranes of 5 kDa MWCO. In the absence of ligand, they could achieve retentions below 30%, while the micelle retention was almost 100% with both kinds of membranes in the presence of TPP. This enhancement attributed to formation of a highly hydrophobic complex with TPP, which incorporates into micelles more effectively than catalyst molecules alone. They achieved better results with membrane C [71].

The separation of hydrophilic small molecules, such as sugars, from aqueous solutions is another current field of research. Mehling et al. studied recovery of some sugars (arabinose, cellobiose, glucose and sucrose) from their solutions by MEUF for the first time and compared the results with those of extraction with organic solvents. Cationic CTAB and TX100/Aliquat 336 nonionic-cationic mixture was used as the surfactants. Phenylboronic acid (PBA) ligand was used as a carrier to solubilize sugars in micelles. They obtained better results than those obtained by extraction [72].

There is a limited number of LM-MEUF study performed for removal of copper. Şahin and Taşcıoğlu explored the effects of 20 azo compounds as complexing agents, on removal of Cu(II) ions from single component solutions. They compared the results of MEUF and LM-MEUF studies carried out at pHs 3, 5 and 7. The most effective ligand was found to be 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ), at pH 5. 6.6×10^{-8} mol/L TPTZ provided complete removal of 5.0×10^{-4} mol/L Cu(II) ions in the presence of SDS with two times lower concentration than that required for complete removal of Cu(II) ions by MEUF. They observed that SDS concentration required for complete removal of Cu(II) ions by LM-MEUF decreased with increase in TPTZ concentration implying that SDS feed concentration can be lowered to a concentration close to SCMC by increasing TPTZ concentration, without any concern of increased TPTZ leakage into permeate since TPTZ-Cu(II) complex is positively charged and TPTZ is sparingly soluble in water [73].

There are some reports in the literature on selective removal of metal ions by LM-MEUF. They obtained much better results for ions with quite dissimilar properties such as Cu(II)-Ca(II) or Cu(II)-Pb(II) than those obtained by MEUF studies. Most of these studies were carried out in the late 1980s and1990s.

Simmons et al. used various ligands and surfactants comprising CPC, CTAB, N, N-dimethyl=dodecylamine-N-oxide (DDAO) and polyoxyethylenenonyl phenyl ether ($NP(EO)_{10}$) for selective separation of Cu(II) and Ca(II) ions. N-(n-hexadecyl)-di-2-picolylamine ligand provided Cu(II) rejections of 99.9, 99.8, 99.7, 97.7 and 98.9% using SDS, CPC, CTAB, DDAO and (NP(EO)10), respectively; with no rejection of Ca(II) [74].

Pramauro et al. studied pre-concentration and selective removal of U(VI), Sr(II) and Cd(II) cations. Radioactive strontium is a fission product which should be separated from uranium. Cadmium originates from some other sources such as vessels exposed to acids. They used TX100 and HTAB as the surfactants. Derivatives of 4-aminosalicylic acid (PAS) and of 1-(2-pyridylazo)-2-naphthol (PAN), rendered hydrophobic by tuning alkyl chains, were used as chelating agents. They formed mixed micelles with surfactants (chelating micelles). Selective recovery of uranyl ions was possible via the multi-step UF approach with PAN derivatives in acidic medium. Effective uranyl retention could be obtained with salicylates only in neutral and basic media. Retention was only 3–5% with TX100 micelles in the absence of ligand. 91% U(VI) ions, 21% Cd(II) and 15% Sr(II) could be rejected from single component solutions in the presence of PAS-C8 derivative at pH 5.5 indicating to a selective complexation of uranyl ions with this ligand. Cd(II) and Sr(II) rejections may be resulted largely from adsorption by the membrane. 99% of uranium ions could be recovered in the presence of PAN-C8 and the authors reported that quantitative separation of uranyl ions from both Sr(II) and Cd(II) ions could be feasible at pH 3 with repeated UF processes [75].

Roach et al. reported that Pb(II) ions can be selectively separated from aqueous solutions containing equimolar Ca(II) ions almost completely in the presence of nitrilotriacetic acid (NTA) derivatives as chelating agents [69].

Ghezzi et al studied Cd(II) removal and recovery from binary solutions containing Mg(II) ions in high concentrations and concluded that Cd(II) ions bind to SDS micelles as Cd-PADA complex, and the presence of Mg(II) ions does not affect heavy metal removal from sea water since they do not complex with PADA [48].

There is only one report in the literature on selective separation of Cu(II) and Cd(II) cations which have quite similar properties. Şahin and Taşcıoğlu explored the feasibility of LM-MEUF as a method for selective removal of 0.5 mM Cu(II) ions from 0.5 mM Cd(II) containing solutions at pH 5 and showed that metal ions of similar properties can be separated simply by an UF process. Cu(II) and Cd(II) ions are expected to interact with complexing agents in the same way under the same conditions, since they have similar chemical and physical properties. But the authors showed that complexation behaviors of these cations with the same ligand can be differentiated in micellar media by the virtue of the "medium effect" of surfactant micelles [1]. On this basis, complexation behaviors of 20 azo compounds with Cu (II) and Cd(II) ions were investigated in SDS micellar medium to determine the ligands which could provide selective removal of Cu(II) ions. The selected ligands were used in LM-MEUF experiments. The most effective ligand in selective separation was found to be TPTZ. Complete removal of Cu(II) ions could be achieved with Cd(II) rejections lower than 10% in the presence of this ligand. Selective separation could be provided at SDS feed concentrations much lower than that required for removal of Cu(II) ions from single component solutions by MEUF. Feed concentration of SDS could be lowered to the values close to the SCMC by increasing the TPTZ concentration. A small rejection of Cd(II) was attributed to adsorption on membrane since Cd(II) was observed not to form complex with TPTZ in SDS micellar media [73].

Patil and Marathe studied selective separation of Ni(II) and Co(II) cations from aqueous stream using SDS and SDS/TX100 mixed surfactant system, and iminodiacetic acid (IDA) as the chelating agent, in a cross-flow UF unit. Under the optimum conditions and in SDS micellar system, 94% cobalt could be rejected while 92% Ni permeated across the membrane. TX100 exerted a negative effect on cobalt rejection such that 84% Co(II) retained in the retentate and 93% Ni(II) was in the permeate in mixed micellar system [76].

Aydinoglu et al. studied extraction and recovery of Au(III). They also investigated feasibility of gold/copper separation. Complete extraction of gold (as $AuCl_4^-$ ions) could be achieved in cationic DTAC micellar medium by electrostatic and hydrophobic interactions in the absence and presence of pyridine-2-azo-p-dimethylaniline (PADA), respectively. $AuCl_4^-$ ions were not retained by negatively charged SDS micelles. But it was possible to provide complete rejection of gold in SDS micellar medium in the presence of PADA due to hydrophobic forces between PADA and micelles and the positive charge of Au(III)-PADA complex. Cu(II) removal could not be achieved by cationic DTAC micelles. But they could provide gold-copper separation by MEUF to a large extent utilizing charge effect of SDS micelles: oppositely charged Cu(II) ions bound to micelles retained on the membrane, while $AuCl_4^-$ ions of the same charge with micelles passed through the permeate [52].

Şahin and Taşcıoğlu explored the feasibility of Cu(II)–Cd(II) separation by LM-MEUF, using the same ligands which they used in Ref. [73] but in the presence of CTAB and TX100 micelles [77]. TX100 was not found to be effective in selective separation. Interestingly, the most effective ligand in removal of Cu(II) ions from single component solutions in the presence of cationic CTAB was TPTZ as it was also the case in the presence of anionic SDS. TPTZ was also the most effective ligand in removal of Cu(II) ions from two component solutions but the authors suggested the use of 2-hydroxy-1-(2-hydroxy-4-sülfo-1-naphthylazo)naphtelene-3-carboxylic acid (CALCA) for selective separation. CALCA provided the lowest R value (6.4%) for Cd(II) ions at complete removal of Cu(II) ions at pH 5. Cd (II) rejection in such a small extent was attributed to the adsorption of Cd(II) ions by the membrane itself, since CTAB micelles cannot bind positively charged Cd(II) ions and CALCA were found not to undergo complexation with Cd(II) ions in CTAB micellar medium. The results obtained in the presence of anionic [73], cationic and nonionic [77] micelles provided evidences for the mechanism of Cu(II) removal by LM-MEUF.

Notes

***Both MEUF and LM-MEUF are research areas which require more interest. There is still much to do to determine the optimum conditions for the removal of ions or organics from aqueous media by these simple and economic techniques. There are a large number of parameters and their combinations that can be altered and optimized while conducting MEUF or LM-MEUF studies.

***It should be noted here that in the majority of MEUF and LM-MEUF studies, the SCMC values of the surfactants have not been determined. Most of the researchers take the CMC values of surfactants in deionized water as a basis, wrongly, while conducting a study and discussing the results. Therefore, the surfactant concentrations given in articles should be evaluated in terms of micelle formation, taking into consideration that surfactants exist in the medium as micellar aggregates in concentrations over SCMC, and the concentrations given in CMC unit such as "2 CMC" should be checked if CMC stands for "SCMC".

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Chapter 6

Fouling of Nanofiltration Membranes

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Additional information is available at the end of the chapter

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Abstract

Despite all promising perspectives and new research in nanofiltration, for example, in drinking water production, in wastewater treatment, the food industry, the chemical and pharmaceutical industry, and many other industries, there are still some obstacles that slow down large-scale applications. Fouling is an irreversible and time-dependent phenomenon, and it is related to the characteristics of the membrane and solute-solute and solute-membrane interactions. Therefore, an understanding of fouling mechanisms such as fouling characteristics and consequences, fouling mathematical models, and physical-chemical and processing factors affecting fouling, are very important. As a result, the aim of this chapter is to present some phenomena that contribute to fouling: physical-chemical interactions, pore mechanical blocks, and deposit of suspension material on membrane surface.

Keywords: nanofiltration, fouling, fouling membranes, fouling characteristics, membrane process

1. Introduction

Nanofiltration (NF) is defined as “a process intermediate between reverse osmosis and ultrafiltration that rejects molecules which have a size in the order of one nanometer.” In general, the use of membrane process is limited by fouling, which reveals itself as a decrease in flux with time of operation. Fouling probably is the most important reason for the minimal acceptance of nanofiltration and other membrane processes in large-scale processing [1, 2].

A number of factors contribute to fouling and are strongly interlinked. Organic, inorganic, particulate, and biological fouling are some of the main fouling categories. Also important are metal complexes, for example, Fe, Al, Si. Despite many research traditionally focusing on one category or fouling mechanism at a time, it is well accepted that in most cases, it is not one single category that can be identified. In most real-life applications, all four types of fouling go hand in hand [2, 3]. Fouling is an irreversible and time-dependent phenomenon; it is related to the characteristics of the membrane and solute-solute and solute-membrane interactions that cause an irreversible decline in the flow of permeate, which can only be recovered by the chemical cleaning of the membrane. In addition, some process parameters like equipment design, temperature, feed concentration, flow, and pressure can also contribute to membrane fouling.

2. Nanofiltration and membranes

The singularity of these membranes is highlighted by their ability to selectively reject different dissolved salts; they have a high rejection rate of low molecular weight, dissolved components. Nanofiltration membranes with low transmembrane pressure, operating pressure of generally 5–30 bar, were developed to achieve high divalent ion rejection. It is expected that the rejected molecules can have a molecular weight of 200 $g.mol^{-1}$; this corresponds to an equivalent of Stokes diameter of approximately 1 nm [3, 4].

Nanofiltration membranes are neither entirely dense nor entirely porous, so their retention mechanisms are determined by both size exclusion (porous membranes) and sorption and diffusion (dense membranes). Also, these kinds of membranes are principally used to partially soften potable water, allowing some minerals to pass into the product water, thus increasing the stability of the water and preventing it from being aggressive to distribution piping material. Additionally, NF membranes are discovering increasing use in purifying industrial effluents and minimizing waste discharge. The key to using NF membranes for particular applications is the selection of a membrane with the appropriate rejection characteristics and the design of a suitable process. In general, NF membranes are characterized by a high charge density and pore sizes in the range of nanometers; the surface charge is most often negative and has the greatest effect on the selective passage nature of these membranes. New studies have been developed, and new membranes having unique properties, including a varying range of hardness rejection and fouling resistance manufactured [2, 4].

3. Characteristics of fouling and consequences of fouling

The efficiency of the nanofiltration process is affected by fouling on the membrane and other factors like tangential velocity, pressure, temperature, turbulence, feed particles size, concentration polarization changes in membrane properties, and membrane characteristics [2].

Fouling phenomenon is the result of the interaction between solutes adsorbed onto the membrane and solutes present in the feed flow, or even between the membrane and diverse solutes present in the solution. Fouling can be the result of three main factors or the interaction between them: the properties of the material constituting the membrane, the properties of the solute, and the operational parameters [2, 3, 5].

The interaction between solute and membrane, the interaction among molecules of solute present, and the chemical constitution of the membrane structure must be identified to understand the phenomenon of fouling. Notably, the interaction between solute and membrane will determine the fouling formed by the adsorption of solute onto the membrane surface [6, 7].

In contrast to polarization of concentration, which is considered a reversible phenomenon and independent of process time, fouling is an irreversible phenomenon and dependent on time. Fouling can be defined as a deposition or adsorption of retained particles, colloids, macromolecules, salts, etc., on the membrane surface and/or aggregation in the pores, causing partial or even total blockage of the pores, resulting in a continuous decline of flow. The different ways in which the pores become blocked are a function of the size and form of the solute in relation to the pore size distribution of the membrane. Partial blockage of the pores occurs when isolated macromolecules or groups of them partially seal the pores, with the possibility of forming a deposit on the membrane surface, increasing the resistance to permeation. When chemical species are deposited or adsorbed on the inside of the membrane pores, it reduces the volume available for passage of the permeate; there is internal blockage of the pores. Complete blockage of the pores occurs when the particles that deposit on the membrane surface are larger than the membrane pores, completely obstructing them [8, 9].

This phenomenon, related to the characteristics of the membrane and solute-solute and solute-membrane interactions, causes an irreversible decline in the flow of permeate, which is only recovered by the chemical cleaning of the membrane. **Figure 1** shows some types of blocks [2, 8, 9].

Observing and analyzing **Figure 1**, it is possible to understand the different ways in which the membrane can be blocked and compare concentration polarization. When hydrocolloids, macromolecules, or other particles with larger dimensions as compared to the diameter of the membrane pore, are rejected and accumulate on the surface of the membrane, concentration polarization occurs. An increase in resistance to solvent passage occurs by this accumulation, and consequently leads to a greater local osmotic pressure. In general, concentration polarization occurs in any selective transport process such as classical filtration and tangential filtration. In tangential flux, concentration polarization stabilizes quickly and this provokes an additional resistance to mass transfer by the membrane, and as a result a decline in flux permeate [10, 11].

The precipitation of organic solutes on the membrane surface is known as gel formation. This process usually occurs when the wall concentration due to concentration polarization exceeds the solubility of the organic solute. It is very important to consider that gel formation does not necessarily mean irreversible flux decline. The gel polarization model is based on the fact that at steady state, flux reaches a limiting value, where an increase in pressure no longer increases the flux. Conforming to the gel polarization model, at this limiting value, the solubility limit of the solute in the boundary layer is reached and a gel formed [5, 12].

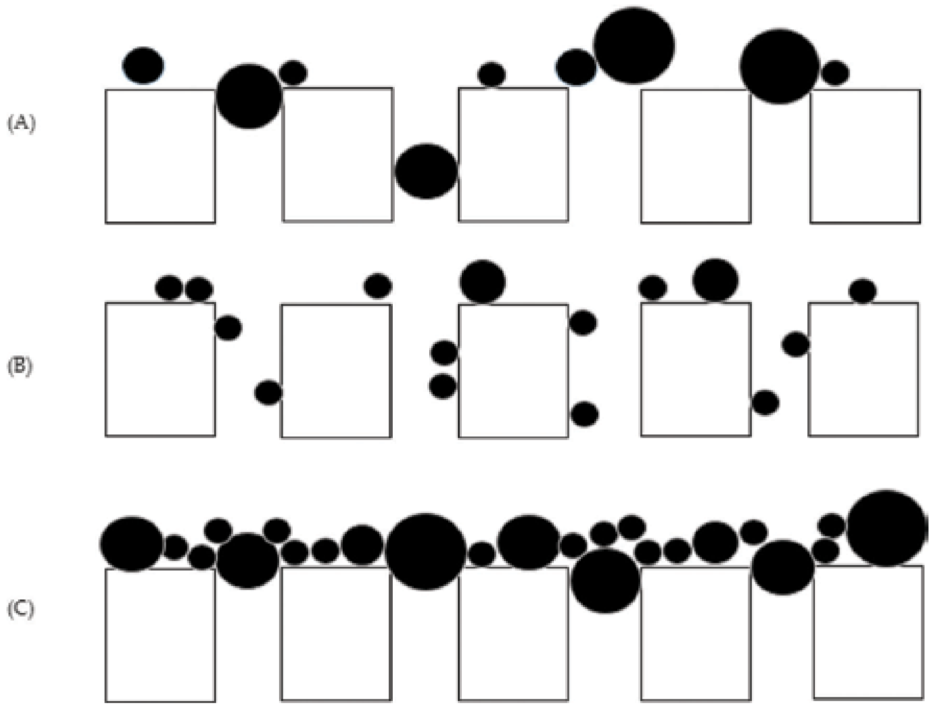

Figure 1. Inlay membrane mechanism: (A) complete blockage of pores; (B) partial (internal) blocking of pores; (C) polarized layer.

The typical permeation flux curves can be described in three different stages. The first stage (I) is characterized by a sudden drop in flux in the first minutes due to the polarization of the solutes by concentration on the surface of the membrane. At this stage, loss of flow is reversible. In the second stage (II), the flow variation decreases, varying with the pore diameter of the membrane. The precipitation of the accumulated solutes begins, which leads to the blocking of the pores and the adsorption of the components in the membrane, causing the formation of the polarized layer and the incrustation. The decrease in flow due to this latter phenomenon is irreversible. Finally, the third stage (III) is the consolidation of incrustation; in this stage, the flow decreases continuously and slowly. **Figure 2** shows each step described here [13].

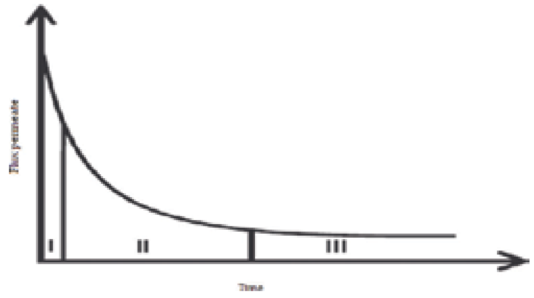

Figure 2. Typical permeation flux curves described in three different stages (adapted from Marshall and Daufin [13]).

4. Physical and chemical factors affecting fouling

Nanofiltration membranes retain substances with molar masses higher than ~300 g mol^{-1} and multivalent ions. The retention characteristics depend largely on how much free volume there is in the membranes, which can for some membranes be related to the flux. As nanofiltration membranes have characteristics of both ultrafiltration as well as reverse osmosis membranes, their fouling characteristics are also rather unique [12, 14].

It has already been discussed that fouling is initiated by solute-membrane material interactions; however, Van der Waals forces, chemical binding, and Lewis acid-base interactions are the major phenomena involved in the interactions resulting between surfaces and solutes on a molecular level. As a result, physicochemical properties of membrane surfaces are changed and this facilitates the deposition of other molecules and other aggregates. Membrane-solvent interactions can be expected to diversify with changes in the solvent properties, such as molecular size, surface tension, viscosity, and dielectric constant [11, 14, 15].

The relationship between the type of solvent, polar or non-polar, and the type of membrane, hydrophilic or hydrophobic, used in separation processes, must be judiciously analyzed. The flow rate of polar solvents is significantly higher (8–10 times) than that of non-polar solvents in processes carried out with hydrophilic membranes [9].

The relationship between the components of solute molar mass and rejection by the membrane can be observed from the results obtained in the analysis of the rejection of triacylglycerols present in *n*-hexane solution, where the percent rejection obtained was higher for larger molar masses [9].

Fouling of nanofiltration membranes has been studied very extensively up to date and many studies have tried to explain what happens in each situation. Because fouling can decrease the flux drastically, it is important to investigate what types of foulants should be avoided in NF [13].

It is necessary to identify the foulants in order to reduce or eliminate fouling. This objective can be achieved by a characterization of the fouled membrane or by fouling studies in the laboratory. Once the foulants are identified, suitable control strategies can be adapted. An overview of foulants and appropriate control strategies are summarized in **Table 1**. The strategies include a number of categories, for example: module design, operation mode and cleaning, membrane selection like non-fouling materials/coatings, feed pre-treatment, suitable surface charge, porosity, hydrophilicity chlorine compatibility, and surface roughness [5, 11].

Important factors that differentiate nanofiltration from other processes of membranes separation are as follows:

- Rejection of multivalent negative ions, such as sulfates, and phosphates;
- Rejection of sodium chloride (0–70%) in systems of complex mixtures;
- Rejection of particles without loads, dissolved materials, and positive charge ions in solution is related to the size and shape of the molecule in question.

Foulant	Fouling control
General	Hydrodynamics/shear, operation below critical flux, chemical cleaning
Inorganic (scaling)	Operate below solubility limit, pre-treatment, reduce pH to 4–6 (acid addition), low recovery, additives (antiscalants); some metals can be oxidized with oxygen
Organic	Pretreatment using biological processes, activated carbon, ion exchange, ozone, enhanced coagulation
Colloids (<0.5 μm)	Pre-treatment using coagulation and filtration, microfiltration, ultrafiltration
Biological solids	Pretreatment using disinfection (e.g., chlorination/dechlorination), filtration, coagulation, microfiltration, ultrafiltration

Adapted and modified from Fane et al. [19].

Table 1. Foulants and their control strategies in nanofiltration processes.

Therefore, the efficiency of a nanofiltration process depends on the size of the particles present in the solution and molecular loads [5].

It is also known that mineral salts have a deep influence on the fouling of ultrafiltration and nanofiltration membranes. These components can interact with the membrane directly or precipitate on the membrane and cause a reduction in flux. However, mineral salts contribute to the ionic strength of the solution, which in turn affects the conformation and dispersion of the proteins and consequently, the fouling of the nanofiltration membrane [2, 5, 6].

Many studies report the effect of pH on membrane fouling. Flux is lowest at the isoelectric point of the protein and is higher as the pH moves away from the isoelectric point. Changes in pH affect proteins in solubility, which is generally lowest at the isoelectric point and increases as pH is adjusted away from it; conformation, because of the interaction between proteins and membranes, also changes with pH membranes. Thus, these effects of pH on flux should not be unexpected, especially in view of the effect on solubility of salts [2, 6].

In general, in many industrial or laboratory test processing cases, membrane fouling may be caused by pectins, proteins, tannins, starch, cellulose, and hemicellulose. Moreover, it is very necessary to consider biofouling in membranes. Biofouling is a term used to describe all instances of fouling where biologically active organisms are involved. Whilst the different forms of chemical fouling reflect largely passive deposition of organic or inorganic materials on membrane surfaces, biofouling is a dynamic process of microbial colonization and growth, which results in the formation of microbial biofilms. Biofilms are microbial communities that grow attached to surfaces. Biofilm formation constantly precedes biofouling, which becomes an issue only when biofilms reach thicknesses and surface coverages that reduce permeability. In some cases, biofilms may cause total blockage of feedwater channels and mechanical collapse of modules by telescoping [2, 6, 15–22].

5. Processing factors affecting fouling: temperature, pressure, feed concentration, flow rate and turbulence

It is important to consider that other factors can affect fouling, and not just the complex physical-chemical interaction of feed components.

The main physical operational parameters that affect the permeate flow rate are: pressure, temperature, viscosity and density of the feed fluid, and the tangential velocity [23].

The temperature effect is not completely clear and can influence fouling in two different ways. It is possible that as temperature is increased further, the beneficial effects (lower viscosity, higher diffusivity) will outweigh the harmful effects (loss of solubility of salts) and may result in a net increase in flux. It could also result in a decrease in flux for certain feeds, due to decreases in solubility of feed components at higher temperatures. Evidently, for biological systems, too high temperature will result in protein denaturation and other heat damage, which will provoke lowering of the flux [2, 10].

An increase in feed concentration alters the viscosity, density, and diffusivity of the feed solution, causing a decrease in permeate flow rate. The permeate flow rate is directly proportional to the pressure applied and inversely proportional to the viscosity. Viscosity can be controlled by two factors: solids concentration in the feed and temperature [24, 25].

As is known, an increase in pressure results in a greater convective rate for the transport of solute to the membrane surface, increasing its concentration at the interface, causing an increase in diffusivity of the solute in the opposite direction to that of the process pressure, and thus decreasing the permeate flow rate [26–29]. It is important to emphasize that there is a linear relationship between flow rate and the inverse of the solvent viscosity for nanofiltration and ultrafiltration membranes, revealing that the main mass transport mechanism in these systems is convection [2, 30].

Moreover, an increase in tangential velocity increases the permeate flow rate by provoking greater turbulence, causing a dispersion in the solute molecules concentrated on the membrane surface, and reducing the thickness of the gel layer. High shear rates generated at the membrane surface tend to shear off deposited material thus reducing the hydraulic resistance of the fouling layer. This is one of the simplest and most effective methods to control the effect of concentration polarization. Severe decreases in flux can sometimes be observed at too low velocities [2, 6, 31].

6. Resistance and mathematical models of fouling

Because of concentration polarization and fouling, there is a reduction on flux permeate value compared with pure solvent. As a result, both represent additional resistances to mass transfer by the membrane. The kinetic that is relativity slow for some phenomes and that provokes fouling, can explain the long time it takes to reach a possible stationary state. **Figure 3** is presented as an illustration of these phenomes. Thus, the relation between permeate flux and pressure variation applied on both sides of the membrane can be expressed by Eq. (1):

$$J = \frac{1}{n R_T} \Delta P \tag{1}$$

where

$$R_T = R_m + R_a + R_b + R_g + R_{cp} \tag{2}$$

Here R_m, resistance of transport by the membrane; R_a, additional resistance due to adsorption phenomenon; R_b, additional resistance of physical pores blocks; R_g, additional resistance due to formation of gel layer on the membrane surface; R_{pc}, additional resistance due to polarization concentration phenomenon; R_T, total resistance due of mass transfer through the membrane; n, solution viscosity that permeates through the membrane.

Despite the resistance-in-series model being used frequently, in which permeation flux declines due to membrane fouling and concentration polarization resistance on the membrane surface, other mathematical models to predict the flux behavior can also be used. A number of mathematical models are available in the literature that attempt to describe the mechanism of transport of particles through membranes such as Brownian diffusion, inertial lift, shear-induced diffusion, flowing cake and surface transport, and cake layer models [32].

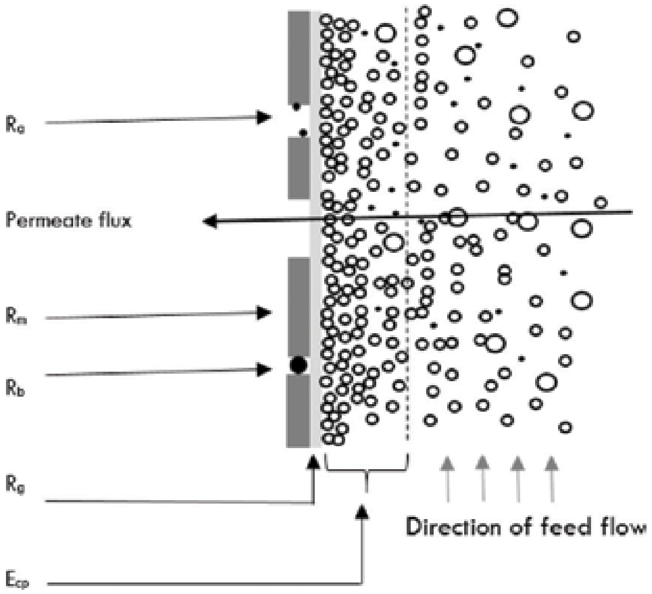

Figure 3. Resistances of mass transfer in membrane provoked by fouling and concentration polarization. Additional resistance: R_m, membrane resistance; R_a, adsorption; R_b, blocked pore; R_g, gel layer; E_{cp}, concentration polarization.

The most elementary type of model relates the flux to the time and volume permeated. Most of them are based on the assumption that the build-up of fouling layer is a first order reaction [2].

Decrease in permeate flux with time has been related to the volume concentration factor (VCR), defined as the initial volume divided by the retentate volume at any time ($VCR = V_0/(V_0 - V_P)$), where V_0 is the initial volume and V_P is the permeate volume [33].

In general, almost any data (flux vs. time) will adequately fit almost any of models reasonably well, but since they are semi-empirical in nature, they do not help to explain or understand the phenomenon itself [2].

7. Fouling and cleaning

According to the characteristics and factors described before, fouling reveals itself to be a decline performance, commonly a decline in flux under constant operating conditions, processing, and probable modification in the permeate properties of the membrane. The optimum way to reduce fouling will depend on the fouling process [34].

Membrane fouling problems can also be cleaning problems. For food processes, the membrane material, and all other food contact surfaces, should be compatible with normal food and food cleaners [2, 34].

Reducing membrane fouling must include an attention to the chemical nature of the membrane such as physical-chemical properties of feed stream. Some studies reported that hydrophilic membranes normally foul less than hydrophobic membranes [34].

To decide about the cleaning process, it is very important to consider the type of foulant, that is, the cleaning agents to use will depend on the material that causes the fouling. Moreover, the cleaning cycle can be incorporated into the design of nanofiltration plant as automatic cleaning operation. The membrane system is considered clean when the original water flux has been restored [2].

8. Final considerations

Nanofiltration technology has been widely applied in the desalination and concentration, separation and purification of drinking water, wastewater treatment and other industrial processes [36–41]. This process already plays an important role in a variety of cases in the water treatment, the dairy industry, biomedical processes and, so on. It is important to note that the ability of nanofiltration to separate monovalent and multivalent ions is a key feature in environmentally related processes. Operations with high pressure membranes are already established technologies for the treatment of waste water that aim at the production of purified water for recycling or reuse and recovery of valuable compounds [12, 35, 42–46].

Among these example applications, a number of factors have been contributing to the increasing interest in using membrane processes for water treatment. The essential factor is the stringent water quality regulations, which can be met to some extent, in an economically viable way, by membrane processes [5].

Furthermore, the food industry was one of the first industries to introduce membrane filtration into its commercial processes since membrane processes are potentially nondestructive, relatively energy efficient (no phase change), and even cheaper than conventional treatment [36–41]. However, nowadays, the cost of application and industrial processes by membranes is still expensive.

Researches reveal that in practice, industrial application of membranes becomes more attractive and competitive when combined processes, i.e., classical processes and membrane processes, are used together. In this way, each process acts in the most efficient part, and thus, the results are more advantageous than when applying technologies alone [5].

It is also necessary to improve the competitiveness of the process for filtration of drinking water, wastewater treatment, the food industry, the chemical and pharmaceutical industry, purification of biodiesel, and many other industries. It is important to improve the technological process and products and to reduce costs.

Fouling of membranes is important as it limits the competitiveness of the process due to an increase in costs caused by an increased energy demand, additional labor for maintenance and chemical costs for cleaning as well as a shorter lifetime of the membranes. Essential for effective fouling control is a proactive operation of the nanofiltration (NF) plant where an early indication of fouling is acted upon and a good identification of the type of fouling is carried out. On the other hand, nanofiltration technology can be applied in many industrial sectors in many different ways. The use of membrane technology appears as a relevant alternative to conventional processing in a huge variety of annexed processes.

NF membranes are also finding increasing use for purifying industrial effluents and minimizing waste discharge. The possibility of waste treatment, the preservation of compounds of importance from them, the reduction in energy consumption and of chemical products stand out among the principal advantages of NF membranes.

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Electrically and Electrochemically Assisted Nanofiltration: A Promising Approach for Fouling Mitigation

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Additional information is available at the end of the chapter

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Abstract

Membrane fouling is regarded as the most critical bottleneck for the widespread application of membrane separation technology. The application of electricity to the surface of membrane provides a promising alternative for fouling mitigation, which may involve the following effects such as electrophoresis, electroosmosis, and electrooxidation. Electrophoresis and electroosmosis influence the movement of charged species (ions or molecules) or movement of fluid adjacent to charged surface under the applied electric field, while electrooxidation functions by degrading species accumulated in the concentration polarization layer and fouling layer to resume permeate flux. Different membrane modules have been developed to satisfy the requirement of electrode assembly. Meanwhile, this coupled process also promotes the development of stable and conductive electrodes including membrane electrodes. Successful applications have been found in the areas of ion separation and treatment of dye wastewater, arsenic contaminated wastewater, antibiotic contaminated wastewater, etc. Compared with microfiltration (MF) and ultrafiltration (UF), existing research in the nanofiltration (NF) is still limited. The increasing applications of NF in practice because of its unique separation capability will definitely trigger more investigations on this electrically or electrochemically combined antifouling technique.

Keywords: membrane antifouling, electrophoresis, electrooxidation, nanofiltration, membrane module

1. Introduction

Nanofiltration (NF) can distinguish species based on their size and/or valence [1]. The major drawback of NF lies in inherent membrane fouling caused by concentration polarization and

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pore blockage, similar to other typical membrane separation processes. Membrane fouling significantly decreases permeate flux with time and shortens membrane service life, requiring mechanical or chemical cleaning or even complete replacement of the membrane elements after certain operation time [2]. Therefore, effective antifouling technique is in high demand to make the membrane separation processes economically more competitive.

The electrically or electrochemically combined separation process has been presented as an effective fouling control strategy through in situ membrane cleaning. The utilization of an external adjustable electric field in membrane filtration was first investigated and denoted as electrofiltration, which has been thoroughly studied for decades [3]. It is the combination of two driving forces: pressure and electric field, which are mainly used for the separation of charged molecules or particles. Most studies published previously in the literature refer to electro-microfiltration (EMF) or electro-ultrafiltration (EUF) with the feed solutions of minerals [4], emulsions [5], macromolecules [6], etc. It functions by dragging the charged foulants away from the membrane surface within the electric field. The electroosmosis flow generated by the superimposed electric field may also contribute to the enhanced permeate flux.

Compared with electrofiltration, there are relatively fewer studies about the combination of electrooxidation with membrane separation. However, the effectiveness of such electrochemically assisted separation process in membrane fouling control has drawn increasing attention with more research focus shifted to this area. With the contribution of electrochemical degradation of organic foulants concentrated at the membrane surface, the permeate flux could be resumed, and the permeate quality could be improved at the same time. The organic foulants treated by this coupled technique include oily emulsion [7], dyes [8, 9], phenols [10], natural organic matters [10], etc.

There are relatively fewer reports about electrically and electrochemically assisted NF than MF and UF. Moreover, corresponding module designs for such coupled NF process are limited as well, mainly presented as the "sandwich" configuration of membrane between two electrodes, whereas more compact module design with membrane performing dual functions of filter and electrode has already been well developed in MF and UF. This chapter aims to present the electrically and electrochemically assisted filtration process from the working principles first and then the existing developed membrane modules with different designs for embedded electrodes, followed by typical applications of coupled NF process. Toward the end, some possible aspects for future research are discussed in order to make the electrically and electrochemically assisted NF more practical and economically competitive.

2. Working principle

2.1. Electrophoresis and electroosmosis

Most particles acquire a surface charge when in contact with a polar (e.g., aqueous) medium because of ion adsorption or ion dissolution. This surface charge influences the distribution of nearby ions of opposite charge and leads to the formation of an electrical double layer at the interface between the particle and the dispersion medium. The double layer contains two parts, the stern layer and the diffuse layer, with boundary named slipping plane. The zeta potential ξ is the electric potential at the slipping plane relative to a point in the bulk fluid. If electric voltage is applied, the charged particle (plus ions within the slipping plane) will likely be repelled toward the electrode of opposite charge, which is termed as electrophoresis. The velocity of charged particles (plus ions within the slipping plane) closely depends on the zeta potential ζ and the strength of the electric field [11]. The electrophoretic mobility, which is defined as the electrophoretic velocity per electric field, has a positive correlation with the zeta potential according to the Smoluchowski equation Eq. (1). This equation is valid in most cases for particles or colloids in aqueous media [12],

$$u_e = \frac{\zeta\,\varepsilon_0\,\varepsilon_r}{\mu} = \frac{v_e}{E} \tag{1}$$

where u_e is the electrophoretic mobility of charged particles ($m^2 \cdot s^{-1} \cdot V^{-1}$), ζ the zeta potential (V), ε_0 the permittivity of free space ($F \cdot m^{-1}$), ε_r the dielectric constant (dimensionless), μ the viscosity of the fluid (Pa·s), v_e the electrophoretic velocity ($m \cdot s^{-1}$), and E the magnitude of electric field ($V \cdot m^{-1}$).

Electroosmosis is the motion of liquid under an applied potential across a porous material such as membranes. Similar to the electric double layer in a charged particle, the electric double layer also exists on the surface of porous material, which could be ionized when in contact with a polar medium. Ions in the diffuse layer migrate toward the electrode with opposite charge. Since ions are solvated, the solution is also dragged along, producing the electroosmotic flow [13].

When electrophoresis is combined with membrane separation, the combined system is usually termed as electrofiltration in short. Electrophoresis-assisted membrane was first mentioned by Bier as the so-called forced-flow electrophoresis for the reduction of membrane pore blockage, followed by similar research for the treatment of different feed solutions [5, 14–16]. The electrofiltration method is the consequence of the fact that charged droplets or particles in the feed solution could migrate away from the membrane surface in the electric field, which helps to reduce concentration polarization and mitigate membrane fouling. A typical schematic representation of electrophoresis-assisted filtration (electrofiltration) configuration is shown in **Figure 1** for the removal of negatively charged particulates using polysulfone membrane [17]. Besides flux enhancement by applied electric filed, an electroosmotic flux is expected toward the cathode because of the negative charges carried by the membrane under neutral condition. However, if the membrane elements are utilized as both the electrode and the filtration media, the electroosmosis flow could be regarded as zero because there is no electric potential difference across the membrane [5]. Electrofiltration requires low conductivity of feed solution as well as high applied electric field to achieve high mobility of charged particulates and hence high productivity of the filtration process. The antifouling effects of electrofiltration membranes depend on many factors, such as magnitude of the electric field, concentration of the feed solution, electrode material and arrangement, size and zeta potential of the feed particles, etc.

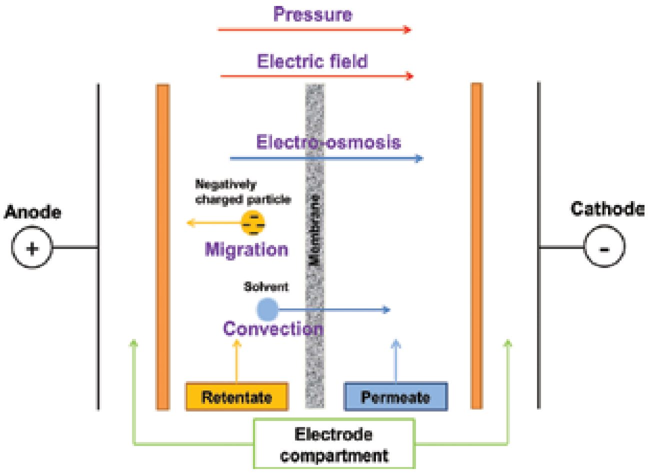

Figure 1. Schematic diagram of the electrofiltration process [18] (reproduced with permission).

2.2. Electrooxidation

Electrooxidation could be divided into indirect and direct electrooxidation processes. Indirect electrooxidation could be achieved by electrochemically generated chlorine, hypochlorite, hydrogen peroxide, or ozone [19]. It is also possible to use mediators, which are metal ions oxidized on an anode from a stable and low valence state to a reactive and high valence state, to treat mixed and hazardous wastes [20]. For direct electrooxidation process, the anode surface could generate either physisorbed active oxygen (MO_n·OH·) or chemisorbed active oxygen (MO_{n+1}). Physisorbed oxygen reacts directly with oxidizable organic compounds acting as a source of hydroxyl radicals. β-PbO_2, Sb-doped SnO_2, and Boron-doped diamond (BDD) exemplify this type of anode. Chemisorbed active oxygen is generated if the anode material MO_n is oxidizable and MO_n·OH· is further oxidized to MO_{n+1}, which initiates oxidation process by a two-electron transfer mechanism. Examples of this kind of anode are IrO_2/Ti, RuO_2/Ti, etc. In general, ·OH is more effective for pollutant oxidation than O in MO_{x+1}. The two mechanisms are illustrated as below Reactions (2)–(5) [21].

Oxidation by physisorbed active oxygen:

$$H_2O + MO_x \rightarrow MO_x(\cdot OH) + H^+ + e^- \quad (2)$$

$$R + MO_x(\cdot OH)_z \rightarrow CO_2 + zH^+ + ze^- + MO_x \quad (3)$$

Oxidation by chemisorbed active oxygen:

$$MO_x(\cdot OH) \rightarrow MO_{x+1} + H^+ + e^- \quad (4)$$

$$R + M\,O_{x+1} \rightarrow RO + M\,O_x \tag{5}$$

The essential part of an anodic oxidation process is the selection of anodic material. An ideal anode should possess high electro-catalytic activity, high electrochemical stability, and affordable material cost. Meanwhile, it should also have a high overpotential for O_2 evolution so that Reactions (2) and (4) can proceed with high current efficiency. Otherwise, most of the electric current supplied will be consumed in splitting water.

Graphite and Pt electrodes can be effective only at very low current densities or in the presence of high concentrations of chlorides or metallic mediators [22]. PbO_2 is the most widely investigated anode material because of its relatively low cost and high current efficiency [23]. However, it suffers from severe electrochemical corrosion and causes secondary Pb^{2+} pollution. SnO_2 has been reported to have a high overpotential of oxygen evolution. Its stability is very poor [24]. Sb-doped SnO_2 electrodes have been developed including Ti/SnO_2-Sb, Ti/SnO_2-Sb-CNT [9] and Ti/SnO_2-Sb_2O_3-Y [25]. However, the performance still needs further improvement. Although IrO_2-based anodes (including dimensionally stable anodes (DSA)) have also been used for anodic oxidation of organic pollutants [26–28], such type of electrodes would have low current efficiency because of low overpotential of oxygen evolution. Meanwhile, because chemisorbed active oxygen is mainly generated at the IrO_2-based anodes, partial degradation of certain pollutants in wastewater has been mostly achieved, instead of complete mineralization [21, 26]. Boron-doped diamond (BDD) electrodes are attractive candidates for electrooxidation because of their high electrochemical stability, large electrochemical window, and high electrochemical activities for the degradation of pollutants. However, the fabrication process usually involves complex preparation procedures, severe operation conditions, and high equipment cost. It is also a challenge to deposit the diamond layer on common electrode substrate such as titanium [24, 29–31]. Another material worth mentioning is Magnéli titanium suboxides. They have high corrosion resistance and are capable of conducting mineralization reactions of organic pollutants such as trichloroethylene [32], *p*-nitrosodimethylaniline [33], *p*-benzoquinone (BQ) [33], coumarin [34], phenol [35], etc. The most conductive phase of Magnéli titanium suboxides, Ti_4O_7, has similarly large O_2 evolution potential to BDD electrode. With nanotube array morphology, it even possesses comparable electrochemical activity to BDD as well [35]. The preparation temperature of Ti_4O_7 is over 800°C requiring H_2 atmosphere. Partial oxidation may occur if the electrodes have been utilized multiple times. Therefore, it is still highly needed to develop new electrodes with high electrooxidation efficiency, high electrochemical stability, as well as acceptable material and fabrication cost.

The combination of electrooxidation with membrane filtration has been studied for a couple of years. With the contribution of electrochemical degradation of organic foulants concentrated at the membrane surface, the permeate flux of the hybrid membrane filtration process could be significantly enhanced. One schematic diagram of the membrane separation with electrooxidation assistance is shown in **Figure 2**. In order for electrooxidation effect to occur, many

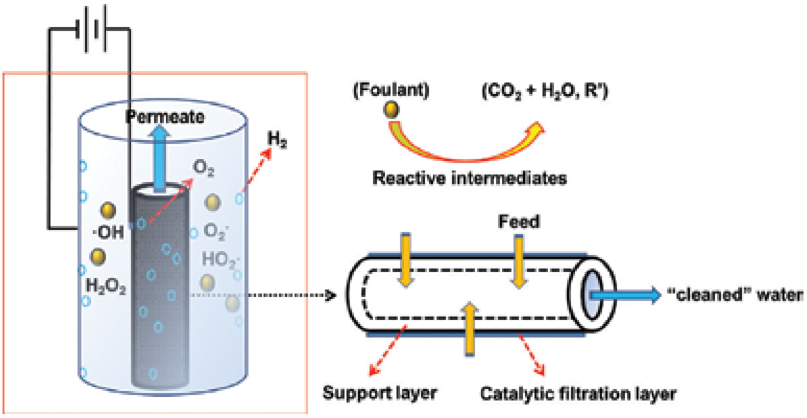

Figure 2. Schematic diagram of electrooxidation-assisted filtration [18] (reproduced with permission).

researchers developed conductive membrane electrodes to serve as the anode. However, O_2 gas may be induced if the applied potential is above the overpotential window, resulting in bubbling resistance to adversely affect the permeate flux [36, 37]. One possible solution is to locate the anode in close vicinity with the membrane surface to minimize the bubble resistance. With such kind of configuration, the induced O_2 gas may make the fluid near the membrane surface turbulent and further reduce concentration polarization and/or gel layer resistance [7, 38]. The detailed mechanism for the coupled process is still not well understood, requiring further fundamental investigation.

3. Electrically/electrochemically assisted membrane module design

3.1. Membrane material

Different from the porous membranes for UF and MF, the membranes in NF are mostly dense with pore sizes from 1 to 10 nm. Generally speaking, organic polymers present a fixed electric charge, which is mostly negative. Inorganic ceramics can be positively or negatively charged depending on the pH of bulk solution and isoelectric point of the membrane material [1].

3.2. Electrode material

For electrically assisted membrane filtration (electrofiltration), the anode and the cathode are normally separated from the membrane element. To date, the most commonly applied anodic material has been reported to be noble metal/metal oxides (e.g., platinum, iridium oxide)-coated titanium [39–41]. Graphite or stainless steel may also be used [1, 42, 43], but electrode corrosion is likely to occur after long-time operation. There is usually a wide range of selection for the cathodic material.

When the membrane itself serves as the electrode (i.e., membrane electrode) during electrofiltration, the membrane support layer or the modified layer could serve as the electrode. Conductive polymers are possible candidates which may provide membranes with electrical conductivity. Typical conductive polymers include polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), polyphenylene vinylene (PPV), etc. Their good conductivity is owing to the high electron mobility in the conjugated p-orbitals upon doping. Long-term stability should be considered when using conductive polymers as membrane electrodes. Meanwhile, the high hydrophobicity of these polymers may have a negative impact on filtrations of organic feed solutions. With much higher thermal and chemical stabilities, conductive inorganic materials, such as carbon- (used as membrane support), noble metal-, or metal oxides-based composites (used as modified layer), are possible alternatives of membrane electrodes for electrofiltration [44]. Electrochemical corrosion in alkaline condition is the common problem for carbon membranes [45]. The cost issue should be considered for noble metal- or metal oxides-based composites as conductive modified layers [36]. Magnéli Ti_4O_7 has also been utilized as membrane electrodes for electrofiltration [35, 46, 47]. The issue that should be considered for Magnéli Ti_4O_7 membrane electrode is partial oxidation to other Magnéli titanium suboxides with higher oxidation states if the electrolyte conductivity used for electrofiltration is high.

For electrooxidation-assisted membrane filtrations, polymers are seldom utilized, and the anodic materials are mostly composed of carbon, noble metal/metal oxides, doped SnO_2, or BDD. Typical fabricated membrane electrodes for electrochemically assisted MF and UF include the TiO_2/carbon composite membrane developed for oily water filtration [7]; the Boron-doped diamond (BDD)/Ti membrane developed for the treatment of Disperse Blue 2BLN powder [8]; the carbon nanotube (CNT)/Al_2O_3 flat sheet composite membrane developed for the filtrations of silica spheres, latex particles, phenol, and natural organic matter (NOM) [10]; and the Ebonex membrane (mixture of the Magnéli phases of Ti_4O_7 and Ti_5O_9) for the removal of organic pollutant such as *p*-methoxyphenol [48]. Issues to consider when using these developed membranes include electrochemical instability of carbon membranes (usually graphite) [45, 49], sophisticated fabrication of BDD in membrane modification [10], and also possibly oxidation of Ebonex to higher oxidation states after repeated use. Up to now, the research on NF with electrooxidation assistance is limited. One typical research is conducted by Xu and coworkers using doped SnO_2 as anode in vicinity of membrane surface to degrade membrane foulants simultaneously with the separation process [25, 38]. Better performance may be achieved if replacing the electrode in their research with the materials developed for electrooxidation-assisted MF and UF or other typical materials for electrooxidation as mentioned in Section 2.2.

3.3. Membrane module configuration

Membrane module design is essential for the realization of electrically or electrochemically assisted membrane filtration. The styles of electrode assembly into the module should consider several parameters, including the types of membrane elements, the major working effect for membrane antifouling, and possible side effects brought to the feed or permeate solution. Generally speaking, most membrane modules with electrophoresis as the main antifouling mechanism are constructed with flat sheet membrane elements with exerted electric field provided between two separate electrodes on either side of the membrane [4, 15, 16, 40, 41, 50]. Some electrooxidation-assisted membrane module also follows this style of electrode assembly with the anode in close vicinity of the membrane element [25, 38]. To make the system more compact and energy efficient, the membrane element itself could serve as both the electrode and the filtration media via the utilization of a conductive membrane support [5] or the modification of a conductive layer on a non-conductive membrane support [36]. The compact module design also promotes the development of electro-catalytic membranes (usually as membrane anode) as well, which could degrade foulants accumulated on the membrane surface simultaneously with the separation process through electrooxidation [7, 8, 51, 52], leading to higher permeate flux and better permeate quality.

The membrane modules presented below are some typical examples. Actually, these electrically or electrochemically assisted module designs should be applicable to all kinds of pressure-driven separation processes including MF, UF, NF, and RO, but the membrane elements and operation conditions should change accordingly.

3.3.1. Flat sheet membrane module

Figure 3 presents a flat sheet module design for electrophoresis-assisted arsenic wastewater treatment. The design utilized solid graphite plate as the anode and perforated graphite as the cathode. The electric contacts to external power supply were also made of graphite. With cathode located in the permeate side, it was possible to repel negatively charged $H_2AsO_4^-$ and $H_2AsO_3^-$ away from the membrane surface and retain relatively higher flux for longer operation time with applied electric field [43].

3.3.2. Tubular membrane module

According to the study of Wakeman and coworkers, tubular geometry modules would have the most effective use of electrical power when used as an aid to prevent membrane fouling [14]. Because of the annular structure of tubular membrane elements, the module design for the hybrid process is more complex compared with flat sheet membrane module. In general, a rod or wire needs to be inserted into the inside of membrane and fixed at two terminals.

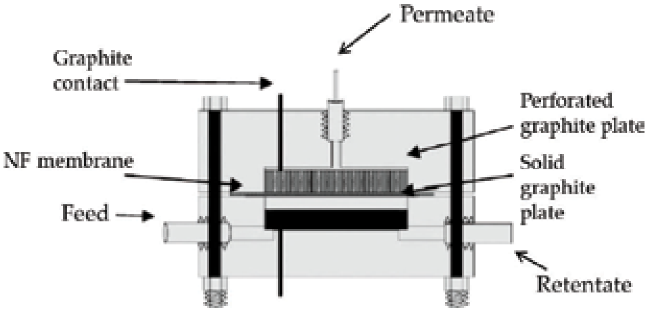

Figure 3. Flat sheet membrane module designs with electrophoresis assistance [43] (reproduced with permission).

Cylindrical netting is then required to surround the outer surface of membrane as the other electrode. Part of a typical tubular module design is shown in **Figure 4**, with rod electrode and cylindrical netting electrode composed of the same or different materials. The electric field distribution is more complex compared with flat sheet membrane module where the electric field distribution resembles that of a typical parallel-plate capacitor.

3.3.3. Module with functional membrane element

Just as mentioned before, in order to make the module more compact, the membrane element can also be utilized as one electrode if the inner or outer surface is conductive. Corresponding electric contact needs to be designed to connect with external power supply. The authors have developed one kind of membrane module that could act as membrane elements with either inner or outer surface conductive [18]. As shown in **Figure 5**, the electric contacts of (2) and (3) could connect the inner and outer surfaces of membranes, respectively, to the power supply. Both electric contacts were provided through stainless steel rods combined with graphite rods. The other non-membrane wire electrode could be inserted through the module terminals which were sealed with silicone rubbers.

3.3.4. Separate compartment of electrodes

For electrophoresis-assisted membrane filtration, low conductivity of feed solution is usually required. However, electrolysis is generally unavoidable at the high potential applied for electrophoresis. Similarly, electrolysis will occur if the voltage supplied exceeded the electrochemical window for electrooxidation-assisted filtration. Due to gas formation and other electrochemical reactions that occurred at the electrodes, alteration of pH may occur, which may damage the components within the feed or permeate solutions (e.g., biomolecules). Besides using buffer solution, external compartments can be placed on either side of the electrodes to avoid changes in the process streams. These compartments are separated from the retentate and permeate compartments normally by cellophane or ion-exchange membranes. Meanwhile, an additional rinsing cycle can be used within each compartment to wash away electrolysis products and prevent particle deposition at the electrodes.

A typical design with separate compartment of electrodes and rinsing cycle is displayed in **Figure 6**. If the feed solution is negatively charged, a cation-exchange membrane could be put on the cathode side and an anion-exchange membrane on the anode side in order to avoid

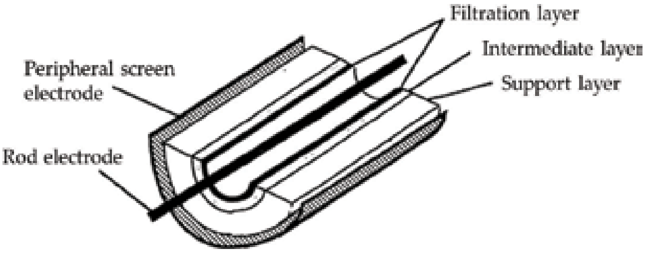

Figure 4. Typical tubular electrically assisted NF membrane module design.

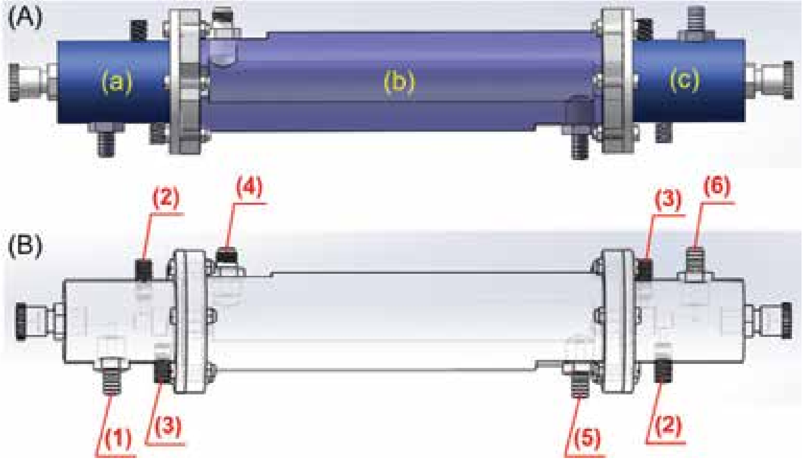

Figure 5. Three-dimensional (A) and perspective view (B) of (a) tubular membrane module with electric contact for inner and outer membrane surface, (b) compartment used for permeate collection, (c) symmetrical compartments for the flow of feed solution and retentate. (1) Inlet opening for feed solution, (2) electricity connectors in contact with the inner surface, (3) electricity connectors in contact with the outer surface, (4) pressure gauge connector in the permeate side, (5) opening for permeate, (6) outlet opening for retentate [18] (reproduced with permission).

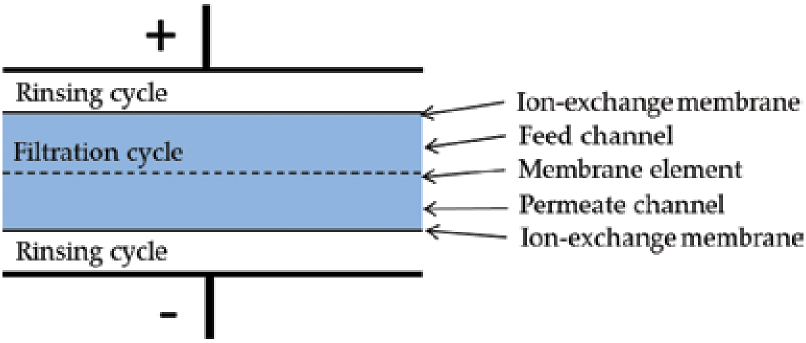

Figure 6. Membrane module design with separate compartment of electrodes and rinsing cycle.

increase of ion concentration in the filtration cycle. As reported by Weigert and coworkers, a tenfold increase of permeate flux was achieved using this process design [53].

3.4. System energy consumption

The additional energy consumed by DC power supply should be considered for the electrically or electrochemically combined NF system. The total energy consumption should include energy required for operating the pump and for electrophoresis or electrooxidation. Normally, the energy consumption is written as total specific consumption per unit volume of permeate flux, with the equation below [25]:

$$E_{total} = \frac{Q\,\Delta P}{JA\eta} + \frac{VI}{JA\,\eta_{DC}} \tag{6}$$

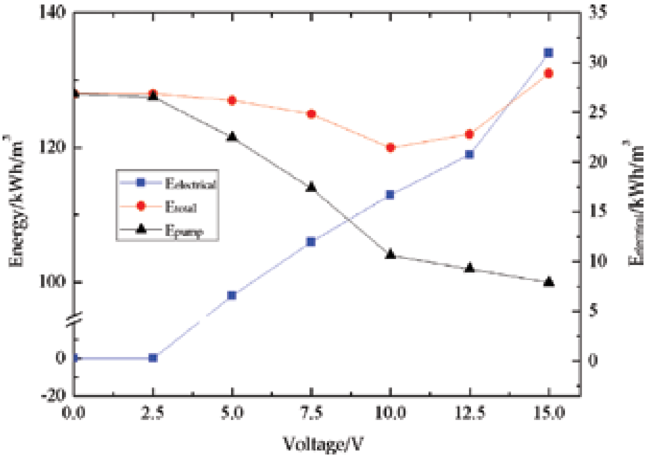

Figure 7. Variation of energy consumption per unit volume of permeate with applied potential at TMP of 0.8 MPa and CFV of 0.0258 m·s^{-1} [25] (reproduced with permission).

where Q was the flow velocity (m^3·s^{-1}), ΔP the TMP (Pa), V the applied voltage (V), I the electric current (A), J the permeate flux (L·m^{-2}·s^{-1}), A the membrane area (m^2), η the efficiency of pump, and η_{DC} the efficiency of DC power supply. Despite the additional costs brought by electrooxidation or electrophoresis, total energy consumption may be reduced due to the significant increase of specific permeate flux and the decrease of required treating time or membrane surface area.

A typical graph showing individual and total energy consumptions is presented in **Figure 7**. Although the energy consumed by electrooxidation increased with applied voltage, lower energy is required for the operation (the pump energy) because of the enhancement of permeate flux. As a result, the total energy demand shows a "V" curve with the minimum value at around 10 V. At higher electric potential, the decrease in concentration polarization and fouling layer became less obvious resulting in insignificant increase in permeate flux. Therefore, the total energy increased with higher voltage [25].

4. Application

4.1. Ion separation and alteration of membrane property

Pupunat and coworkers present the first results obtained by superimposing an electric field on a classical NF operation with single salt or mixed solutions of Na_2SO_4 and NaCl (fixed Na^+ concentrations of 10 and 50 mol·m^{-3}) over an estimated potential range from 0 to 1.9 × 10^3 V·m^{-1} (0–7.5 V). The detailed experimental conditions are listed in **Table 1** with the same module design shown in **Figure 4**. The membrane was created from an α-alumina macroporous support, an intermediate mesoporous titania substrate, and a very thin microporous film of negatively charged Nafion. The anode is a stainless steel rod at the center of tubular membrane, while the cathode is a stainless steel cylindrical wire netting stuck on the membrane support. The anode was put inside in order to promote a pumping effect of Na^+

Membrane element	Anode	Cathode	Application	Conditions	Ref.
Organo-inorganic tubular membranes	Stainless steel rod	Stainless steel cylindrical wire netting	Single salt and mixed solutions of Na_2SO_4 and NaCl with fixed Na^+ concentrations of 10 and 50 $mol{\cdot}m^{-3}$	CFV: 3 $m{\cdot}s^{-1}$ TMP: 5, 10, 20, 30 bar Electric field: 0 to 1.9×10^3 $V{\cdot}m^{-1}$	[1]
NF45 and BQ01 flat polymeric membranes	Stainless steel wire lattice	Porous, stainless-steel disk	Direct red dye with an average molecular weight of 1373 $kg{\cdot}kmol^{-1}$	TMP: 6.9 bar CFV: 0.5 $m{\cdot}min^{-1}$ Electric field: 0 to 1.5×10^4 $V{\cdot}m^{-1}$	[41]
BQ01 flat polymeric membranes	Stainless steel wire lattice	Porous, stainless-steel disk	3.08, 17.11 and 59.88 $mol{\cdot}m^{-3}$ NaCl solution	TMP: 6.9 bar Electric field: 0 to 2.67×10^4 $V{\cdot}m^{-1}$	[54]
Self-prepared negatively charged polyamide nanofiltration membrane NF-PS-3	Solid graphite	Perforated graphite plate	0–1000 ppb As (V) and As (III) solutions	TMP, 80–180 psig; CFV, 3.785 $L{\cdot}min^{-1}$; electric potential, 0 to 2 V	[42]
NF90 flat polymeric membrane	Mesh Ti/ SnO_2-Sb	Ti Mesh	250 $mg{\cdot}L^{-1}$ tetracycline hydrochloride with NaCl of 0.06 $mol{\cdot}L^{-1}$	TMP, 0.4–1.2 MPa; CFV, 10–60 $L{\cdot}h^{-1}$; electric current, 10–50 $mA{\cdot}cm^{-2}$	[37]
Polyamide polymeric membrane	Mesh Ti/ SnO_2-Sb_2O_3-Y	Ti Mesh	0.3–0.8 $g{\cdot}L^{-1}$ Acid Red 73 solution with 0.1 $mol{\cdot}L^{-1}$ Na_2SO_4	TMP, 0.4–1.2 MPa; CFV, 0.0086 to 0.043 $m{\cdot}s^{-1}$; electric potential, 2.5–15 V	[24]

Table 1. Summary of typical researches on electrically and electrochemically assisted NF.

through the porous medium. As expected, the experimental results clearly indicate that the electric field could strongly modify the kinetics of ionic transport through the membrane. The selectivities of $S_{Na+/Cl-}$ and $S_{Na+/SO42-}$ continuously increased with higher electrical voltage at $[Na_2SO_4]/[NaCl]$ of 1 and transmembrane pressure (TMP) of 10 bar. Meanwhile, the directions of variations of $[Na^+]$, $[SO_4^{2}-]$, and $[Cl^-]$ rejections were found to be independent of $[Na^+]$ concentration whether it was 10 or 50 mol m^{-3}. The most significant difference in NF and electrically assisted NF was observed at lower TMP. At TMP of 5 bar and voltage of 7.5 V, the rejection of $[Na^+]$ strongly decreased from 30 to −367% (minus means passage of $[Na^+]$), while the rejection of $[Cl^-]$ increased from −27 to 81% and $[SO_4^{2-}]$ from 56 to 90% [1]. This may be because the electrophoretic force was much more significant compared with the competitive hydrodynamic force [37]. However, under practical consideration, it is better to control the boundary voltage within 4 V because rapid increase in current density and strong variations of pH values were observed.

Different from the study of Pupunat and coworkers, a very small fractionation was obtained with applied electric field by Moël and coworkers using BQ01 membrane (polymeric membrane from Osmonics). Before the application of electricity, higher permeability was achieved for NaCl separation (dynamic permeability) compared with pure water (pure water permeability), which was explained by the swollen effect. After electricity was applied, they found that dynamic permeability decreased. The loss in dynamic permeability increased with higher NaCl concentration but was not affected by the magnitude and polarity of electric field. The researchers suggest that the electric field could induce favorable conditions for cross-linkage on the polymeric membrane surface. The smallest electric potential of 1.33×10^4 $V{\cdot}m^{-1}$ was sufficient to establish the polymer conformation, which explains the absence of significant variations with magnitude. The possibility of controlling pore size by an external force like an electric field represents an interesting opening in the field of NF and deserves further investigation [54].

4.2. Treatment of dye wastewater

A major problem in the textile industry is the discharge of dyehouse effluents without proper treatment, which will limit aquatic plant growth and affect the esthetic merits of water [55]. Efficient color reduction has been achieved by NF [56, 57], but the fouling issue remained to be tackled. Moël and coworkers studied the electrically assisted NF process for a textile direct dye solution with Stokes-Einstein radius of 1.2 nm and concentrations of 0.2 and 12 $kg{\cdot}m^{-3}$. Two types of membranes, BQ01 (polymeric membrane from Osmonics) and NF45 (polymeric membrane from Dow Chemical), were employed. Although both membranes can have 100% dye rejection, they showed different behaviors. With low red dye concentration of 0.2 $kg{\cdot}m^{-3}$, fouling was reversible for BQ01 but irreversible for NF45. For BQ01 membrane, a 1.25×10^4 $V{\cdot}cm^{-1}$ electric potential is needed to avoid fouling, while for NF45, 6×10^3 $V{\cdot}cm^{-1}$ is sufficient. With much higher red dye concentration of 12 $kg{\cdot}m^{-3}$, a reversible fouling is obtained using BQ01 with an electric field of 1.33×10^4 $V{\cdot}cm^{-1}$, whereas a partially reversible fouling is observed without an electric field. The authors suggested that electric field could delay the formation of fouling layer and may interact with the structure of the red dye layer leading to a more reversible fouling [42].

Xu and coworkers developed a coupled separation process with electro-catalytic oxidation to treat C.I. Acid Red 73 wastewater [25]. Flat sheet module design was adopted with anode located in close vicinity of membrane surface to achieve electrooxidation-assisted antifouling filtration. A Ti net was fixed behind the membrane in the permeate side serving as both the cathode and the support for membrane, while a Ti/SnO_2-Sb_2O_3-Y net with electro-catalytic activity was positioned at the feed side serving as the anode. With electrical supply, dyestuff in the wastewater can be directly degraded at the anode; meanwhile, the rising of bubbles may also result in turbulence of liquid around membrane surface and enhance the antifouling performance. The authors investigated the enhanced flux from electrooxidation by coating the anode with insulating varnish. With the application of electro-catalytic oxidation reaction, both permeate flux and dye retention were improved. Besides electrooxidation, electrophoresis and electroosmosis may also account for the flux increase at relatively higher applied potential. The study revealed that the electro-catalytic permeation flux increased with applied potential, initial feed concentration, TMP, and cross-flow velocity (CFV). However, the increment became slower when the applied potential exceeded 8 V and CFV was greater than 0.035 $m{\cdot}s^{-1}$. The authors further quantified the individual and total energy consumption required to run the pump and supply electric potential for electrooxidation. From their estimation, the optimal energy consumption could be obtained at 10 V, 0.6 MPa with low CFV [25].

4.3. Treatment of arsenic-contaminated water

Arsenic is highly toxic to humans, with As (V) and As (III) most likely to be encountered in potable water solutions. The prevailing pH ranges of As (III) and As (V) are 2–9 and 7–11.5, respectively [58]. As (III) was found primarily as H_3AsO_3 and hard to be ionized, which explains the reason why As (III) was difficult to be removed from water using ordinary processes like ion-exchange and electro-cross-flow membrane system [43]. Compared with As (III), As (V) was easier to be removed (H_3AsO_3, pKa = 9.13; H_3AsO_4, pKa = 2.22), so chlorine or oxygen was usually added to treat arsenic-contaminated feed [43].

Pérez-Sicairos and coworkers found that rejection of As (V) and As (III) can be enhanced by applied potential across the electro-cross-flow NF membrane system. The module design is presented in **Figure 3**. The rejection of As (V) was increased slightly from 97.3 to 98.6% when the applied potential was increased from 0 to 2.0 V at initial As (V) concentration of 1000 ppb. The rejection of As (III) was increased from 52.3 to 70.4% when the applied potential was increased from 0 to 2.0 V at initial As (III) concentration of 1000 ppb due to enhanced dissociation of the neutral species H_3AsO_3 to form H^+ and $H_2AsO_3^-$. Applied pressure and type of salt in the feed under investigation did not obviously affect the rejection of arsenic by the electromembrane system [43]. Better As (III) removal should be achieved with As (III) oxidized to As (V) prior to the electrically assisted NF process.

4.4. Treatment of wastewater containing antibiotics

Xu and coworkers applied the technique of electro-catalytic oxidation enhanced NF to reduce membrane fouling in the treatment of tetracycline hydrochloride wastewater. The mesh catalytic anode was put on the intercept side and in close vicinity of the membrane. The application of electrooxidation through the generation of hydroxyl radicals to the NF process brought obvious higher permeate flux and lower flow resistance. For instance, at TMP of 0.4 MPa, CFV of 30 $L \cdot h^{-1}$, and current density of 20 $mA \cdot cm^{-2}$, the total filtration resistance decreased from 14.54 to 3.84×10^{13} m^{-1} with the assistance of electrooxidation effect. The apparent retention of tetracycline hydrochloride was slightly increased as well (from over 97% to over 99%). Within the experimental range, higher permeate flux was obtained at higher TMP and higher current density. The enhancement became less obvious at TMP of over 1.2 MPa and current density of over 40 $mA \cdot cm^{-2}$. For the coupled process, the effect of CFV on permeate flux was insignificant because the concentration polarization layer was very thin. Compared with NF alone, better filtration performance could be obtained at lower TMP and CFV, indicating the process may be energy saving as well [38].

5. Concluding remarks and future perspectives

There is still a long way to go for the investigation of electrically and electrochemically assisted NF process because existing research is quite limited compared with MF and UF. The increasing application of NF in industry will surely trigger the development of in situ cleaning technique for fouling mitigation, with the electrically and electrochemically assisted filtration process as a very important part of the technique.

Here are some areas that worth further studies. First, for most of existing research, the investigation time is less than 3 hours or even shorter. Longer time should be investigated in order to see the coupled effect in the long run. Second, more fundamental research should be conducted to investigate in depth the basic mechanism of this coupled process. Third, most developed modules are only applicable to single membrane element. In order to increase the feasibility of this coupled technique in practice, it is highly suggested to develop membrane modules with multiple membrane elements (tubes or flat sheets) compacted together, which definitely requires more complicated design of electricity connection. Fourth, more practical and compact designs of membrane modules with separate compartment of electrodes are needed because it is necessary to maintain the conditions of feed and permeate constant. Fifth, new electrode materials are still required which should possess the following qualities: electrochemically stable, corrosion resistant, economically acceptable, and electro-catalytic. It is even better if such material could be placed on the membrane surface. Moreover, energy consumption is still a key aspect to consider when determining the optimal operation condition. In order to minimize energy consumption, pulsed electric field instead of constant electric field could be used as suggested by some researchers. More research is still needed to further reduce total energy consumption from the aspects of operation condition, membrane module design, and membrane materials development.

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The nanofiltration technique lies between ultrafiltration and reverse osmosis techniques, and it is considered a low-cost process and is capable of removing pesticides, organic matter, desalination of sea water, oil process and pollutants from industrial wastewater. However, the main challenge in implementation of nanofiltration membrane is its ability towards fouling and low performance at high temperature. The use of nanoparticles in the manufacturing of membranes allows for a high degree of control over membrane fouling. Nanoparticle-based membranes can be developed by assembling engineered nanoparticles into porous membranes or blending them with polymeric or inorganic membranes. This book covers topics from multiple ranges from manufacturing of nanofiltration membranes and their applications in wastewater treatment, drinking water treatment, and removal of pollutants, to addressing the fouling issues.

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