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## Review

## Removal of contaminants of emerging concern by membranes in water and wastewater: A review



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## ABSTRACT

This review summarizes comprehensive recent studies on the removal of contaminants of emerging concern (CECs) by forward osmosis (FO), reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF) membrane treatments, and describes important information on the applications of FO, RO, NF, and UF membranes in water and wastewater (WW) treatment. The main objective of this review was to synthesize findings on membrane treatments of CECs in water and WW, and to highlight upcoming research areas based on knowledge gaps. In particular, this review aimed to address several key parameters, including the physicochemical properties of CECs (solute molecular weight/size/geometry, charge, and hydrophobicity), water quality conditions (pH, solute concentration, temperature, background inorganics, and natural organic matter), and membrane properties and operating conditions (membrane fouling, membrane pore size, porosity, charge, and pressure) that influence the removal of CECs during membrane filtration. Future research directions regarding membrane treatment for the removal of CECs from water and WW are also discussed.

## 1. Introduction

To meet the increasing demand for water due to climate change, population growth, and over-consumption, water authorities are considering and implementing water recycling schemes. The fate of contaminants of emerging concern (CECs), such as endocrine-disrupting compounds (EDCs) and pharmaceuticals (PhACs)/personal care products (PPCPs), in water resources is a matter of significant concern according to increases in the consumption of CECs and the intensity of water recycling [1]. Stumm-Zollinger and Fair (1965) and Tabak and Bunch (1970) were the first to address concerns regarding the possible adverse effects of PhACs in municipal wastewater (WW), demonstrating

that several steroids are unlikely to be removed by conventional WW treatment processes [2,3]. The United States Environmental Protection Agency (USEPA) established the Endocrine Disruptor Screening Program for EDCs in 1998, which advised that both human and wildlife influences be evaluated, and estrogen, androgen, and thyroid endpoints be examined [4]. There is no current federal regulation for PhACs in drinking or natural water, while assessment of PhACs associated with ecological testing is required by the United States Food and Drug Administration if the environmental concentration in water is anticipated to exceed  $1 \mu\text{g L}^{-1}$  [5]. Only a few EDCs and PPCPs, including erythromycin (ETM), estrone (E1), 17 $\beta$ -estradiol (E2), 17 $\alpha$ -ethinyl estradiol (EE2), and estriol (E3), are currently listed in the USEPA's Drinking

**Abbreviations:** 4CP, 4-Chlorophenol; AC, Activated carbon; ATZ, Atrazine; CBM, Carbamazepine; CECs, Contaminants of emerging concern; CFV, Cross-flow velocity; CMC, Carboxymethyl cellulose; CRW, Colorado River water; CTA, Cellulose triacetate; DCF, Diclofenac; DI, Deionized; DOC, Dissolved organic carbon; DS, Draw solution; E1, Estrone; E2, 17 $\beta$ -Estradiol; E3, Estriol; EDCs, Endocrine-disrupting compounds; EE2, 17 $\alpha$ -Ethinyl estradiol; ETM, Erythromycin; FO, Forward osmosis; FRT, Fluoranthene; HA, Humic acid; IBP, Ibuprofen; MBR, Membrane bioreactor; MTP, Metoprolol; MW, Molecular weight; MWCs, Molecular weight cut-off; NPX, Naproxen; NF, Nanofiltration; NOM, Natural organic matter; ORW, Ohio River water; PCBA, Parachlorobenzoic acid; PhACs, Pharmaceuticals; PHN, Phenol; PPCPs, Pharmaceuticals/personal-care products; PVV, Passaic Valley water; RO, Reverse osmosis; SRW, Suwanee River RO isolate NOM water; SMX, Sulfamethoxazole; SUVA, Specific UV absorbance; TFC, Thin-film composite; TCS, Triclosan; UF, Ultrafiltration; USEPA, The United States Environmental Protection Agency; UV, Ultraviolet; WTPs, Water treatment plants; WW, Wastewater; WWTPs, WW treatment plants

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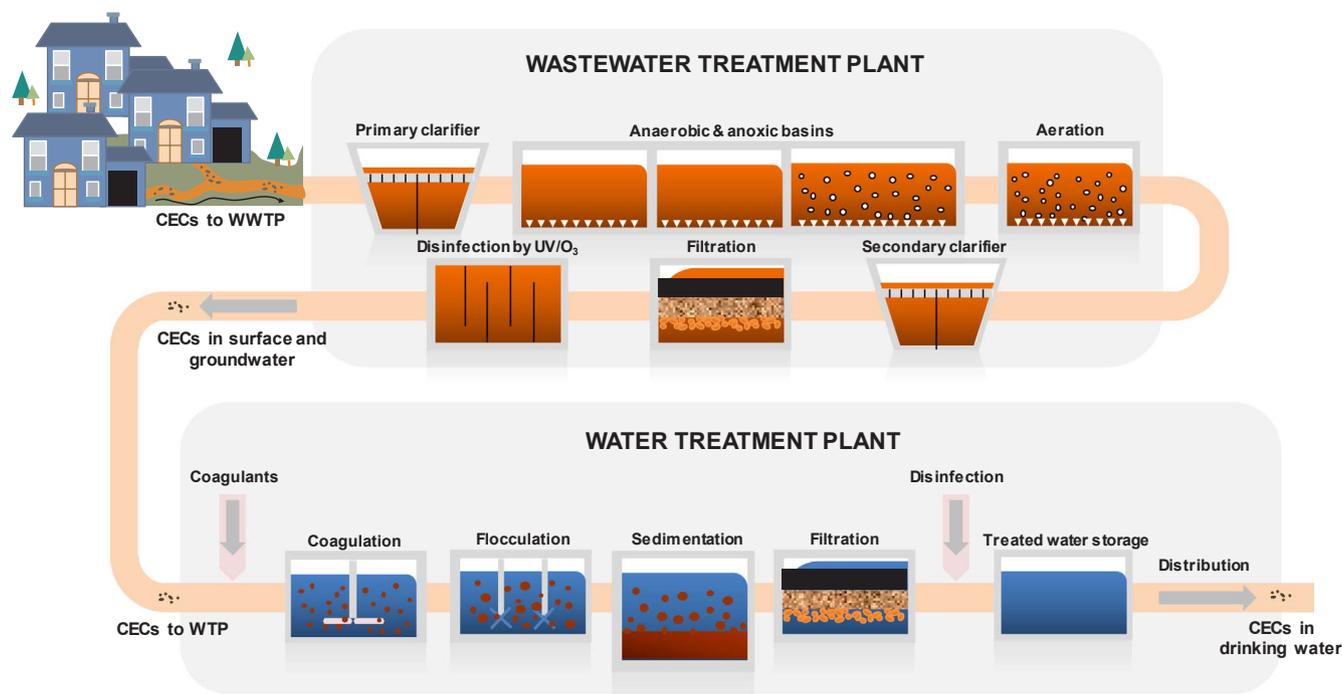


Fig. 1. Possible fate and transport of CECs in typical drinking water treatment and WW treatment processes modified from [8].

Water Contaminant Candidate List 4 [6]. The State of California has evaluated the potential influence of EDCs and PPCPs on indirect potable reuse of municipal WW effluent [7].

The potential fate and transport of CECs in typical drinking water treatment and WW treatment processes are described in Fig. 1 [8]. Both environmental scientists and engineers need to understand the removal mechanisms of CECs to assess potential human exposure to CECs, and to design more effective and specific water and WW treatment processes. Numerous studies have revealed that conventional water treatment plants (WTPs) [9–13] and WW treatment plants (WWTPs) [14–17] incompletely remove many CECs, while advanced technologies involving activated carbon (AC), ozonation, ultraviolet (UV) irradiation, sonodegradation, and membrane filtration enhance the removal of CECs [10,11,18–20]. Table 1 summarizes the estimated performances of different technologies used in both WTPs and WWTPs, based on literature reports of specific classes of compounds or similarities to other

CECs that have been examined in detail. In WWTPs, it is fairly complicated to assess the various different removal mechanisms due to the physicochemical properties of CECs (e.g., hydrophobicity, pKa, size, shape, and charge) and factors associated with the WW treatment technology used (e.g., aerobic/anaerobic/anoxic biodegradation, sludge adsorption, and oxidation by O<sub>3</sub>/chlorine) [21]. Table 2 summarizes the removal efficiencies for target CECs in the treatment concept, a representative sample of the existing literature concerning biodegradability, and trends regarding adsorption to sludge and oxidation by chlorination [21].

Membrane processes, including forward osmosis (FO), reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF), have been widely used in water and WW treatment processes [22–25]. The main advantages of FO are the production of high-quality permeate due to a high removal of various CECs and the ability to operate under an osmotic driving force without requiring a hydraulic pressure difference

Table 1  
Unit processes and operations used for CEC removal.

Group	Classification	AC	BAC	O <sub>3</sub> /AOPs	UV	Cl <sub>2</sub> /ClO <sub>2</sub>	Coagulation/flocculation	FO	RO	NF	UF	Degradation {B/P/AS} <sup>a</sup>
EDCs	Pesticides	E	E	L-E	E	P-E	P	F-E	E	G	P-F	E {P}
	Industrial chemicals	E	E	F-G	E	P	P-L	F-E	E	E	P-F	G-E {B}
	Steroids	E	E	E	E	E	P	F-E	E	G	P-F	L-E {B}
	Metals	G	G	P	P	P	F-G	F-E	E	G	P-F	P {B}, E {AS}
	Inorganics	P-L	F	P	P	P	P	F-E	E	G	P-F	P-L
PhACs	Antibiotics	F-G	E	L-E	F-G	P-G	P-L	F-E	E	E	P-F	E {B} G-E {P}
	Antidepressants	G-E	G-E	L-E	F-G	P-F	P-L	F-E	E	G-E	P-F	G-E
	Anti-inflammatories	E	G-E	E	E	P-F	P	F-E	E	G-E	P-F	E {B}
	Lipid regulators	E	E	E	F-G	P-F	P	F-E	E	G-E	P-F	P {B}
	X-Ray contrast media	G-E	G-E	L-E	F-G	P-F	P-L	F-E	E	G-E	P-F	E {B and P}
	Psychiatric control	G-E	G-E	L-E	F-G	P-F	P-L	F-E	E	G-E	P-F	G-E
PCPs	Synthetic scents	G-E	G-E	L-E	E	P-F	P-L	F-E	E	G-E	P-F	E {B}
	Sunscreens	G-E	G-E	L-E	F-G	P-F	P-L	F-E	E	G-E	P-F	G-E
	Antimicrobials	G-E	G-E	L-E	F-G	P-F	P-L	F-E	E	G-E	P-F	F {P}
	Surfactants/detergents	E	E	F-G	F-G	P	P-L	F-E	E	E	P-F	L-E {B}

Source: Modified from [7].

BAC = biological activated carbon; AOPs = advanced oxidation processes.

<sup>a</sup> B = biodegradation, P = photodegradation, AS = activated sludge; (solar); E = excellent (> 90%), G = good (70–90%), F = fair (40–70%), L = low (20–40%), P = poor (< 20%).

**Table 2**  
Removal efficiencies of selected CECs in order by log  $K_{ow}$  at WWTP under dry weather conditions with examples of previously published literature related to biodegradability, tendency of adsorption to sludge, and tendency of oxidation by chlorination.

Compound	Use	MW (g mol <sup>-1</sup> )	pK <sub>a</sub> <sup>b</sup>	log K <sub>ow</sub> <sup>c</sup>	Inf. (ng L <sup>-1</sup> )	Eff. (ng L <sup>-1</sup> )	Rem. (%)	Bio.	Ads.	Oxi.	Ref.
Triclocarban	Antibiotic	315.6	NA	4.90	198	33	83	L	H	NF	[111] <sup>B</sup> , [112] <sup>A</sup>
Gemfibrozil	Anticholesterol	250.2	4.7	4.72	45	33	27	H	M	H	[113] <sup>B,A</sup> , [10] <sup>O</sup>
Triclosan	Antibiotic	289.6	8 (7.9)	4.76	190	63	67	L	H	H	[113] <sup>B,A</sup> , [10] <sup>O</sup>
Ibuprofen	Analgesic	206.1	4.5 (4.9)	3.97	2724	241	91	H	M	M	[114] <sup>B</sup> , [115] <sup>A</sup> , [116] <sup>O</sup>
Diphenhydramine	Antihistamine	255.5	9.0	3.27	171	142	17	L	M	NF	[117] <sup>B</sup> , [112] <sup>A</sup>
Naproxen	Analgesic	230.1	4.5 (4.2)	3.18	5113	482	91	M	M	H	[113] <sup>B</sup> , [112] <sup>A</sup> , [116] <sup>O</sup>
Benzophenone	Ultraviolet blocker	182.2	< 2	3.18	88	47	47	L	M	L	[118] <sup>B</sup> , [119] <sup>A</sup> , [120] <sup>O</sup>
E1	Steroid	270.4	10.3 (10.5)	3.13	ND	ND	NA	H	M	H	[113] <sup>B,A</sup> , [10] <sup>O</sup>
Propylparaben	Preservative	180.2	8.5	3.04	520	7	99	H	H	H	[118] <sup>B,A</sup> , [121] <sup>O</sup>
TCPP	Fire retardant	327.6	NA	2.89	585	434	26	L	L	L	[122] <sup>B,A</sup> , [120] <sup>O</sup>
Diltiazem	Calcium channel blockers	414.5	12.9	2.79	ND	ND	NA	M	M	L	[123] <sup>B</sup> , [124] <sup>A</sup> , [125] <sup>O</sup>
Atrazine	Herbicide	215.1	< 2 (1.6)	2.61	ND	ND	NA	L	M	L	[113] <sup>B,A</sup> , [116] <sup>O</sup>
Carbamazepine	Analgesic	236.3	< 2	2.45	188	156	17	L	L	H	[126] <sup>B</sup> , [115] <sup>A</sup> , [10] <sup>O</sup>
DEET	Insect repellent	191.3	< 2	2.18	47	46	2	M	L	L	[113] <sup>B,A</sup> , [10] <sup>O</sup>
Simazine	Herbicide	201.7	1.62	2.18	ND	ND	NA	H	M	M	[127] <sup>B,A</sup> , [128] <sup>O</sup>
TCEP	Fire retardant	285.5	NA	1.44	439	348	21	H	M	L	[122] <sup>B,A</sup> , [113] <sup>A</sup> , [116] <sup>O</sup>
Benzotriazole	Heterocyclic	119.2	8.2	1.44	88	47	47	M	L	L	[129] <sup>B,A</sup> , [130] <sup>O</sup>
Trimethoprim	Antibiotic	290.1	6.3, 4.0, < 2 (7.1)	0.91	150	118	21	L	L	H	[131] <sup>B</sup> , [132] <sup>A</sup> , [10] <sup>O</sup>
Sulfamethoxazole	Antibiotic	253.1	2.1 & < 2 (5.7)	0.89	400	117	71	L	H	H	[113] <sup>B,A</sup> , [10] <sup>O</sup>
Primidone	Anticonvulsant	218.3	11.5	0.73	100	40	60	M	L	H	[133] <sup>B</sup> , [134] <sup>A</sup> , [125] <sup>O</sup>
Meprobamate	Anti-anxiety	218.3	< 2	0.70	ND	ND	NA	M	L	L	[113] <sup>B,A</sup> , [116] <sup>O</sup>
Diclofenac	Arthritis	318.1	(4.2)	0.7	6897	359	95	L	L	H	[135] <sup>B</sup> , [115] <sup>A</sup> , [10] <sup>O</sup>
Atenolol	Oral beta blocker	266.3	9.6	-0.03	1040	529	49	M	L	L	[127] <sup>B,A</sup> , [125] <sup>O</sup>
Caffeine	Stimulant	194.2	6.1	-0.07	8810	236	97	H	H	M	[113] <sup>B</sup> , [124] <sup>A</sup> , [10] <sup>O</sup>
Sucralose	Sweetener	397.6	NA	-1.00	5289	4043	24	L	L	L	[136] <sup>B,A,O</sup>
Acetulfame	Sugar substitute	201.2	2.0	-1.33	3863	3705	4	L	L	L	[137] <sup>B,A</sup> , [138] <sup>O</sup>
Iopromide	Contrast agent	790.9	< 2 and > 13	-2.10	11133	12895	-16	L	L	L	[113] <sup>B,A</sup> , [116] <sup>O</sup>
Iopamidol	Contrast agent	777.1	10.7	-2.42	8518	10091	-18	L	L	NF	[139] <sup>B,A</sup>
Iohexol	Contrast agent	821.1	11.7	-3.05	14432	16008	-11	L	L	L	[139] <sup>B,A</sup>

Source: Modified from [21].

Inf. = influent; Eff. = effluent; Rem. = overall removal; Bio. = biodegradation (<sup>B</sup>); Ads. = adsorption to sludge (<sup>A</sup>); Oxi. = oxidation by chlorine (<sup>O</sup>); Ref. = references; H = high; M = medium; L = low; ND = not determined because under detection limit (ND values = 15 ng L<sup>-1</sup> for E1, 50 ng L<sup>-1</sup> for diltiazem, 5 ng L<sup>-1</sup> for atrazine, 1.5 ng L<sup>-1</sup> for simazine, and 0.5 ng L<sup>-1</sup> for meprobamate); NA = not available or not applicable; NF = not found.

[26]. The permeation of CECs through RO membranes involves adsorption of the CECs onto the membrane surfaces, dissolution of the CECs into the membrane, and subsequent diffusive transport of dissolved CEC molecules through the membrane matrix [27]. While complete or near-complete removal of a wide range of CECs can also be predicted by NF membranes, the retention of CECs by NF membranes greatly depends on the physicochemical properties of CECs, which can be affected by solution chemistry (*i.e.*, mainly by the solution pH) [28]. UF membrane processes, used in WW reclamation and drinking water to remove CECs, were investigated via existing separation mechanisms (*e.g.*, size/steric exclusion, hydrophobic adsorption, and electrostatic repulsion) [11,29]. While the majority of CECs are organic compounds, several studies have examined the transport mechanisms of toxic ions of inorganic CECs (*e.g.*, chromate, arsenate, and perchlorate) through membranes [30,31]. Unlike organic CECs, the degree of removal of inorganic CECs is mainly governed by both size exclusion and electrostatic exclusion, while adsorption plays a minimal role in their removal.

While numerous studies have reported the removal of both inorganic and organic CECs by membrane treatments, a systematic understanding of the removal mechanisms and effects of operating conditions on the transport of CECs through FO, RO, NF, and UF membranes is lacking. Therefore, a broad review of CEC removal by membrane treatment is important, since the transport of both inorganic and organic CECs by membranes is significantly affected by the unique properties of CECs, as well as water quality conditions and membrane type. The main objective of this review was to combine present findings on membrane treatments of CECs in water and WW and to highlight upcoming research areas according to knowledge gap. Particularly, this review aimed to address several key parameters, including the physicochemical properties of CECs (*e.g.*, solute molecular weight (MW)/size/geometry, charge, and hydrophobicity), water quality conditions (*e.g.*, pH, solute concentration, temperature, background inorganics, and natural organic matter (NOM)), and membrane properties and operating conditions (*e.g.*, membrane fouling, membrane pore size, porosity, charge, and pressure) that influence the removal of CECs during membrane filtration.

## 2. Membrane treatment of various CECs

### 2.1. Removal by FO membranes

#### 2.1.1. Effect of the physicochemical properties of CECs

The FO process uses an osmotic pressure difference caused by the concentrated draw solution (DS) to permeate water from the feed solution to the DS across the membrane, whereas RO, NF, and UF processes use a hydraulic pressure difference as the driving force to transport water through a semipermeable membrane [26]. Thus, the transport of water through the membrane in FO is coupled with the transport of the draw solute in the opposite direction [32]. The transport of 20 PhACs assessed in closed-loop FO systems weakly correlated with retention and size/MW, suggesting that, aside from steric hindrance, solute-membrane interactions also affect retention [33]. While CEC transport and retention in FO likely share many characteristics (*e.g.*, membrane material and pore size) with the RO and NF processes, the reverse permeation of the draw solute and high salinity of the DS may affect the retention of diverse solutes and transport mechanisms [32].

The bench-scale FO retention of 23 nonionic and ionic EDCs and PPCPs was 40–98%, which depended primarily on size and charge (80–98% for positively and negatively charged compounds and 40–90% for nonionic compounds) [34], and gave rise to the following general observations: (i) relatively small compounds are able to partition into the relatively hydrophilic FO membrane and diffuse through the membrane active layer; (ii) a membrane surface fouling layer separates and hinders the interaction between hydrophobic compounds, which consequently increases retention [35]; and (iii) the retention of charged

compounds is usually high due to electrostatic interactions (*i.e.*, repulsion) arising from the negative surface charge of the FO membrane [36]. While the mechanism underlying the retention of positively charged compounds is somewhat unclear, a high retention of > 90% is promising [28]. The retention of four PhACs (carbamazepine (CBM), diclofenac (DCF), ibuprofen (IBP), and naproxen (NPX)) by FO membranes increased with increasing hydrophobicity [37], indicating that hydrophobic interactions between selected PhACs and cellulose triacetate (CTA) membranes may represent the dominant short-term removal mechanism [38]. Therefore, the relatively poor retention of NPX by FO membranes may be due to its lower affinity (lower  $\log D$  value at pH 6 = 1.37) to the membrane polymer. However, the retention of CBM (MW = 236 g mol<sup>-1</sup>) is significantly greater than that of IBP (MW = 206 g mol<sup>-1</sup>) due to its relatively larger MW, while they share similar hydrophobicity ( $\log D$  at pH 6 = 2.45 for CBM and 2.43 for IBP); this suggests that size exclusion also contributes to the retention of PhACs and that the MW of IBP may be close to the MW cut-off (MWCO) of CTA-based FO membranes.

For selected organic compounds, the average retention by FO membranes followed the order: sulfamethoxazole (SMX, 67–90%)  $\approx$  CBM, 68–83%)  $\gg$  atrazine (ATZ, 34–49%) > 4-chlorophenol (4CP, 28–39%) > phenol (PHN, 21–22%) [39]. The retention of relatively large MW and negatively charged dominant compounds (CBM = 236.3 g mol<sup>-1</sup>, neutral; SMX = 253.3 g mol<sup>-1</sup>, negative at pH = 7.0) was approximately 70%, while that of the relatively small MW and nonionic compounds (PHN = 94.1 g mol<sup>-1</sup> and 4CP = 128.6 g mol<sup>-1</sup>) was inconsistent, ranging from ~ 20 to 35%. This is presumably due to the combined effects of the relatively small MW and low hydrophobicity of PHN and 4CP, which allow them to readily diffuse through the active layer in osmotically driven processes. In addition, the small retention of ATZ by FO membranes (vs. CBM and SMX) could be attributed to its lower affinity for the membrane polymer and size exclusion contributions, because the MW of ATZ (215.7 g mol<sup>-1</sup>) is relatively less than that of CBM, while they are comparably hydrophobic [39].

Retention of > 99% was achieved for various heavy metal ions (*e.g.*, As, Cd, Cr, Cu, Hg, and Pb) under FO processes [40]. The very high retention of heavy metal ions under FO could be attributed to several factors: (i) the key mechanism for heavy metal transport across the FO membrane is solution-diffusion, since the influence of convective flow is minor for heavy metal transport in the FO process; therefore, heavy metal ions with larger hydration radii are removed readily because diffusivity decreases with increasing hydrated radius and (ii) the Donnan equilibrium effect could hinder the degree of ionic permeation of the feed ions due to the presence of highly concentrated bulk DSs across the active layer [41].

#### 2.1.2. Effect of water quality conditions

The retention of tract PhACs (metoprolol (MTP), SMX, and triclosan (TCS)) is pH-independent of the modified FO membrane by integrating nano-TiO<sub>2</sub> [42], as follows: (i) the degree of retention of MTP (positively charged) is lower than that of TCS (neutral) and SMX (negatively charged), mainly due to electrostatic interactions between the compounds and the negatively charged membrane; (ii) the retention of SMX increased with increasing pH, since the speciation of SMX from a neutral species at pKa1 < pH < pKa2 to a negatively charged entity at pH > pKa2 results in pH-dependent behavior; and (iii) upon comparing the performance of pristine and modified membranes at an average retention value, the performance of the modified membrane was better than that of the pristine membrane. The negatively charged/relatively hydrophilic FO CTA membrane enhanced the retention of E1 and E2 (*i.e.*, undissociated/uncharged hormones at the feed solution pH 6.5) in the presence of an anionic surfactant (sodium cocoyl *N*-methyl taurate) [26]. Given these conditions and properties, it is hypothesized that hydrophobic attractions occur between the surfactant tail and the membrane surface, resulting in adsorption of individual surfactant

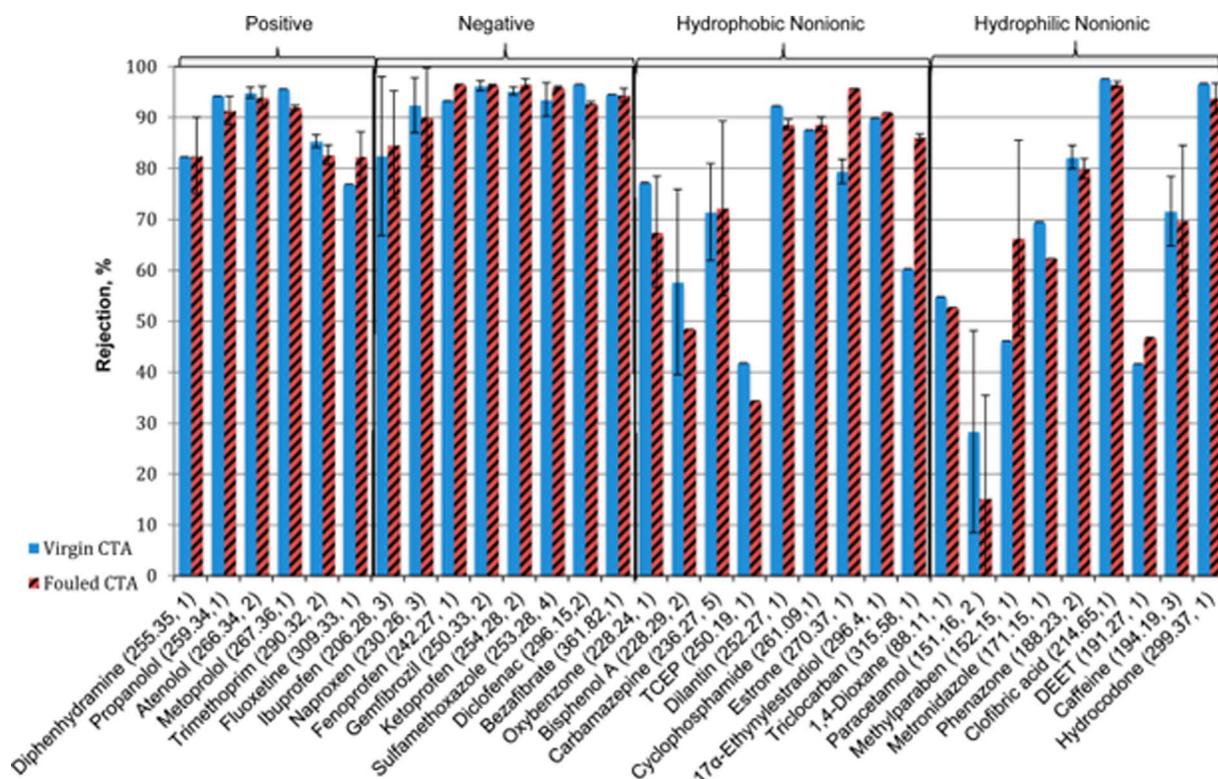


Fig. 2. Average retention of EDCs and PPCPs by virgin and fouled FO CTA membranes tested at the bench scale . adopted from [47]

molecules to the membrane [43]. Two mechanisms may enhance hormone transport by the FO membrane in the presence of anionic surfactants: (i) a small amount of hormones are available for adsorption onto the membrane because they are adsorbed onto the hydrocarbon chains of the micelles in the bulk feed solution, and (ii) the anionic surfactant adsorbs to the membrane surface due to hydrophobic interactions and enhances resistance to hormone transport by hindering hormone adsorption to the membrane [26].

The effects of organic fouling on CEC retention depend on the foulants. When the FO membrane was fouled by alginate, the retention of some PhACs (e.g., SMX and NPX) was significantly lower, whereas the change in retention was negligible for the majority of the 20 tested PhACs [33]. This result is presumably due to alginate forming a cake that is somewhat porous in comparison with the FO membrane, therefore only slightly contributing to PhAC retention. Hindered PhAC diffusion back to the bulk feed solution within the foulant layer results in cake-enhanced concentration polarization, which causes low apparent retention [44]. Therefore, decreases in the retention of CECs by fouled FO membranes could exert a substantial influence in closed-loop FO applications. In a separate study, the presence of humic acid (HA) increased the retention of SMX for pristine and modified FO-TiO<sub>2</sub> membranes [42], by shielding the membrane surface charge [45]. However, no substantial effect on the retention of TCS was observed for neutral TCS, since the degree of permeation of TCS was considered in the absence of electrostatic interactions. The presence of HA resulted in a decrease in the retention of MTP for both pristine and modified FO membranes [42], since positively charged MTP at pH 7 was enriched on the HA layer and readily diffused through the membrane barrier to the permeate side [46]. In a separate study on 32 EDCs and PPCPs, the retention of negatively charged EDCs and PPCPs positively correlated with increasing MW and retention, as shown in Fig. 2 [47]. Negatively charged compounds were also more easily retained by the FO membrane due to electrostatic repulsion by the negatively charged membrane surface. The retention of nonionic compounds decreased in all but two cases, as proposed by Linares et al. [48], while the retention of

hydrophobic nonionic compounds varied significantly.

A lab-scale FO system was employed to evaluate the performances of thin-film inorganic FO membranes for the retention of several heavy metals (Cd, Cu, Pb, and Zn) at a range of DS concentrations (0.5–2.0 mol L<sup>-1</sup> NaCl) and initial FS concentrations (50–1,000 mg L<sup>-1</sup>) of heavy metal ions [49]. The thin-film inorganic membrane was proficient at removing heavy metal ions, with an average retention efficiency of approximately 95%. The retention of heavy metals was less dependent on the DS concentration applied. The retention efficiency decreased from 95% to less than 85% with an increase in the initial concentration of the heavy metal (50–1,000 mg L<sup>-1</sup>), which was likely because the increasing FS concentration enhanced the diffusion of heavy metal ions across the membrane [49].

### 2.1.3. Effect of membrane properties and operating conditions

In addition to the physicochemical characteristics of CECs and water chemistry conditions, CEC retention is also influenced by membrane properties (e.g., charge, hydrophobicity, structure, and pore size) and operating conditions (e.g., pressure, dead-end/cross-flow, and bench/pilot scale). For all selected PhACs, the thin-film composite (TFC) polyamide membranes showed greater retention than the CTA membranes [37], whereas for CBM and DCF, the effects of membrane properties on their removal performance were somewhat insignificant. For NPX and IBP, the degree of retention was clearly higher with TFC polyamide membranes than with CTA-based FO membranes considering the water flux effect. The greater retention by TFC polyamide membranes is presumably due to: (i) the higher size exclusion effect indicated by the higher degree of glucose retention of TFC membranes and (ii) the electrostatic interactions (i.e., repulsion) between the deprotonated (negatively charged) NPX/IBP and the negatively charged surface of the TFC polyamide membranes at pH 6 [37]. Bench- and pilot-scale FO experiments revealed the different retention trends of 23 EDCs and PPCPs; the retention of EDCs and PPCPs during pilot-scale experiments (80–>99%) was significantly higher than those for bench-

scale experiments (40–98%) under all conditions tested [34]. Although the reason for this difference is somewhat unclear, it is presumably due to the formation of a fouling layer, membrane compaction, and the enhanced hydrodynamic conditions used in the pilot-scale system.

Active layer structures of the CTA and TFC FO membranes differed considerably, which could play a significant role in the retention of PPCPs [50]. The TFC membrane exhibits greater hindrance to PPCP diffusion compared to the CTA membrane [41]. The TFC membrane showed a greater PPCP retention than the CTA membrane due to its relatively high membrane surface charge, in association with the pore hydration that is manifested by a layer of water molecules permanently attached to the negatively charged membrane surface via hydrogen bonds [51]. The CTA membrane possessed relatively less surface charge since its pore hydration was significantly inhibited due to the higher ionic strength in the membrane pore [52], whereas TFC membrane pores remained hydrated in FO mode, resulting in greater PPCP retention compared to the CTA membrane. Therefore, the retention performance of FO membranes could be enhanced significantly by modifying the surface charge associated with the active layer structure [50].

Since the membranes were rapidly saturated and adsorption decreased over long-term operation, the initial membrane adsorption of CECs may be insignificant. Nevertheless, it is important to evaluate the impact of initial adsorption and predict the CEC retention accurately to determine the correlations between membrane and CEC properties [53]. The compounds showed the following adsorption trend at equilibrium with a contact time of 96 h: EE2 (91.7%)  $\gg$  4CP (39.4%) > CBM (31.2%) > SMX (27.7%) > ATZ (22.8%)  $\gg$  PHN (6.9%) [39]. The relatively hydrophilic CECs (SMX, CBM, and ATZ) showed lower adsorption affinities on the FO membrane than EE2, while SMX, CBM, and ATZ showed no correlation based on the  $\log K_{OW}$  values. Phenolic compounds such as PHN and 4CP (*i.e.*, relatively low MWs compared with the other compounds used) showed different adsorption trends (6.9% for PHN and 39.4% for 4CP) due to variation in their physicochemical properties (*i.e.*, PHN is highly soluble in water vs. 4CP). The adsorption of 4CP ( $\log K_{OW} = 2.39$ ) was greater than that of PHN ( $\log K_{OW} = 1.67$ ), as anticipated based on the hydrophobicities of these two compounds [39]. The electrostatic repulsion caused by deprotonation, which occurred because the solution pH was higher than the compound dissociation constant ( $pK_a$ ), did not significantly influence the adsorption process in either membrane compared with  $\log K_{OW}$ . In a separate study, the retention of E1 and E2 was > 99% until 20% recovery was reached for FO experiments involving simulated WW feed solutions [26]. From 20 to 45% recovery, the retention decreased slowly to 95–96%, while from 45% recovery to the end of the experiments (70% recovery), the retention increased slowly to 96–97%.

Cross-flow velocities (CFVs) are one of the key membrane operating conditions that significantly affect the transport of CECs during FO membrane filtration. A previous study showed that SMX retention was higher with a CFV of  $58.8 \text{ cm s}^{-1}$  than  $9.8 \text{ cm s}^{-1}$ , since SMX transport associated with diffusion was influenced more by higher water flux states (*i.e.*, a CFV of  $58.8 \text{ cm s}^{-1}$ ) when the FO membrane was negatively charged [39]. In addition, these findings agreed well with previous studies [34,42], indicating that the increase in concurrent CFVs has a significant effect on diffusive movement (hindered diffusion of compounds) and increases solute retention in the FO process by decreasing concentration polarization effects. Solute retention is comparatively constant regardless of CFV in the solute retention performance of the membrane, while water flux depends on the osmotic driving force, which also contributes to the increased compound retention under high CFV operating conditions. In addition, it has been reported that reverse salt flux influences the increase in organic compound retention in osmotically driven processes, because the retarded forward diffusion phenomenon from reverse salt flux hinders the diffusive transport of organic compounds [32].

## 2.2. Removal by RO membranes

### 2.2.1. Effect of the physicochemical properties of CECs

While high pressure-driven separation of RO membranes is being increasingly used in water and WW treatments and reclamation, solute–membrane interactions, such as steric exclusion (sieving effect), electrostatic interactions (charge effect), and hydrophobic/adsorptive interactions, should be evaluated for CECs varying in size, charge, and hydrophobicity [54]. In the RO membrane (BW30; Dow FilmTech), the average retention followed the order: ATZ (93.7%) > CBM (84.3%) > SMX (75.2%) > 4CP (60.9%) > PHN (47.3%) [39]. In that study, in general, the RO membrane had a greater retention efficiency than the FO membrane (CTA; Hydration Technologies). The higher retention efficiency of the RO membrane could be attributed to the positively coupled effects arising from size exclusion, electrostatic repulsion (Donnan exclusion), and hydrophobic/supramolecular interactions (*i.e.*, hydrogen bonding and  $\pi$ - $\pi$  stacking) of the RO membrane polymer, which mainly consists of an aromatic polyamide, whereas the relatively small water flux in the RO membrane negatively affects target compound retention [39]. The retention of the relatively large MW compounds (CBM, SMX, and ATZ) was > 75%, while the retention of the nonionic and small MW compounds (PHN and 4CP) ranged from 45 to 60%. Among similarly sized compounds, the lower  $\log K_{OW}$  of SMX showed a weak influence on its lower retention; an increase in retention with increasing  $\log K_{OW}$  was observed in the cases of CBM and ATZ. This phenomenon is in agreement with a previous study [55], which reported that the retention of most hydrophobic molecules by an aromatic polyamide membrane material was enhanced with increasing affinity of the solute for the membrane.

E1 and E2 are currently listed in the USEPA Drinking Water Contaminant Candidate List 4. While there are fairly insignificant differences between E1 and E2 retention (> 85%) by RO membranes, the variance shows a small experimental error ( $\sim 3\%$ ) [56]. Although E1 and E2 contain a 17-keto group and a 17-hydroxyl group, respectively, they share similar molecular structures. These results suggest that the 3-oxygen atoms of the first ring of E1 and E2 may participate in hydrogen bonding with the membrane polymer. This is somewhat consistent with the findings of Le Questel et al. [57] in their study of the hydrogen bond formation between progesterone and its human receptor. The findings in that study suggested that the 3-oxygen atom of progesterone was the key hydrogen bonding acceptor. In a separate study, an examination of PhAC (SMX, sulfamethazine, trimethoprim, clarithromycin, and roxithromycin) retention rates by RO revealed that this filtration technique removes antibiotics at a very high rate, because the results from all of the applied fluxes were below the limits of quantification [58]. Regardless of their high degree of retention, however, antibiotic concentrations exceed the limits of detection in most cases. These findings indicate that several molecules of antibiotics penetrate the RO membrane, and thus it can be concluded that RO cannot serve as an absolute barrier to antibiotics.

The RO process combined with a membrane bioreactor (MBR) has been effectively applied for the treatment of raw sewage and secondary effluent [59,60]. An RO-MBR system showed that the overall retention rates of 20 PhACs studied in the influent were > 99% [61], while RO alone showed a very effective degree of retention of numerous micropollutants (*e.g.*, atenolol, clarithromycin, ETM, and MTP) to below the detection limit ( $\leq 10 \text{ ng L}^{-1}$ ) [62]: CBM (> 99%) [63], SMX, MTP, and sotalol (> 98%) [64], and antibiotics, psychiatric control, and anti-inflammatories (> 90%) [7]. The retention of CECs by RO is determined by somewhat complex interactions of electrostatic and other physical forces between the target solute, the solution and the membrane itself. In particular, key retention mechanisms in RO membranes include steric hindrance, electrostatic interactions (repulsion), and hydrophobic interactions (adsorption) between the CECs and the membrane [54].

The retention of relatively hydrophilic PhACs ( $\log K_{OW} < 3$ ) is also very high (> 99%), whereas hydrophilic compounds do not adsorb to the membrane polymeric matrix [65]. Since the MWCO of the RO membrane (TR70-4021-HF) is approximately 100 Da, one of the potential removal mechanisms involved is steric hindrance (size exclusion). In addition, electrostatic interactions (attraction or repulsion) may affect the retention of some PhACs in an RO membrane due to their charge (e.g., positive charge of macrolide antibiotics and negative charge of SMX) [61].

### 2.2.2. Effects of water quality conditions

The presence of NOM and colloidal particles could significantly affect membrane performance. The E1-binding ability of hydrophobic HA is the key contributor to its significant enhancement of E1 retention by RO membranes (DL and CK, Osmonics) [66]. It is widely known that divalent cations (e.g.,  $\text{Ca}^{2+}$ ) affect the binding of trace CECs by humic substances [67]. Therefore, the  $\text{Ca}^{2+}$  concentration in a feed solution is believed to affect the E1 retention in HA-containing solutions. Although the presence of HA could enhance the retention of E1, a higher  $\text{Ca}^{2+}$  concentration tends to reverse this effect [66]. Particularly, the addition of 0.3 mM  $\text{Ca}^{2+}$  in feed solution enhanced the effect of HA on E1 retention by the membrane, decreasing to 180% compared to an enhancement of 30% in the absence of  $\text{Ca}^{2+}$ . When the  $\text{Ca}^{2+}$  concentration was increased to 0.6 mM, HA showed no noticeable improvement in E1 retention. In another study, the pH dependence of E1 speciation closely mirrored the pH dependence of E1 retention, with the retention decreasing noticeably at high pH for the RO membrane [68]. This decrease was not the result of changes in membrane characteristics due to high pH, because the flux was largely constant over the entire pH range examined. This finding corroborates the earlier suggestion that adsorptive effects (presumably mediated by hydrogen bonds between the hydroxyl and/or carbonyl groups of E1 and the membrane) are major contributors to the retention of E1 on these membranes; it is to be expected that adsorption would be highest under conditions where charge repulsion is lowest. At high pH, adsorption would decrease and, depending on the pore size, retention would decrease as charge repulsion increases [68]. In the absence of colloidal silica particles, the decrease in E2 retention appeared to be linear, whereas for the case with colloidal fouling, the retention decreased severely initially, followed by a moderate linear decline [44]. However, unlike E2, progesterone retention decreased severely initially but gradually slowed down until the end of the experiment. These findings suggest that the formation of a colloidal cake layer on the membrane surface restricts back diffusion of the compounds, causing a significant reduction in their retention.

The concentrations of CECs found in sewage are in the order of  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$ . Therefore, the effect of initial CEC concentration on removal reflects the behaviors of the CECs.

The effect of initial concentration (ranging from 1 to 1000  $\text{ng L}^{-1}$ ) on the retention of E1 by several RO membranes is insignificant, which is presumably due to the constant partition coefficient for E1 at high concentrations between the membrane and bulk solution [68], indicating that the membrane surface sites may not become saturated. A similar finding, in which the retention of several pesticides was somewhat independent of the initial feed concentration, was also reported [69].

The pH of the feed water influences the membrane surface charge, the characteristics of the solutes in the feed water, and the membrane separation performance for solutes [70]. Variations in  $\text{Ni}^{2+}$  retention during RO filtration at varying pH conditions are somewhat insignificant. While the  $\text{Ni}^{2+}$  concentrations in the influent varied between 8.22 and 10.29  $\text{mg L}^{-1}$ , its concentrations in the pretreatment effluent decreased to between 4.07 and 6.56  $\text{mg L}^{-1}$ . However, the  $\text{Ni}^{2+}$  concentrations in pretreatment + RO were below the detection limit. While the feed exhibited high  $\text{Ni}^{2+}$  concentrations at pH 5.5–7,  $\text{Ni}^{2+}$  showed much larger decreases under other pH conditions in the permeate from

pretreatment. For  $\text{Zn}^{2+}$ , the same effects were also observed at pH = 6.  $\text{Zn}^{2+}$  concentrations in the feed ranged between 10.7 and 13.7  $\text{mg L}^{-1}$ , and its concentrations in permeate pretreatment decreased to between 7.14 and 9.56  $\text{mg L}^{-1}$ .  $\text{Zn}^{2+}$  concentrations in the permeate did not change much with pH (mostly less than 0.88  $\text{mg L}^{-1}$ ) [70].

### 2.2.3. Effects of membrane properties and operating conditions

For RO membranes, the retention governed by the adsorption affinity of compounds correlates with their hydrophobicity, except for phenolic compounds, which have different characteristics (the adsorption affinity of 4CP to the RO membrane was remarkably higher, and 4CP reached a pseudo-equilibrium state faster than the other compounds examined) [39]. The compound adsorption affinities on the RO membrane showed the following order (% removal): 4CP (93.8%) > EE2 (89.9%)  $\gg$  PHN (69.8%) > ATZ (55.2%) > CBM (31.8%)  $\gg$  SMX (6.2%). For phenolic compounds, the greater retention by the polyamide RO membrane was caused by the following aspects [71–74]: (i) the retention is depending on physicochemical properties, including the functional groups (–OH and –Cl), solubility, and hydrophobicity, which impart high affinity for polyamide materials; (ii) the chlorine functional group of 4CP is an electron-withdrawing group; therefore, the reaction affinity with the membrane polymer may dominate; (iii) water solubility generally correlates with  $\log K_{OW}$ , indicating that the adsorption capacity of 4CP to the RO membrane increased with lower solubility; and (iv) many studies of membrane adsorption have reported that organic compound adsorption onto membranes is influenced by the membrane surface, as well as by the support layer and membrane pores. In addition, Yoon et al. [75] reported that adsorption was related to the membrane pore radius, consequently allowing relatively low MW organic compounds (e.g., PHN and 4CP) to access and diffuse into the membrane's internal adsorption sites. Therefore, from these results, we conclude that a weak correlation exists between all CECs. Moreover, regarding phenolic compounds and other CECs, a strong correlation between hydrophobicity and adsorption capacity was observed.

Understanding the influence of operating variables on the retention of CECs is very significant from a design, as well as an operational, perspective. In general, retention by the RO membrane increases with increasing CFV, since an increase in CFV decreases the concentration polarization at the membrane–bulk solution interface. However, no CFV effects on E1 retention were observed [56] since the E1 concentration within the membrane could be higher than that of the polarization layer due to E1 adsorption onto the membrane surface. Therefore, the concentration polarization effect appears to be minimal in this case. Generally, solute retention increases with pressure up to an asymptotic value. However, E1 retention decreases by 15% with increasing pressure (10–25 bar) [56], which is presumably due to the strong interaction with membrane polymers for organic compounds [76,77]. Solute-membrane interactions can be supported by friction associated with hydrodynamic conditions and diffusion associated with a chemical concentration gradient. Because the RO membrane has an average pore radius of 0.7 nm [77], those interactions are critical since it is in the same order of magnitude as the molecular size of E1. The drag force within the membrane pores increases, since an increase in pressure causes an increase in permeate flux. Therefore, the desorption of E1 improves, or the time for adsorption decreases due to the lower residence time in the membrane, which may contribute to the reduction in retention [56]. A low-pressure RO membrane is a pressure-driven membrane dominated by an increase in permeate flux against increasing transmembrane pressure. The retention of several heavy metals increased with an increase in transmembrane pressure [78], which may be due to a decrease in the average pore size on the membrane surface and an increase in the favored sorption of pure water at a higher pressure (e.g., solvent permeability increases compared with solute at a high pressure, causing increased retention) [79]. Retention is also dependent on the valency of the metal ion. Cr(IV) was removed (99.9%)

more than  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  (both > 99.5%) at 500 kPa pressure [78].

### 2.3. Removal by NF membranes

#### 2.3.1. Effect of the physicochemical properties of CECs

Similar to FO and RO membranes, the influence of the physicochemical properties of CECs on retention by NF membranes is also significant. The retention of BPA by an NF membrane (NE4040-70; Saehan, MWCO = approximately 200 Da) was much lower (74.1%) than that of IBP or salicylic acid (98.1 and 97.0%, respectively), quickly decreasing with operation time and reaching an asymptote [80]. BPA ( $\text{pK}_a = 9.6\text{--}10.2$ ) remains as an uncharged species at the tested pH 7, while IBP ( $\text{pK}_a = 4.9$ ) and salicylic acid ( $\text{pK}_a = 2.9$ ) should be mostly deprotonated, resulting in a negative charge. Therefore, the sieving effect (size exclusion) is the dominant mechanism of BPA retention, while the low BPA retention could be attributed to the absence of electrostatic interactions (repulsion) between the membrane surface and BPA. However, while IBP ( $\text{MW} = 206 \text{ g mole}^{-1}$ ) and salicylic acid ( $\text{MW} = 138 \text{ g mole}^{-1}$ ) have smaller MWs than BPA ( $\text{MW} = 228 \text{ g mole}^{-1}$ ), IBP and salicylic acid exhibited much greater retention than BPA due to both size exclusion and electrostatic repulsion. In addition, the fast decrease in BPA retention with operation time is presumably because hydrophobic and uncharged BPA readily adsorbs to the hydrophobic membrane surface until saturation. However, IBP and salicylic acid exhibited minor decreases in retention with operation time, although these compounds have higher  $\log K_{ow}$  values than BPA, presumably due to electrical repulsion between the compounds and the membrane [80].

In addition to the chemical speciation of CECs governed by solution pH and  $\text{pK}_a$ , the physicochemical activities of CECs for their retention are significantly influenced by their functional groups [54]. The degree of retention of three PhACs (CBM, SMX, IBP) by two NF membranes (NF-90 and NF-270; FilmTech) varied significantly due to their different physicochemical properties [28]. The retention of neutrally charged CBM ( $\text{pK}_a = 2.3$ ) by both the NF-90 and NF-270 membranes was relatively constant, since retention is exclusively governed by steric (size) exclusion in the absence of charged functional groups. In the absence of electrostatic interactions (repulsion), the compound physicochemical properties can influence retention performance. SMX, which contains two functional moieties at both sides of the sulfonamide linkage, shows two dissociation constants: one involving the protonation of the primary aromatic amine  $-\text{NH}_2$  and the other corresponding to the deprotonation of the sulfonamide  $-\text{NH}$ . The retention of the neutral SMX by the loose NF-270 membrane was significantly lower than that of CBM, despite the higher MW of SMX compared to CBM, since SMX has a higher polarity (dipole moment) than CBM. Organic molecules with high dipole moments (above 3 D) can show lower retention than molecules with a similar MW but with a lower dipole moment [81]. This finding suggests that the compound dipole moment plays a significant role in the retention by NF membranes, via affecting molecule orientation as it approaches the membrane pores.

#### 2.3.2. Effects of water quality conditions

The effects of seasonal changes, ionic strength, and spiked concentration on the retention of CBZ by an NF membrane (NF270) were examined with MBR effluents [63]. The removal of CBZ from the effluents was seasonally dependent despite a spiked concentration (3600, and  $1000 \mu\text{g L}^{-1}$ ), with a higher retention in the summer (approximately 85–90%) compared to the winter (approximately 50–55%). Variations in the effluent organic matter seasonally produced during the biological stage could describe this phenomenon. In addition, metabolic rate changes due to low temperature were reported to influence organic matter degradation, particularly hydrolysis yields [82]. In another study, it was reported that solute–solute interactions in tertiary effluent significantly improved the retention of PhACs for the NF membrane (NF-270) due to the association between PhACs and organic

macromolecules in the effluents [83]. Therefore, bound PhACs are rejected by NF membranes more readily by size exclusion and/or electrostatic interactions (repulsion) occurring between the complexes and the membrane surface, as previously reported for various contaminants [84]. The association between organic PhACs and organic macromolecules is believed to be a result of hydrogen bonding and hydrophobic interactions [85]. It was also observed that PhAC binding by effluent organic matter was favored in WW effluent, presumably due to higher biopolymers (soluble microbial polymers) [86].

The presence of calcium in the feed water reduces the removal of organic EDCs and PhACs in NF membranes [87], whereas the removal of PhACs with NF membranes was noticeably increased in the presence of a high calcium concentration [83]. Comerton et al. observed that the retention of hydrophilic PhACs ( $\log K_{ow} < 4$ ) by NF in MBR effluent decreased significantly when cations were doubled [88]. Increases in ionic strength and divalent cation concentrations result in changes in effluent organic matter conformation, which may alter the presentation of sites for compound association, leading to a decrease in organic matter–compound complexation [87]. This phenomenon could be explained by the fact that NOM has a stretched and linear configuration in low ionic strength solutions and in the absence of divalent cations, while NOM has a more inflexible, compact and coiled configuration in high ionic strength solutions and in the presence of divalent cations [89]. The presence of NaCl in the deionized (DI) water matrix had a minimal effect on the overall retention of CBZ by NF270 (MWCO = 155 Da), while the fluctuations in CBZ retention can be attributed to the dehydration of CBZ in the presence of  $5 \text{ g L}^{-1}$  NaCl, which produces a smaller molecule that can more easily leak through the membrane pores [63]. Schäfer et al. also observed only a negligible effect for NaCl (0–100 mM) and  $\text{CaCl}_2$  (0–5 mM) on the retention of E1 by the TFC-SR2 (Koch) membrane from DI water [68]. It was hypothesized that ionic strength affects solute retention by two integrated and comparable effects: (i) the presence of salt could screen the charge associated with the polar functional groups of PhACs and decrease the apparent size of the molecule, and (ii) it can shield the electrostatic potential of the membrane surface and reduce electrostatic interactions (repulsion). The reduction of IBP by an NF membrane (MWCO = 150–300 Da) was reported with increasing ionic strength with MBR effluents [90], while divalent salt ( $\text{CaCl}_2$  and  $\text{CaSO}_4$ ) had an insignificant effect on pesticide retention by an NF-Desal DK membrane (Osmonics, MWCO = 150–300 Da), which was presumably due to blockage of membrane pores as a result of divalent ion retention [91].

A fouled NF membrane (UTC-60; Toray) was used to evaluate the degree of retention of several PhACs in WW effluent and DI water [86]. In that study, the effect of the association between the PhACs and organic macromolecules in WW effluents was likely significant in the case of MBR effluent, particularly for primidone and CBM. Organic macromolecules in MBR effluent appeared to increase the removal of PhACs by the NF membrane due to their association. After silica fouling, the retention of PPCPs was increased by the tight NF90 membrane (MWCO = 200 Da), but decreased by the loose NF270 membrane (MWCO = 270 Da) [92]. With or without silica fouling, the solution pH negligibly influenced the retention of both relatively hydrophilic and hydrophobic compounds by NF90, but significantly influenced the retention of those compounds by NF270. PPCP retention was enhanced after silica fouling due to the additional steric hindrance effect provided by the fouling layer, thus decreasing the permeation of PPCPs across the membrane surface. For NF90, both steric exclusion and electrostatic interactions (repulsion) occurred synergistically to enhance the retention of PPCPs after fouling and with an increase in pH. However, for NF270, electrostatic repulsion was the mechanism governing the transport of PPCPs as the pH increased, with or without silica fouling. Although a fouling layer may provide additional steric hindrance for loose NF270, its influence was overwhelmed by the accompanied cake-enhanced concentration polarization phenomenon. The cake-enhanced concentration polarization phenomenon hindered the back-diffusion of

PPCPs into the feed solution, and trapped and accumulated PPCPs on the membrane surface to enhance their diffusion across the membrane [93].

### 2.3.3. Effects of membrane properties and operating conditions

As described earlier, CEC adsorption onto the membrane is the main removal mechanism at the initial stage of filtration while, at the later stage, the retention of CECs is less than expected based only on a steric/size exclusion mechanism. While size exclusion is the main retention mechanism at the later stages of membrane filtration, it was proposed that partitioning and subsequent diffusion through the membrane polymer matrix causes a fairly lower rate of retention [77]. In that study, a clear deviation of retention based on size exclusion was observed, while the diffusive transport of hormones (E1, E2, progesterone, and testosterone) was slow through the polyamide skin layer (15–40 nm) of the NF-270 membrane. In addition, although the “tight” NF-90 and “loose” NF-270 membranes have different membrane pore sizes based on their MWCOs, the similar retention rates of natural hormones by those membranes may be explained by their comparable active layer thicknesses that influence the diffusion behaviors of hormones [94], as follows: (i) although the contribution of convective flow to the transport of hormones across the membrane is somewhat small, the presence of water plays a significant role in allowing the diffusion process [95] and (ii) hormone diffusion in the dense polymeric phase occurs, which can be caused by switching between two bonding sites, or from a hydrophobic bond to a substrate and a hydrogen bond to water [96].

A chemically modified NF via graft polymerization significantly improved BPA retention (74.1% (raw membrane) to 96.9% for the polymerized membrane) [80]. Since BPA is an uncharged species at the tested pH 7.2, the enhanced retention was attributed to the steric hindrance associated with the polymer chains. Greater steric hindrance was achieved for the membrane polymerized for 60 min compared to that polymerized for 15 min, since the longer polymerization time produced longer polymer chains. In addition, BPA retention by the polymerized NF membrane decreased more slowly versus that by the raw membrane, which was presumably due to the increased adsorption of BPA associated with the relatively hydrophilic polymerized membrane. The retention of IBP and salicylic acid (negatively charged solutes) by the polymerized NF membrane improved from 98.1% to 99.7% and from 97.0% to 99.1%, respectively, indicating that the increased negative surface charge and increased steric hindrance of the polymerized NF membranes were directly responsible for the enhanced retention [80].

## 2.4. Removal by UF membranes

### 2.4.1. Effect of the physicochemical properties of CECs

The retention of seven different PhACs by a UF membrane (pore size = 0.1  $\mu\text{m}$ ) was investigated using the pilot-scale municipal WW reclamation system [97]. In that study, MW,  $\log D$ , and charge at a neutral pH of the PhACs were considered major parameters affecting their retention by the UF membrane. Most of the target PhACs were not effectively removed using the UF membrane (< 35%), with the exception of DCF and SMX. However, there was no significant relationship between the retention of target PhACs by the UF membrane and their MW,  $\log D$ , or charge at neutral pH. In a separate study, inconsistent degrees of retention for 16 PhACs by a UF membrane (MWCO = 100 kDa) were obtained with municipal WW, while a somewhat small overall retention (< 29%) was achieved [98]. In particular, acetaminophen, caffeine, IBP, and NPX remained unchanged at the membrane permeate since the UF membrane has a much larger pore size than the target PhACs (< 400  $\text{g mole}^{-1}$ ). In addition to size exclusion, membrane surface adsorption associated with compound hydrophobicity ( $\log K_{\text{OW}}$ ) is another key mechanism by which UF removes PhACs. It is believed that PhACs are unlikely to be adsorbed on the

membrane surface when PhACs have high hydrophilicity ( $\log K_{\text{OW}} = < 2.6$ ), while the opposite effect of PhACs adsorbed onto membrane surfaces is obtained for highly hydrophobic PhACs ( $\log K_{\text{OW}} = < 4.5$ ) [99], consistent with the finding that the high retention of TCS was due to its very high  $\log K_{\text{OW}}$  value (4.76, the highest among all target PhACs) [98]. Although DCF, IBP, and NPX have relatively high  $\log K_{\text{OW}}$  values (4.4, 3.97, and 3.3, respectively), both the retention and adsorption caused by the membrane were almost negligible, presumably due to the reduced hydrophobicity of these PhACs once they are deprotonated [12].

For dead-end stirred-cell experiments, the sulfonated polyethersulfone UF membrane (nominal MWCO = 8 kDa) showed a fluoranthene (FRT) retention of > 95% in the absence of NOM, presumably due to hydrophobic adsorption [75]. FRT adsorption (15–25% for the UF membrane) was lost in the presence of NOM, presumably due to competition for adsorption sites and pore blockage by NOM. In that study, E2 retention by the UF membrane was reduced from 60 to > 95% in the absence of NOM, and to 10–20% in the presence of NOM due to competition for adsorption sites. A model species (parachlorobenzoic acid, PCBA) was employed to verify that hydrophobic interactions (attraction) occurred between a hydrophobic compound and the hydrophobic membrane. A PCBA retention of approximately 30% in the presence of NOM, and 50% in the absence of NOM, was obtained by the UF membrane, while PCBA is less hydrophobic. These findings indicate that an electrostatic exclusion mechanism could be more dominant than hydrophobic adsorption for PCBA retention [75]. In a separate study, the concentrations of 52 CECs and conventional contaminants were lower in the permeate than those in initial feed samples. The feed concentrations of the compounds ranged from 16 to 234  $\text{ng L}^{-1}$  [11]. Numerous permeate concentrations of both CECs and conventional contaminants were below the limit of detection, indicating a high degree of retention by the UF membrane (MWCO = 8 kDa), except for a few compounds (e.g.,  $\alpha$ - and  $\beta$ -BHC, FRT, hydrocodone, metolachlor, and musk ketone) that were poorly removed. In most cases, the concentrations of EDC/PPCPs followed the order: initial feed > retentate > permeate, except for a few compounds (e.g., DCF, ETM, E3, gemfibrozil, IBP  $\alpha$ -chlordane, and dieldrin). Because the retentate concentration was lower than the initial concentration, these findings indicate that significant amounts of compounds in the retentate were adsorbed in the test. Assuming negligible loss due to degradation and/or adsorption onto the glassware, this could be due to adsorption to the membrane surface and into membrane pores. Previous studies have shown that the retention of relatively hydrophobic compounds and hormones/steroids (e.g.,  $\log K_{\text{OW}} > 3.0$ ) by RO, NF, and UF membranes is governed significantly by adsorption [56,77,100,101]. In these studies, some polar and less hydrophobic compounds were also adsorbed onto the membrane surface, which was dependent on the membrane material and feed solution pH.

A polymer (carboxymethyl cellulose, CMC)-enhanced UF (polyethersulfone, MWCO = 10 kDa) process was used to evaluate the removal of toxic heavy metals, such as Cu(II), Ni(II), and Cr(III), from synthetic WW solutions [102]. Comparable retention effects were obtained for both Cu(II) and Cr(III) ions from a mixed solution versus the single solutions. Upon increasing the metal ion concentration from 10 to 100  $\text{mg L}^{-1}$ , the metal retention rates varied from 98 to 98.5% and from 99 to 97.1% for Cu(II) and Cr(III), respectively. However, a higher separation effect was observed for Ni(II) ions from the mixed solution versus the single solution. Increasing the initial Ni(II) ion concentration from 10 to 100  $\text{mg L}^{-1}$  caused the metal retention rates to vary from 99 to 76.4% in the mixed solution, and from 99.1 to 57% in the single solution. The higher retention efficiency of Ni(II) ions in the simultaneous solution could be attributed to the association of the Ni-CMC complex with the other two complexes of Cu(II) and Cr(III) with CMC [102].

#### 2.4.2. Effects of water quality conditions

Similar to FO, RO, and NF membranes, CEC retention by UF membranes can also vary depending on feed water chemistry, as previously shown [56,103]. Because four feed waters having diverse water chemistry conditions were employed to evaluate the retention of 52 CECs and conventional contaminants with UF membranes, it is somewhat difficult to compare the retention trends for each compound [11]. Therefore, in that study, compound retention was compared to several major parameters, including dissolved organic carbon (DOC), specific UV absorbance (SUVA), conductivity, and pH. For more polar and hydrophilic compounds, the retention for the UF membrane followed this order (MWCO = 8 kDa): Passaic Valley water (PVW, relatively low pH and high conductivity) > Ohio River water (ORW, relatively low SUVA and low conductivity) ≈ Colorado River water (CRW, relatively low SUVA and high conductivity) > Suwanee River RO isolate NOM water (SRW, relatively high DOC and high SUVA). However, for less polar and highly hydrophobic compounds, the UF membrane retained these compounds somewhat more from ORW and CRW than from SRW and PVW, which could be due to more competition between the NOM in SRW and PVW and compounds for the membrane adsorption sites than ORW and CRW. The SRW contained the most DOC with the highest SUVA, usually indicating more hydrophobic and larger-MW NOM than the other waters with lower SUVA values. In addition, SRW contained the lowest total CEC spiked concentration (1789 ng L<sup>-1</sup>) compared to ORW (6586 ng L<sup>-1</sup>), CRW (5670 ng L<sup>-1</sup>), and PVW (5849 ng L<sup>-1</sup>). Therefore, SRW had the lowest competition among those compounds for membrane adsorption sites [11].

The retention (5–34%) of five EDCs (E1, E2, E3, EE2, and BPA) by a fouled UF membrane was higher than those (10–76%) of a clean membrane (MWCO = 100 kDa), indicating that membrane fouling may influence EDC removal [104]. For the fouled membrane, BPA had the highest removal degree (64–76%), followed by EE2 (42–53%), E1 (28–46%), E2 (24–63%), and E3 (10–17%). Fouling reduced membrane pore size [105], which enhanced the retention of EDCs due to size exclusion. In addition, EDCs–HA sodium matrix forms as EDCs adsorb to humic particles, which were then co-rejected by the membrane [87]. While the BPA molecule was the smallest, it showed the highest retention efficiency, presumably because BPA exhibits the strongest electropositivity, resulting in its tight bond with humic particles [104]. EE2 had comparable electropositivity with E1, E2, and E3; however, it is larger than the others and therefore had a higher retention rate. In addition, cake layers formed under different pressures had differing abilities to retain different EDCs [54]. The cake formed at 50 kPa showed the best effect on EDC retention, while cakes formed at 25, 30, and 75 kPa exerted a relatively insignificant effect on EDC retention [104]. After fouling, membranes with cakes formed under different pressures still presented electronegativity, which differed from the clean membrane, where there were adsorptive sites not only on the membranes but also on the cakes. Therefore, adsorption still contributes to the retention of EDCs. In addition, membrane fouling significantly influences membrane characters, such as porosity and hydrophilicity. Lower porosity and stronger hydrophilicity were favored for EDC retention by a fouled membrane [104]. This is presumably because the cake with a lower porosity underwent additional severe compression and had a greater number of small pores, so that the EDCs were more difficult to penetrate through. Furthermore, hydrophobic EDCs were more repulsive to more hydrophilic cake, consistent with previous findings [12].

The retention of inorganic CECs (Cr(VI), As(V), and ClO<sub>4</sub><sup>-</sup>) by the UF membrane (MWCO = 8 kDa): (i) decreased with increasing solution conductivity due to the decreasing negative membrane charge; (ii) increased with pH due to the increasing negative membrane charge; and (iii) decreased in the presence of divalent counter ions (Ca<sup>2+</sup>) due to a less negative membrane charge [31]. In addition, a general trend in which the retention of these toxic ions increased as the solution pH increased from 4 to 10 was also observed. These findings can be

explained by electrostatic exclusion, since the membrane charge became more negative with increasing pH, resulting in increased electrostatic repulsion between the target ions and the membranes, thus increasing ion retention. However, for As(III), the retention by the UF membrane only varied marginally over a range of pHs below 10, because As(III) exists mostly as an uncharged species below pH 9.13 (*i.e.*, its pKa). In contrast, As(III) retention increased considerably at pH 10, when it became anionic, indicating that steric/size exclusion was the mechanism determining the uncharged As(III) species until it became anionic at pH > 9.13, where an electrostatic exclusion mechanism began to play an important role [31].

#### 2.4.3. Effects of membrane properties and operating conditions

The minimal retention of steroidal hormones (*e.g.*, E1, E2, progesterone, and testosterone) by UF membranes in the absence of organic matter was predicted due to the small size of the hormones relative to the membrane pore sizes of 0.8–0.9 and 1.6–18.2 nm (MWCO = 10 and 100 kDa, respectively) [106]. However, up to 28% retention was observed, with retention increasing with a decreasing membrane MWCO (1 kDa) influencing size exclusion. Retention was also related to membrane adsorption, with higher retention by lower MWCO membranes due to longer experimental durations. In addition, an increase in organic matter concentration was anticipated to enhance E1 retention due to greater partitioning with the higher organic matter mass. These results indicate an increase in E1 retention as organic matter concentration increases from 12.5 to 125 mg L<sup>-1</sup> for both 10 and 100 kDa membranes [106]. In a separate study, the retention of 16 EDCs and PPCPs was evaluated during UF of natural surface waters at four different surface shear stress regimes: no shear stress, low peak shear stress associated with continuous coarse bubble sparging, sustained peak shear stress associated with intermittent coarse bubble sparging, and high peak shear stress associated with large pulse bubble sparging [107]. Overall, surface shear stress conditions somewhat influenced compound retention, while the average retention for all EDCs and PPCPs under the conditions tested (no shear stress, continuous coarse, intermittent coarse, and pulse bubble sparging) was 32, 18, 22, and 34%, respectively.

The effects of membrane type were investigated at fixed heavy metal ion (Zn and Cd) concentrations of 50 mg L<sup>-1</sup> [108]. For both metals, the flux of treated water decreased, as expected, with decreasing membrane pore diameter, having very small values for the UF membrane. Therefore, polysulfonamide membranes are not recommended for most applications, although they provide very high retention coefficients. Due to the small differences in pore size of Versapor membranes, the retention coefficients were very similar. The lowest retention coefficient of Zn was obtained using dextrin as a complexing agent due to its low MW. Polyethylene glycol and diethylaminomethyl cellulose were more effective complexing agents, with constant retention coefficients with all three membranes [108]. For the UF (MWCO = 8 kDa) membrane, As(III) retention was fairly constant over the entire pH range (7–11%) [31], presumably because steric/size exclusion was dominant for the UF membrane. While the retention of uncharged As(III) was the lowest among the ions tested, ClO<sub>4</sub><sup>-</sup> retention was significantly lower than Cr(VI) and As(V) for the UF membrane, presumably because the hydrated divalent ions have a larger size (0.27 nm for HAsO<sub>4</sub><sup>2-</sup>) and/or a greater charge than the hydrated monovalent perchlorate ion (ClO<sub>4</sub><sup>-</sup>, 0.14 nm). The solute radii were calculated using the Stokes–Einstein equation [109]. For target toxic ions, the RO membrane with a small pore size (the measurement of which was discussed in a previous report [110]) exhibited the highest retention (> 90%), indicating that size exclusion was at least partially responsible for retention. However, the UF membrane with a relatively large pore size exhibited the lowest retention, ranging from 7% to 43% [31]. Table 3 summarizes the removal efficiencies of selected CECs by FO, RO, NF, and UF membranes under various experimental conditions and water types. In addition, a retention diagram of organic CECs

**Table 3**  
Summary of selected CEC and heavy metal removal by FO, RO, NF, and UF membranes.

Membrane class	CEC class	Experimental condition	C <sub>0</sub> and water type	Key removal (%)	Key finding	Ref.
FO	PHN, 4CP, ATZ, CBM, SMX	Cross-flow HTI-CTA CFV = 58.8 cm s <sup>-1</sup>	2 μM SDW	SMT (89.7), CBM (82.6), ATZ (48.7), 4CP (38.6), PHN (21.9)	Compared to the polyamide-based RO membrane, the CTA-based FO membrane exhibited superior water flux performance due to the optimized properties of its active and support layers in FO-mode. Experiments revealed that membrane consistently retains both E1 and E2 at or above 99.5%, independent of feed composition.	[39]
		Cross-flow CTA, DS = NaCl Recovery = 0–70% Cross-flow, CTA DS = NaCl, MgSO <sub>4</sub> , glucose CFV = 9 cm s <sup>-1</sup>	1,000 ng L <sup>-1</sup> SDW	> 95 (E1) 75–95 (E2)	Experiments revealed that membrane consistently retains both E1 and E2 at or above 99.5%, independent of feed composition.	[26]
	Twelve EDCs PPCPs	Cross-flow HTI-CTA DS = NaCl Bench scale Pilot scale DS = NaCl	2,000 ng L <sup>-1</sup> SDW	30–90	Retention of charged organics by the CTA membrane was generally high and was governed by both electrostatic interaction and steric hindrance.	[50]
		Cross-flow HTI-CTA DS = NaCl Bench scale Pilot scale DS = NaCl	2,000 ng L <sup>-1</sup> SDW	80–90 (positive) 50–85 (neutral) > 95 (negative) 70–95 (positive) 60–95 (negative) 40–90 (hydrophobic nonionic) 40–95 (nonionic)	Fouling by long-term biofilm growth caused FO retention to vary in function of biofilm age, although overall biofilm influence was limited. Retention of EDCs and PPCPs during pilot-scale experiments was significantly greater than observed for bench-scale experiments under all conditions evaluated.	[33]
	Eighteen PPCPs charged (positive, neutral, and negative) Twenty three EDCs and PPCPs (positive, negative, hydrophobic nonionic, nonionic) MTP, SMX, TCS	Cross-flow TiO <sub>2</sub> modified FO DS = NaCl	500 μg L <sup>-1</sup> SDW	> 99 (MTP) > 99 (SMX) > 97 (TCS)	The retentions of triclosan and sulfamethoxazole were higher than metoprolol in the FO mode due to their different speciation characteristics and membrane surface charges at different pH values.	[42]
		Cross-flow Cellulose acetate Polyamide TFC DS = NaCl	250 μg L <sup>-1</sup> SDW	65–> 95 (CBM > DCF > IBP > NPX)	For commercial cellulose acetate based FO membranes, size exclusion and hydrophobic interaction between the compounds and membrane dominate their retention under acidic conditions.	[37]
	Twenty four PhACs	Cross-flow DS = NaCl CFV = 20.4 cm s <sup>-1</sup>	100 μg L <sup>-1</sup> SDW	> 60 (retention increases with increasing water flux)	For all PhACs, the retention ratio increased with the increase of the draw solute concentration, although the increase became marginal when the draw solute concentration was higher than 1 M.	[14-0]
		FO + electrochemical oxidation DS = NaCl CFV = 8 cm s <sup>-1</sup>	200 μg L <sup>-1</sup> SWW	50–90 (facing DS mode) 90–95 (facing feed solution mode)	The FO process with function of electrochemical oxidation has the capability to thoroughly remove trace antibiotics from wastewater.	[14-1]
	BPA, TCS, DCF	Cross-flow FO/RO mode DS = NaCl, MgSO <sub>4</sub>	500 μg L <sup>-1</sup> SWW	> 80 (BPA) > 95 (TCS) > 90 (DCF)	The difference in the separation behavior of these hydrophobic trace organics in the FO (when NaCl was used as the draw solute) and RO modes could be explained by the retarded forward diffusion of feed solutes within the membrane pore.	[32]
		Cross-flow COD	20–500 μg L <sup>-1</sup> Landfill leachate	48–59 (Zn) 63–86 (Cu) > 99.5 (Cd)	Among the investigated metals, Cu and Zn exhibit a significant removal, while Cd removal seems not to be affected by the presence of organic compounds in the leachate.	[14-2]
Cr, As, Pb, Cd, Cu, Hg	Cross-flow DS = NaCl, Na <sub>4</sub> Co (C <sub>6</sub> H <sub>4</sub> O <sub>7</sub> ) <sub>2</sub>	1,000–5,000 mg L <sup>-1</sup> SWW	99.87 (Cr), 99.74 (As), > 99.9 (Pb), 99.78 (Cd), 99.77 (Hg)	The proposed FO process maintains high retentions under high concentrations of heavy metal ions. Even when 5,000 mg L <sup>-1</sup> feed solution was used, the retentions were maintained at 99.5%.	[40]	
	Cross-flow, TFI DS = NaCl	200 mg L <sup>-1</sup> SWW	> 94 (Cu > Cd > Zn > Pb)	The retention efficiency reached 94% on average for four typical divalent heavy metals as investigated herein when their massive concentration was below 200 mg L <sup>-1</sup> .	[49]	
Ni	Cross-flow CTA, TFC DS = NaCl	100 mg L <sup>-1</sup> SWW	> 96 (CTA ≥ TFC)	Heavy metals Ni <sup>2+</sup> promoted the formation of concentration polarization, and then decreased the water flux. However, this effect decreased with the increase of FS salinity and membrane hydrophilicity.	[14-3]	
	Cross-flow Dow Filmtec-BW-30	2 μM SDW	ATZ (93.7), CBM (84.3), SMT (75.2), 4CP (60.9), PHN (47.3)	For the RO membrane in FO-mode, internal concentration polarization was severe and attributed to the lower porosity of the support layer of the RO membrane. The lower porosity played a dominant role in the reduction of water and/or reverse salt flux.	[39]	

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Table 3 (continued)

Membrane class	CEC class	Experimental condition	C <sub>0</sub> and water type	Key removal (%)	Key finding	Ref.
	Twenty six EDCs and PPCPs	Spiral wound Sahan-RE4040-FL	10–11,500 ng L <sup>-1</sup> WWE	> 90–99	In order to efficiently remove micro-contaminants, processes including granular AC and MF with RO are suggested due to their high removal rates. Ultimately, a multi-barrier approach using MBR followed by RO could prove the most effective in contaminant removal.	[14–4]
	E1	Cross-flow Polyamide Cellulose acetate	100 ng L <sup>-1</sup> WWE	> 90 (polyamide) 30–90 (cellulose acetate)	The removal efficiency can be enhanced significantly in the presence of effluent organic matter in feed solution. The hydrophobic fraction played a paramount role in the ‘enhancement effect’.	[66]
	E2 E3	Cross-flow Dead-end	100 ng L <sup>-1</sup> SDW WWE	> 85 (E2) > 80 (E3) Cross-flow > dead-end	The presence of organic matter appears to enhance hormone retention. This enhancement is apparently stronger in natural water, in which organic matter generally has larger molecular weight, than that in secondary effluent.	[56]
	E1	Dead-end Four RO membranes	100 ng L <sup>-1</sup> SDW	> 95	It appears that both size exclusion and adsorptive effects are instrumental in maintaining high retention of E1 on a variety of RO membranes over a range of solution conditions.	[68]
	Six antibiotics/three pharmaceuticals/BPA/cholesterol	Spiral wound MBR + RO pilot	< 1,500 ng L <sup>-1</sup> WWE	> 93	The RO removal mechanism is based on the characteristics of the membrane, the molecule being removed, and the background fluid. Despite significant differences between the tested membrane pressures, all were removed at high rates.	[58]
	Twelve EDCs PPCPs	Cross-flow, CTA DS = NaCl, MgSO <sub>4</sub> , glucose CTV = 9 cm s <sup>-1</sup>	2,000 ng L <sup>-1</sup> SDW	~60– > 95	The observed higher retention of neutral organics by the TFC membrane to a more favorable active layer structure as indicated by the larger active layer thickness to porosity ratio parameter, $l/\epsilon$ , and the negative membrane surface charge that induced pore hydration.	[50]
	Thirteen EDCs and PhACs	Full-scale WW recycling plant MF + RO Pilot	1–4,000 ng L <sup>-1</sup> WWE	< detection limit to < 500 ng L <sup>-1</sup>	The activated sludge, MF and RO processes proved to be a reliable combination for the removal of the whole range of physicochemical parameters considered.	[1]
	Ten EDCs and PPCPs	MBR-flat sheet MBR-hollow fiber MBR-RO Pilot Polyamide TFC	0.06–59.5 µg L <sup>-1</sup> WWE	4.2– > 99 (MBR-RO > MBR-flat sheet/hollow fiber)	High water quality was obtained using the combined treatments MBR-RO, with removal efficiencies higher than > 90% for salinity and NO <sub>3</sub> <sup>-</sup> . Therefore, the requirements for the reuse of WW can be fulfilled.	[14–5]
	Atenolol, diltiazem, CBM, caffeine, DCF, SMX	Pilot Polyamide TFC	54.1–206.6 ng L <sup>-1</sup> WWE	< 85–95 for all compounds excluding caffeine (~60)	The removal of micropollutants by the RO membrane could be predicted by their molecular weight, Log D, and charge characteristics.	[97]
	Eighteen PPCPs charged (positive, neutral, and negative) Twenty PhACs	Cross-flow ESPA4 Polyamide TFC Pilot MBR + RO	2,000 ng L <sup>-1</sup> SDW	> 95 (positive) > 95 (neutral) > 99 (negative)	Model foulants caused a slight decrease in retention for most compounds, while the retention of some were significantly negatively impacted. The water flux decreased by 10%.	[33]
	Sixteen EDCs and PPCPs	Cross-flow Polyamide	17–2,020 ng L <sup>-1</sup> WWE	50–95 (MBR) > 99 (RO)	Size exclusion and electrostatic attraction or repulsion are supposed to be the main mechanisms involved in the removal of target compounds with RO membranes.	[61]
	Eleven EDCs and PPCPs	Cross-flow Polyamide Cellulose acetate	0.55–610 µg L <sup>-1</sup> NSW SDW	92.5–99.9 for all the compounds excluding trimethoprim (87.1) 57–91 (polyamide) < 1–85 (cellulose acetate)	While CECs with low pKa and high log Kow values usually had greater removal than others, RO filtration, removed more than 90% of most CECs. The dominant retention mechanism for RO membranes would be different depending on membrane material and the physicochemical properties of CECs.	[14–6]
	Ten PCPs	Cross-flow TFC on polyester	1–150 ng L <sup>-1</sup> WWE	< 19–99	RO polished water could be used for environmental use, in aquaculture or even for industrial cooling.	[14–7]
	Ni, Zn	Cross-flow GAC + RO 1,100 kPa	44–169 mg L <sup>-1</sup> (Ni) (Zn)	> 98.5 (Ni) > 90 (Zn)	The metal retentions seem not to be greatly affected by different conductivity and pH. EDTA increased Zn <sup>2+</sup> and Ni <sup>2+</sup> removal, but the effluent conductivity also increased, especially in Zn <sup>2+</sup> removal.	[14–8]

(continued on next page)

Table 3 (continued)

Membrane class	CEC class	Experimental condition	C <sub>0</sub> and water type	Key removal (%)	Key finding	Ref.
NF	Ni, Cr, Cu	Cross-flow Nitto Denko-ES20	50 mg L <sup>-1</sup> SWW	> 98.5 (Cr > Cu > Ni)	The pH is found to influence the retention and flux of heavy metals since the charge property of surface material of polyamide low pressure RO membranes changes with pH.	[78]
	Ni	Cross-flow 75–300 psi	IWW 21 mg L <sup>-1</sup> SWW	93.9, 95.1, 96.7, 96.8 (75, 140, 220, 300 psi)	An appropriate UF pretreatment could be beneficial for reducing the fouling of RO membrane and increased the flux of RO membrane by 30–50%.	[14-9]
	Cr, As,	Cross-flow Polyamide TFC	100 µg L <sup>-1</sup> SDW	> 90 (SDW > NSW)	The Cr, As, and ClO <sub>4</sub> <sup>-1</sup> retentions by the negatively charged RO membranes are significantly greater than expected based exclusively on steric/size exclusion due to electrostatic repulsion.	[31]
	ClO <sub>4</sub>	Cross-flow, ultrathin nanostructured polyelectrolyte-based	10 mg L <sup>-1</sup> SDW	75–95	As for retention, the highest increase was seen on going from the bare membrane to 1 bilayer and after that there was only a slight increase till 3 bilayers.	[30]
	Eleven EDCs and PPCPs	Cross-flow TFC or CA	500 µg L <sup>-1</sup> SDW/WWE	> 70 excluding acetaminophen (< 40)	The effect of pH on the retention of negatively charged compounds was slightly positive for NF membranes due to electrostatic repulsion at high pH.	[15-0]
	E1	MWCOs = 15–300 Da	100 ng L <sup>-1</sup> SDW	10–40 after 10 hr filtration time	The presence of HA in feed solution appeared to improve E1 adsorption on membrane significantly as well as E1 retention.	[15-1]
	Acetaminophen, amoxicillin, cephalixin, indomethacin, tetracycline	Cross-flow TFC	500 µg L <sup>-1</sup> SDW	35– > 99 w/ and w/o alginate	The PhACs retention was influenced by pH, ionic strength, and transmembrane pressure, and those effects were a function of structure and property of the PhACs and properties of the membrane.	[84]
	CBM, acetaminophen, atenolol, diazotrate	Varying pH and pressure Cross-flow Polypiperazine	750 µg L <sup>-1</sup> WWE	90–95 by 0.128 nm pore radius 20–90 by 0.258 nm pore radius	The study of the retention of neutral compounds by virgin and fouled membrane demonstrated that the retention was governed by steric hindrance and then was poorly influenced by fouling.	[83]
	Organic acids including ibuprofen, glutaric acid, acetic acid	Pore radius = 0.128–0.258 nm Cross-flow TFC polyamide	1.5–13.2 mg L <sup>-1</sup> SDW	~30–70 (IBP) ~20– < 95 (glutaric acid) ~10–80 (acetic acid)	The retention of negatively charged organic acids by NF membranes resulted in a larger retention than expected based on steric/size exclusions due to electrostatic repulsion between solute and membrane as driving factor for retention.	[38]
	Ten EDCs and PPCPs	Pilot MBR-flat sheet MBR-hollow fiber MBR-NF	0.06–59.5 µg L <sup>-1</sup> WWE	4.2– > 99 (MBR-NF > MBR-flat sheet/hollow fiber)	While using MBR treatment alone cannot completely remove all the contaminants studied, nicotine, caffeine, ibuprofen and acetaminophen were completely removed from the liquid fraction by this treatment.	[14-5]
Acetaminophen, SMX, TCS	Cross-flow MWCO = 300–550 Da	500 µg L <sup>-1</sup> SDW NOM/calcium ions	< 10 (acetaminophen) 35–80 (SMX) 80–95 (TCS)	For small and neutral-charged target compounds such as acetaminophen, the presence of humic acid and calcium ions increased retention due to an extra hindrance layer provided by the foulants.	[15-2]	
Eleven EDCs and PPCPs	MBR-NF Cross-flow MWCO = 210 Da	26.2–433.9 ng L <sup>-1</sup> WWE	< 1–80 (MBR alone) 78– > 99 (MBR-NF)	The most important factor influencing fouling formation was the characteristics of the dissolved organic matter in the feed water rather than membrane properties.	[15-3]	
Eighteen PPCPs charged (positive, neutral, and negative)	Cross-flow NF270 Polyamide TFC	2,000 ng L <sup>-1</sup> SDW	60–90 (positive) 75–95 (neutral) 85– > 99 (negative)	For positively charged or neutral compounds, the NF retention is more variable and lower. The relatively low retention by NF is likely caused by decreased steric hindrance in NF due to larger pore size.	[33]	
Twelve PhACs	Pilot scale MWCO = 200 Da	< 1–58.8 ng L <sup>-1</sup> NSW	< 1–76 (conventional treatment) 24– > 99 (NF) 53–92 (CBM) 96–98 (diazotrate)	The use of this kind of containerized pilot plant, powered exclusively by a hybrid renewable energy system, allows treating efficiently and sustainably drinking water resources.	[15-4]	
CBM, diazotrate	Cross-flow Polyamide TFC	800 µg L <sup>-1</sup> SDW WWE	75–95 (BPA) > 95 (IBP)	Both season and water matrix influence the dissolved organic matter composition and consequently retention of low molecular weight compounds with medium hydrophobicity by loose membranes.	[63]	
BPA, IBP	Cross-flow Surface modified NF	1000 µg L <sup>-1</sup> SDW		Graft polymerization on the raw NF membrane increased the hydrophilicity and negative surface charge of the membrane in	[80]	

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Table 3 (continued)

Membrane class	CEC class	Experimental condition	C <sub>0</sub> and water type	Key removal (%)	Key finding	Ref.
	Clofibrate acid, DCF, ketoprofen, CBM, primidone	Cross-flow MWCO = 150 Da	100 ng L <sup>-1</sup> SDW WWE	50–70 (deionized water) 90–95 (MBR effluent) 70–95 (tertiary effluent)	proportion to the amount of carboxylic acid in the grafted polymer chains. Two mechanisms for the increase in PhAC removal of caused by macromolecules remaining in the WW effluents: modification of the membrane surface due to membrane fouling and association between the macromolecules and the pharmaceuticals.	[86]
	Eight PhACs	Cross-flow TFC	10 mg L <sup>-1</sup> SDW	99–99.4	Relating the solute retentions to membranes' porosity has shown that the dominant retention mechanism of the examined unionizable antibiotics by all the membranes was the size exclusion effect.	[15-5]
	Ten PCPs	Cross-flow Polyamide TFC MWCO = 150–400 Da	1–150 ng L <sup>-1</sup> WWE	13–99	Membrane filtration provides sufficient removal of chemical contaminants and a potent hygienic barrier for bacteria.	[14-7]
	Seventeen PhACs	Dead-end, NF200 MWCO = 200–300 Da	10 µg L <sup>-1</sup> SDW	35–99 depending on water chemistry conditions	The solution chemistry, organic matter and salinity affect the retention of tetracycline's and sulfanamides and selected hormones by NF membranes.	[15-6]
	ClO <sub>4</sub>	Cross-flow MWCO = 200, 210, 350 Da	100 µg L <sup>-1</sup> SDW	< 5–50 (350 Da) > 90 (200, 210 Da)	The results suggest that the solution chemistry condition of feed water affects perchlorate removal efficiency.	[15-7]
	ClO <sub>4</sub>	Cross-flow, ultrathin nanostructured polyelectrolyte-based	10 mg L <sup>-1</sup> SDW	70–90	The modified membrane had higher permeability, while the perchlorate retention was not significantly enhanced at the same conditions of feed concentration and pressure.	[30]
	Cr, As, ClO <sub>4</sub>	Cross-flow Polyamide TFC MWCO = 200, 400 Da	100 µg L <sup>-1</sup> SDW NSW	45–75 (ClO <sub>4</sub> ) 75–95 (Cr, As)	The results also show that retention of ions by negatively charged NF membranes is significantly influenced by solution pH.	[31]
UF	Herbicides (chlortoluron, isotroturon, diuron, linuron) Benzotriazole, DEET, 3-methylindole, chlorophene, nortripyline Sixteen PhACs	Cross-flow Polyamide TFC MWCOs = 2–20 kDa  Cross-flow Hollow fiber cellulose acetate MWCO = 100 kDa Cross-flow MWCO = 100 kDa	5–50 µM SDW  1 µM SDW WWE  < 10–2,500 ng-L <sup>-1</sup> SDW	35–85 w/ NOM 40–90 w/o NOM  < 5  < 5–95 (UF) 20–95 (PAC + UF)	The retention efficiency of the tested UF membranes followed the sequence linuron > diuron > chlortoluron > isotroturon and agreed well with their values of log Kow and with the sequence of adsorbed mass of herbicide on the membrane. Effluent organic matter competitive effect was more noticeable for the PPCPs less amenable to adsorption; the less hydrophobic compounds, benzotriazole, DEET and methylindole.	[15-8]
	Sixteen EDCs and PPCPs	Hollow fiber Pore size = 0.04 Outside-in	1,000 ng L <sup>-1</sup> Three NSW	< 5–40 (Lake Ontario) 10–90 (Lake Simcoe) 30–90 (Otonabee River)	The combination of PAC and UF in-line treatment yielded an average removal efficiency of 90.3% that tailors the strengths of and eliminates the flaws of the two (PAC and UF) individual techniques.	[98]
	Eleven EDCs and PPCP	Cross-flow Polyamide TFC MWCOs = 2–20 kDa	500 µg L <sup>-1</sup> SDW/WWE	< 60 excluding hydroxybiphenyl (> 90)	The effect of pH on the retention of negatively charged compounds was negative for UF membranes due to the decrease of adsorption at high pH.	[10-7]
	E2	Dead-end Sulfonated PES MWCO = 8 kDa	0.1, 0.5 µM SDW	10–20 w/ NOM 60–95 w/o NOM	E2 removal by UF membranes is clearly governed by hydrophobic adsorption during initial operation due to the hydrophobicity of the compound. However, size exclusion can be a very significant removal mechanism once steady-state operation is achieved.	[15-0]
	Fifty two EDCs and PPCPs	Dead-end Sulfonated PES MWCO = 8 kDa	2–250 ng L <sup>-1</sup> RO isolate NOM water Three different NSW	< 10 (Group I compounds) 30–80 (Group II compounds)	More polar, less volatile, and less hydrophobic Group I compounds had less retention than less polar, more volatile, and more hydrophobic Group II compounds, indicating that retention by UF is clearly governed by hydrophobic adsorption.	[75]
						[11]

(continued on next page)

Table 3 (continued)

Membrane class	CEC class	Experimental condition	C <sub>0</sub> and water type	Key removal (%)	Key finding	Ref.
	E2, E3, progesterone, testosterone	Dead-end MWCos = 1–100 kDa	100 ng L <sup>-1</sup> SDW	20–50 (E2) 15–40 (E3) 35–65 (progesterone) 5–30 (testosterone)	While UF would not be applied to remove micropollutants alone, it can be used as a pre-treatment step prior to RO or as a separation stage in a membrane bioreactor or hybrid process, such as powdered activated carbon-UF.	[10-6]
	Amoxicillin, cefuroxime axetil	Hollow fiber Spiral wound	20 mg L <sup>-1</sup> WWE	70–71 (hollow fiber) 90–91 (spiral wound)	UF was not sufficient for removing either amoxicillin trihydrate or cefuroxime axetil to a safe level.	[15-9]
	Atenolol, diltiazem, CBM, caffeine, DCF, SMX	Pilot Hollow fiber Polyvinylidene fluoride	54.1–206.6 ng L <sup>-1</sup> WWE	< 40 (DCF > SMX > caffeine > others)	Most of the micropollutants were not effectively removed using the UF membrane (< 17%), with the exception of diclofenac and sulfamethoxazole.	[97]
	E1, E2, E3, EE2, BPA	Dead-end MWCO = 100 kDa	100 µg L <sup>-1</sup> WWE	10–90 (BPA > EE2 ≥ E2 ≥ E1 > E3)	Membrane fouling improved EDCs removal by 0%–58.3% and different enhancements were owing to the different porosity and hydrophilicity of cakes that grew under different pressures.	[10-4]
	Ten PCPs	Cross-flow MWCO = 1 k, 10 kDa	1–150 ng L <sup>-1</sup> WWE	< 1–99	Since the nominal pore sizes of the applied UF membranes are in range of 1–10 kDa, the size exclusion was not a major mechanism in removal of CECs having molecular sizes in range of 200–400 Da.	[14-7]
	SMX, CBM, carbamazepine, mecoprop, DCF, benzotriazole	Pilot PAC-UF Pore size = 20, 40 nm	200–4,300 µg L <sup>-1</sup> WWE	35–95	Both UF membrane systems proved to be well compatible with the application of PAC showing no sign of abrasion, pore blockage or other negative impacts.	[16-0]
	Cr, As, ClO <sub>4</sub>	Cross-flow MWCO = 8 kDa	100 µg L <sup>-1</sup> SDW NSW	30–60 (ClO <sub>4</sub> ) 40–70 (Cr) 7–90 (As)	The retention of the target toxic ions decreases with increasing solution conductivity for the membrane due to a reduction of electrostatic repulsion with increasing conductivity.	[31]
	Cu, Ni, Cr	Polymer-enhanced polyethersulfone Hollow fiber UF (10 kDa)	10–100 mg L <sup>-1</sup> IWW	94.4–95.1 (Ni(II)) 98–98.6 (Cu(II)) 98.3–99.1 (Cr(III))	The complexation and filtration processes are pH dependent, the metal retention was more efficient at neutral and alkaline conditions than at acidic one.	[10-2]
	Cd, Zn	Dead-end MWCO = 13 kDa Complexation-assisted UF	50 mg L <sup>-1</sup> SDW	> 95 (Cd) > 99 (Zn)	At varying pH values, it is possible to perform the removal of metals obtaining high retention coefficients resulting in recovery of the concentrated metal present in feed and regeneration of the complexing agent applied.	[10-8]
	ClO <sub>4</sub>	Dead-end MWCO = 3 and 10 kDa	1 mM NGW	10–90	The polyelectrolyte enhanced UF can be an extremely effective alternative to the ion-exchange method if applied with proper engineering skills focusing on environmental aspects.	[16-1]
	ClO <sub>4</sub>	Dead-end Adsorption-UF MWCO = 3 k <sup>-1</sup> 00 kDa	10 mg L <sup>-1</sup> SDW	35–95 (increased with increasing chitosan dosage)	Due to the electrostatic attraction between positively charged chitosan surfaces and negatively charged ClO <sub>4</sub> ions, ClO <sub>4</sub> was trapped by chitosan molecule and then concentrated by UF process.	[16-2]
	ClO <sub>4</sub>	Cross-flow Surfactant modified MWCO = 8 kDa	100 µg L <sup>-1</sup> SDW NSW	80 (SDW) > 5–80 (NSW)	ClO <sub>4</sub> retention by a UF membrane modified with cationic surfactant was greater than expected, based mostly on steric/size exclusion as a result of a decrease of the membrane pore size.	[16-3]

CA = cellulose acetate; C<sub>0</sub> = CEC initial concentration; GAC = granular activated carbon; NOM = natural organic matter; COD = chemical oxygen demand; PAC = powdered activated carbon; SDW = synthetic drinking water; NSW = natural surface water; IWW; industrial wastewater; NGW = natural groundwater; SSW = synthetic wastewater; WWE: WW effluent.

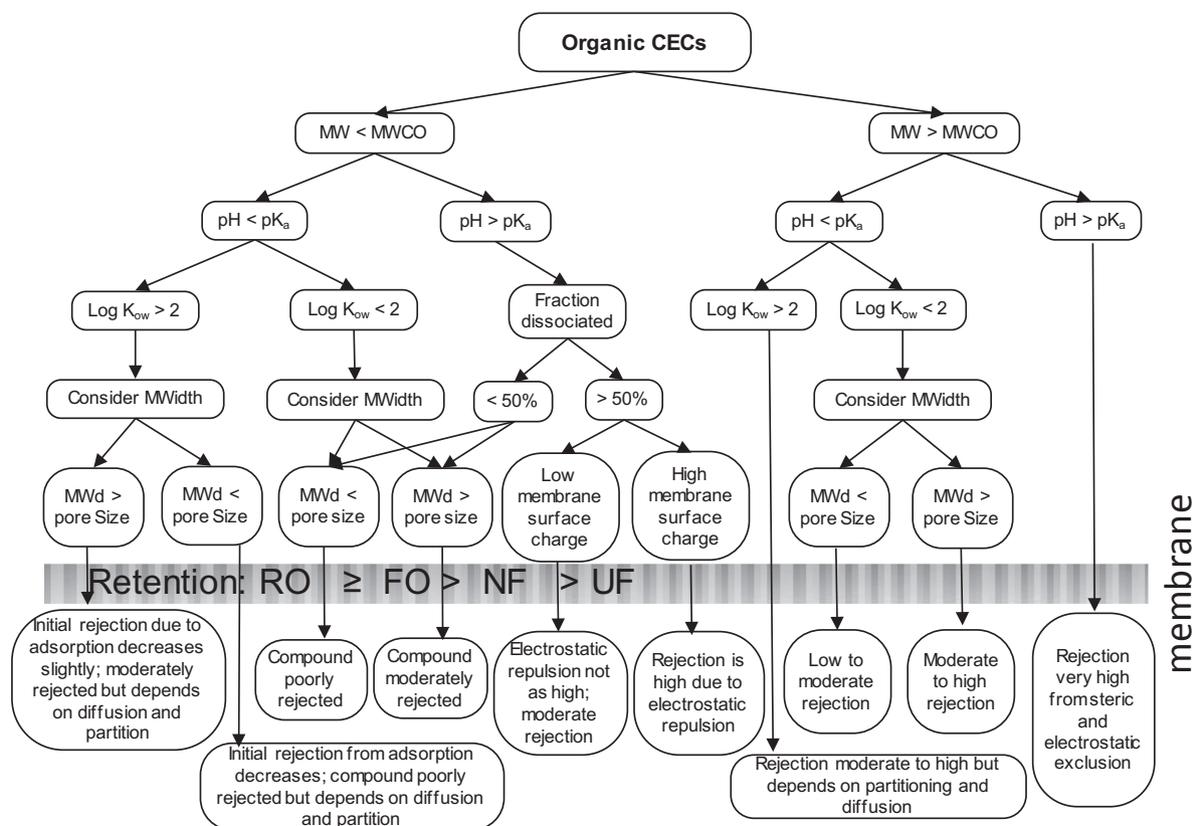


Fig. 3. Retention diagram for organic CECs during membrane treatment based on solute and membrane properties modified from [54].

during membrane treatments based on solute and membrane properties is presented in Fig. 3.

### 3. Conclusions and areas of future research

Overall, the general CEC removal trend was as follows: (i) the removal efficiency for the membranes follows the declining order:  $RO \geq FO > NF > UF$ ; (ii) the retention of CECs by RO and FO membranes is mainly governed by size/steric exclusion, while high retention can still be achieved due to hydrophobic (adsorption) and electrostatic (attraction) interactions for NF and UF membranes; (iii) more polar, less volatile, and less hydrophobic organic CECs have less retention than less polar, more volatile, and more hydrophobic organic CECs; (iv) while, in general, FO and RO membranes show significant metal/toxic anion retention ( $> 95\%$ ) regardless of water quality and operating conditions, metal/toxic anion retention by NF and UF membranes is more efficient at neutral and alkaline conditions than at acidic values; and (v) while UF alone may not effectively remove CECs, it can be employed as a pretreatment step prior to FO and RO.

However, numerous studies were limited to a few membranes (e.g., FO, RO, NF, or UF), focused on synthetic solutions, or examined only a few compounds under limited solution pH/conductivity ranges and operating conditions. Thus, a systematic retention assessment of various CECs is necessary for the following reasons: (i) to investigate the removal mechanisms of FO, RO, NF, and UF membranes in the presence of co- and counter-ions in natural source waters; (ii) to systematically evaluate the influence of DS type, concentration, and reverse permeation rate on CEC retention for FO membranes; (iii) to better understand water conditions in the presence of various NOMs that improve removal, and those for which specific target compounds favor the formation of bound complexes (since determining the optimal solute–solute interactions with organic matter and fouling is critical when designing membrane operations); (iv) to determine whether the accumulation of foulants and retarded diffusion influence the retention of

CECs by membranes having varying fouling degrees in various waters; and (v) to evaluate larger-scale processes because, unfortunately, insufficient information is currently available about FO, RO, NF, and UF membrane processes to allow full-scale implementation.

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