

Treatment Technologies for Wastewater Reuse: Fate of Contaminants of Emerging Concern

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Abstract The presence of thousands of microcontaminants in wastewaters and their potential risks has drawn a large attention of the scientific community during the last years. The presence of these contaminants is especially controversial when wastewater is considered for reuse because a large number of microcontaminants are frequently not totally removed by conventional wastewater treatment processes. As a contribution to the knowledge in this field, this chapter focuses on the application of four well-known and widely used technologies to the elimination of microcontaminants. Membranes, activated carbon, ozonation, and advanced oxidation processes (AOPs) are deeply reviewed to assess their efficiency and safety in the elimination of these contaminants from wastewater effluents. A brief description of each technology is presented together with a review of their real application, mostly in wastewater treatment plants (WWTPs). A deep analysis of the found data allows to conclude that the four presented alternatives can be useful for microcontaminant mitigation although none of them seem to be a universal barrier for microcontaminants when used separately. In addition, each technology presents drawbacks which demand further research to be overcome. Depending on the final use of reclaimed water, the treatment may require the combination of

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several of the studied technologies although that results in an economic impact which cannot be neglected.

Keywords Activated carbon, AOP, Membranes, Micropollutant, Ozone

Contents

1	Introduction	7
2	Existing Technologies for Water Reuse	8
2.1	Membrane Filtration	9
2.2	Ozonation	16
2.3	Adsorption	21
2.4	Advanced Oxidation Processes (AOPs)	26
2.5	Overall Comparison	29
3	Overall Conclusions	29
3.1	Membrane Filtration	29
3.2	Adsorption	32
3.3	Ozonation	33
3.4	Advanced Oxidation Processes	33
	References	33

Abbreviations

AOPs	Advanced oxidation processes
BAC	Biological activated carbon
BDPEs	Bromodiphenyl ethers
CAS	Conventional activated sludge
DEHP	Bis-(2-ethylhexyl)phthalate
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EDCs	Endocrine-disrupting chemicals
EEQ	E2 equivalence factor
GAC	Granulated activated carbon
HRTs	Hydraulic retention times
HS	Compound–humic substance
K _{OW}	Octanol–water partition coefficient
MBR	Membrane bioreactor
MF	Microfiltration
NDMA	<i>N</i> -Nitrosodimethylamine
NF	Nanofiltration
NOM	Natural organic matter
PAC	Powdered activated carbon
PhACs	Pharmaceutically active compounds
PPCPs	Pharmaceuticals and personal care products
RO	Reverse osmosis

SAT	Soil aquifer treatment
SRTs	Sludge retention times
TDS	Total dissolved solid
UF	Ultrafiltration
WWTPs	Wastewater treatment plants

1 Introduction

The lack of surface water for drinking water production is of growing concern and attracts worldwide attention. In response to the water scarcity, treated wastewater is considered a viable alternative water resource. This book chapter focuses on urban wastewater reuses following passage through wastewater treatment plants (WWTPs). The main applications of urban water reuse are direct or indirect potable reuse and direct or indirect non-potable reuse.

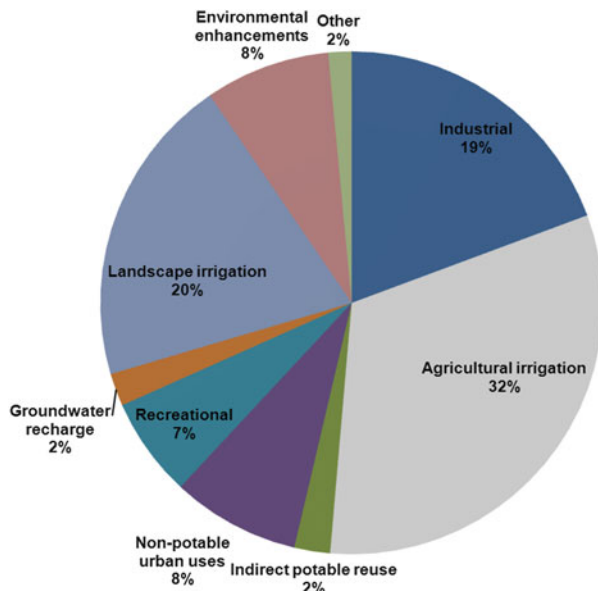
As regards potable water reuse, to our knowledge, direct reuse has been implemented only in Africa [1]. In contrast, indirect potable reuses have been widely accepted by introducing reclaimed water into surface or groundwater bodies. Artificial groundwater recharge is the most widespread practice due to the additional treatment provided by underground transformations and because reclaimed water loses its identity as sewage water. Soil aquifer treatment (SAT) is one of the most regarded practices for indirect potable reuse [2]. To improve wastewater quality, SAT can be combined with preceding advanced treatments. Undoubtedly, the quality of water extracted from a recharged aquifer depends on the introduced water.

Non-potable water reuse includes all water reuse practices other than potable water reuse. Reclaimed water is mainly used for agricultural and landscape irrigation or groundwater recharge. In addition, several cities use reclaimed water for different urban applications such as toilet flushing [3, 4], fire protection, or washing purposes (Fig. 1).

Possible human exposure to reclaimed water puts higher demands on the wastewater treatment in order for the wastewater to be safe for direct or indirect applications. Advanced treatment technologies have been evaluated for improving the quality of reclaimed water in order to prevent potential effects of recalcitrant compounds.

Due to the concern related to the presence of microcontaminants in water sources, several studies on their removal at WWTPs have been carried out at full scale. Nowadays, conventional WWTPs produce water in compliance with major relevant regulations. However, municipal wastewater is considered the primary source of microcontaminants [6] in waterways. A variety of organic microcontaminants, including pesticides, pharmaceutically active compounds (PhACs), personal care products, and estrogens as well as their human metabolites, are not completely removed in WWTPs with conventional treatments, and therefore they are detected in wastewater effluents [7–10]. The presence of microcontaminants is

Fig. 1 Global water reuse
(Figure adapted from
“Municipal Water Reuse
Markets 2010” [5])



especially concerning if treated wastewater is being considered for reuse. It has been seen that traditional biological treatment via activated sludge is not very effective for the removal of several of such contaminants. Thus, studies analyzing the efficiency of conventional WWTPs without advanced treatments are presented herein.

Although the non-potable direct reuse of treated effluents may have beneficial effects (e.g., addition of nutrients to the soil), irrigation with reclaimed water, for example, may cause sorption of microcontaminants and metals in agricultural crops and the contamination of groundwater sources [11–14]. Moreover, several studies reported the presence of microcontaminants in agricultural irrigation networks [11, 12].

2 Existing Technologies for Water Reuse

In the last decade, some researchers investigated the efficiency of different advanced water treatment processes for contaminants of emerging concern (CEC) removal to reduce the impact of discharges of reclaimed water into different water bodies [15]. In this work, we review various available technologies for the removal of microcontaminants showing their advantages and disadvantages. The selected technologies presented in this chapter (membranes, ozone, adsorption, and advanced oxidation processes (AOPs)) are those considered more mature and ready to be applied at WWTPs [16, 17]. In fact, most of them are currently being

used successfully in WWTPs for different purposes. The elimination rate reported proves that these technologies can eliminate a high fraction of the microcontaminants present in water. However, the necessity or not of this step must be carefully studied, since all of them are economically and energetically demanding. Thus, their application can be only considered if water conditions and requirements justify it.

Membrane technologies provide an important solution in reuse and recovery of water. Membrane filtration involves the passage of wastewater, usually from biological treatment, through a thin membrane for the purpose of removing particulate material, pathogens, organic matter, nutrients, and dissolved substances not removed by previous treatment processes. Generally, membrane processes are considered the most powerful technologies for removing microcontaminants, and microfiltration (MF) coupled with reverse osmosis (RO) (MF-RO) has become the most widely used technology together with SAT [18].

Ozone is an unstable gas generally produced by electric discharge in a gas phase. Its stability in water is on the order of minutes, requiring on-site generation. Ozone has been used in drinking water and WWTPs since several decades. Thus, ozonation is a mature and quite reliable technology. Currently, ozone is mainly used for disinfection purposes in the production of drinking water. However, since the concern for the presence of several microcontaminants in wastewater is growing up, ozone is being considered a good alternative to control this problem due to its high oxidizing capacity and the ability of generating hydroxyl radicals.

Adsorption is the process of accumulating substances that are in solution on a suitable interface. During adsorption, molecules of a substance (adsorbate) collect on the surface of another substance (adsorbent). Thus, adsorption is considered to be a mass transfer operation, usually from a fluid phase to solid phase. Adsorption process involves the transfer of the adsorbate molecule from the bulk solution to the adsorption site in the adsorbent. Adsorption treatment of reclaimed water is usually thought of as a polishing process for water that has already received normal biological treatment.

AOPs are generally based on an initial generation of hydroxyl radicals ($\text{HO}\cdot$), which then become the system's main oxidizing agent, able to remove a large number of contaminants. In general, contaminants which exhibit the highest levels of oxidation are characterized by high $\text{HO}\cdot$ rate constants associated with their electron-rich moieties (e.g., phenols, anilines, olefins, and activated aromatic).

2.1 Membrane Filtration

2.1.1 Membrane Technologies

MF and ultrafiltration (UF) membranes are commonly used for the filtration of municipal secondary effluent. The resultant water from these membrane processes may be used for diverse reuse applications after disinfection. The membrane

driving force in MF and UF is the hydrostatic pressure difference or vacuum in open vessels. On the other hand, sieve is the typical separation mechanism. The combination of a biological treatment with MF or UF membranes is called membrane bioreactor (MBR) and is widely used in water reuse systems. MBR is an alternative to the conventional secondary treatment with activated sludge that provides enhanced organic compounds and suspended solid removal. MBRs possess the following advantages over conventional wastewater treatment: high effluent quality, excellent microbial separation ability, absolute control of sludge retention times (SRTs) and hydraulic retention times (HRTs), high biomass content and less sludge bulking problem, low-rate sludge production, small footprint and limited space requirement, and possibilities for a flexible and phased extension of existing WWTPs [19]. The presence of membranes improves the removal of microcontaminants in MBR because of both the intrinsic effect of the membrane and also the increase of SRT. Higher SRTs lead to the diversification of microorganisms, including some slow-growing bacteria such as nitrifying bacteria, which improves the removal of microcontaminants. Sorption to biomass and entrapment in the membrane biofilm are also important mechanisms of elimination.

MBR technology has demonstrated to meet unrestricted irrigation World Health Organization (WHO) standards by means of a supplemental disinfection [20]. Regarding microcontaminants present in municipal wastewater, MBR technology does not efficiently remove them (see the section on “Microfiltration, Ultrafiltration and Membrane Biological Reactor”). Other applications such as aquifer recharge, surface water augmentation, dual water systems in households, and industrial process water require advanced levels of purification nonaffordable with the technologies above mentioned.

MF and UF membranes are also widely used as a pretreatment step to help prevent fouling of the less permeable nanofiltration (NF) and RO membranes. In contrast to MF and UF, solution/diffusion and exclusion separation mechanisms govern the NF and RO separation. In addition, the hydrostatic pressure difference is the only driving force in NF and RO. In terms of water reuse, NF membranes are commonly used to reduce total dissolved solid (TDS) concentration for specific applications. To this end, NF is also used in conjunction with RO. Both NF and RO are also used to treat pre-filtered effluent (typically with MF or UF) for surface water augmentation or indirect potable reuse applications such as groundwater injection. Also, the two-stage scheme MBR–RO/NF is nowadays increasingly accepted for water reuse. Terms “loose” (low rejection) and “tight” (high rejection) are commonly used to define the overall rejection efficiency of NF and RO membranes. Even though most inorganic and organic constituents and microorganisms are removed, disinfection is required to ensure system reliability in the event of a leak or defect in the membrane and to control the growth of microorganisms in the pipelines.

Figure 2 outlines the effectiveness of each membrane technology in removing the different constituents of wastewater as a function of their size.

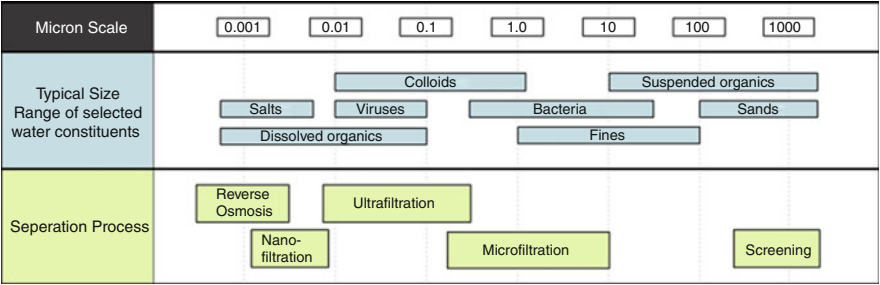


Fig. 2 Size range of constituents in wastewater and operation range of membrane processes

2.1.2 Membrane Separation Mechanisms

Generally, up to four basic mechanisms may be involved in the rejection of solute by membrane processes: sieve, size exclusion (steric effect), adsorption onto membrane, and charge repulsion. To illustrate that, the example of low rejection rate of caffeine by RO membranes due to its physicochemical properties can be used. As a representative of hydrophilic and nonionic compounds, the rejection driven by charge exclusion and adsorption is negligible, and steric exclusion is solely responsible for the retention of caffeine. In addition, the lower molecular weight of caffeine in comparison with other target compounds might result in the decreased removal efficiency during the RO membrane filtration process [21].

These mechanisms are largely dependent on a number of factors, i.e., membrane process type, operating conditions, specific microcontaminant characteristics, membrane fouling, matrix composition, and membrane characteristics. The last factor seems to be more relevant in the case of NF and RO membranes. Although to a lesser extent compared to NF, the retention in RO systems is also membrane type dependent [22].

Recently, major efforts have focused on assessing how matrix characteristics affect the microcontaminant rejection by membranes. According to Nghiem and Coleman [23] and Comerton et al. [24], membrane fouling is likely to contribute to higher rejections of PhACs by NF/RO, especially for some hydrophobic ionogenic compounds. However, other studies reported that organic fouling can both improve and lessen the retention of microcontaminants because membrane fouling has been observed to both increase compound adsorption and decrease mass transport causing higher diffusion of solutes across the membrane [25–27]. The main mechanisms by which fouling seems to influence membrane rejection are the modification of the membrane surface charge, pore restriction, and cake-enhanced concentration polarization.

Regarding the natural organic matter (NOM) present in the matrix, most authors agree with a positive effect over the rejection of microcontaminants. Plakas et al. [28] clarified that an increase in compound rejection may result from the binding of microcontaminants to NOM due to hydrogen bonding, forming NOM–compound complexes that are larger, have an increased negative charge, and/or

have a higher affinity for adsorption to the membrane when compared to the compound alone. Sadmani et al. [29] further analyzed the interactions of major organic matter fractions of NOM with the different microcontaminants as a function of their characteristics. They determined that dissolved organic matter (DOM) fractions interact preferentially with neutral microcontaminants, resulting in increased rejection, presumably due to enhanced size exclusion of compound–humic substance (HS) pseudo-complexes arising from dipole–dipole interactions. The increase in rejection can be also attributed to an increase in the negative surface charge of the membranes due to the presence of NOM (electrostatic repulsion) [30]. According to Sahar et al. [31], NOM interactions could be the explanation for the lower removals observed for the microcontaminants present in lower concentrations in the raw sewage since the matrix effect which influences the removal mechanisms would decrease.

The speciation of microcontaminants may result in a significant change in rejection as a function of pH, with much greater retention occurring for ionized, negatively charged compounds. For uncharged microcontaminants, intrinsic physicochemical properties of the molecules play a role in their retention. UF and NF exhibited much higher removals for less polar microcontaminants [32]. The presence of divalent cations, calcium in particular, can also influence the membrane charge and the interaction of compounds and humic acids with each other and the membrane surface. They can have a positive effect on microcontaminant retention but can also interfere with the microcontaminant–NOM complex reducing its formation and thus retention [24, 28, 33]. According to Sadmani et al. [29], an increase in cation concentration leads to a decrease in removal of neutral compounds probably by decreasing the availability of HS interaction sites.

2.1.3 General Disadvantages of Membrane Technologies

Although membrane processes are effective treatments for removing a wide range of microcontaminants, one of their drawbacks is the generation of huge volumes of concentrates that are commonly discharged to water bodies. Although the discharge of membrane retentates is currently not regulated, safe environmental practices would suggest that such a concentrated waste stream should be treated before its release and dilution into the environment. Treating these concentrates would minimize the environmental impacts associated with their discharge or management [21, 34]. Backwash streams need also to be considered especially if chemicals are used in pretreatment or for membrane cleaning. On the other hand, another important drawback of these filtration systems is the high energy consumption associated to the high operation pressures. These reasons, together with the costs associated to fouling problems and replacement of membranes, prevent these technologies to be truly sustainable.

2.1.4 Full-Scale Application Assessment

MF, UF, NF, and RO have been applied during the treatment of municipal effluents in WWTP for water reuse [30, 35–37].

Microfiltration, Ultrafiltration, and Membrane Biological Reactor

MF and UF are widely used processes to efficiently eliminate turbidity. Regarding the rejection of microcontaminants, adsorption onto membrane polymers, as well as interaction with NOM in wastewater, can improve their removal by MF or UF membranes. An advanced water recycling demonstration plant was studied by Khan et al. [22] in order to investigate the effectiveness of MF in the removal of some commonly prescribed PhACs, as well as natural and synthetic hormones found in sewage. They observed partial reduction in concentration for all target compounds that could be attributable to adsorption on the membrane rather than removal by size exclusion. However, they warned that the adsorption capacity of the membrane for a particular compound can reach saturation, and therefore they would desorb from the membrane when its concentration in the influent becomes lower. Sahar et al. [31] reported that the incorporation of UF after a conventional activated sludge (CAS) system increased the removal of antibiotics (including sulfamethoxazole) by up to 30%, probably due to the activity of the biofilm formed on the membrane surface that incidentally makes the “biomembrane” a tighter physical (enmeshment) and chemical (sorption) barrier. Despite all that, microcontaminants are generally poorly removed during MF and UF because the membrane pore sizes are much larger than the molecular sizes of microcontaminants. Al-Rifai et al. [35] confirmed that MF did not significantly decrease the concentration of 11 PhACs and two nonsteroidal estrogenic compounds. Snyder et al. [36] confirmed that MF and UF membranes have little value for the removal of the vast majority of organic contaminants after studying the removal of a large number of endocrine-disrupting chemicals (EDCs), PhACs, and personal care products. They highlighted the good removal of steroids possibly due to their relatively lower water solubility. However, other compounds did not follow this pattern. The study was evaluated in different pilot- and full-scale plants using secondary non-disinfected effluents and tertiary treated wastewaters.

As commented in Sect. 2.1.1, MBR systems seem to enhance the removal of microcontaminants compared to CAS. Trinh et al. [38] observed good eliminations (>90%) for most of the studied compounds. However, others were incompletely removed (24–68%), including amitriptyline, carbamazepine, diazepam, diclofenac, fluoxetine, gemfibrozil, omeprazole, sulfamethoxazole, and trimethoprim. Similar limited target compound removal was observed in two pilot-scale MBRs using different types of membranes in a WWTP in South Korea. MBR systems were found to be efficient for hormones (e.g., estriol, testosterone, androstenedione) and certain PhACs (e.g., acetaminophen, ibuprofen, and caffeine) with approximately

99% removal. However, the results showed that MBR treatments did not decrease the concentration of the flame retardant TCEP and the PhACs erythromycin, trimethoprim, naproxen, diclofenac, and carbamazepine [39]. Kovalova et al. [40] examined the fate of PhACs and metabolites in a pilot-scale MBR that treated a hospital effluent and reported high removal (>90%) except for the persistent iodinated contrast media. Sahar et al. [31] presented significant but variable eliminations of different microcontaminants in a MBR pilot plant scale operated in a WWTP. Snyder et al. [36] reported that, while the MBRs are effective for reducing the concentration of many EDCs and PhACs from WWTP primary effluents, several compounds remain unaffected, and very few compounds are reduced to below the method reporting limit. They concluded that the removal is likely related to biodegradability of the individual compound.

In summary, MBRs show greater and steadier elimination of microcontaminants compared to CAS systems because of the reasons outlined in Sect. 2.1.1. This improvement is especially evident for hydrophobic compounds. According to Alturki et al. [41], the high removal efficiency for these hydrophobic compounds could be attributed to enhanced residence time in the biological reactor due to ready adsorption to the mixed liquor suspended solids.

From the presented data, it can be concluded that the use of MF or UF membranes alone is not sufficient for microcontaminant removal. Hence, the combination of MF or UF with other processes (e.g., NF or RO) is essential for enhanced elimination of microcontaminants.

Nanofiltration and Reverse Osmosis

Khan et al. [22] compared the effectiveness of NF and RO in the removal of some PhACs and hormones. Retention for individual compounds in NF varies strongly with the membrane type. Comerton et al. [24] studied the rejection of 22 EDCs and PhACs in a MBR effluent. Rejection of EDCs and PhACs by a “loose” NF membrane was poor and variable, which shows that the membrane pore size is large relatively to the compound size. However, the use of a “tight” NF membrane improved the rejection. This was variable and appeared to be influenced by specific compound properties. Rejection was most strongly correlated with compound hydrophobicity, with the more hydrophobic compounds showing higher rejection. Analogue variability was observed for antibiotics by Kosutic et al. [42] for “tight” membranes, with removals higher than 90% and poor removal (<40%) when the rejection of small antibiotic compounds (<200 Da) was assessed. For its part, Yangali-Quintanilla et al. [30] ensured that “tight” NF can be equal to or “better” than RO. The elimination efficiency of NF membranes for different emerging contaminants was very close to that achieved by RO membranes. The average retention efficiency by tight NF was 82% for neutral organic contaminants and 97% for ionic contaminants, while RO was able to achieve 85% removal of neutral contaminants and 99% removal of ionic contaminants. Sang et al. [39] also defended the excellent performance of NF in comparison with RO. RO and NF

showed similar excellent removal (>95%) for all the PhACs and flame retardants studied, being the flame retardant TCEP which presented the lowest rejection.

As commented above, the results undertaken by Khan et al. [22] indicated that the RO process was the most effective in the removal of all tested compounds. Only in one case, one of the PhACs (salicylic acid) was identified in the RO permeate. However, hormones appeared to be more difficult to remove, and traces of those compounds were found in the RO permeates. A polyamide RO membrane provided excellent rejection (>90%) of all EDCs and PhACs investigated in a MBR effluent by Comerton et al. [24]. The authors suggested RO as the final step in a water reuse application, where removal of microcontaminants is of particular concern. Garcia et al. [43] studied the efficiency in the removal of 22 “priority” microcontaminants in a municipal WWTP for water reuse using MF and RO. Although MF was able to remove some compounds by more than 50%, the incorporation of RO significantly enhanced the removal efficiency, ranging from 65% to 90% for most microcontaminants other than naphthalene and ibuprofen. All organics other than EDTA, bis-(2-ethylhexyl)phthalate (DEHP), and bromodiphenyl ethers (BDPEs) were effectively removed by RO to concentrations below 50 ng/L in the permeate. The authors compared their full-scale results for naphthalene and ibuprofen with the ones obtained in pilot plant experiments (>99%) and attributed the differences to the lower feed concentrations at full scale combined with more aged membranes. Sui et al. [44] studied the occurrence and removal of 15 PhACs and consumer products in four WWTPs of Beijing, China. Whereas the eliminations achieved by UF did not exceed 50%, all the target compounds except caffeine were not detected in the effluent of the WWTP equipped with RO. Again, Drewes et al. [21] found that in two full-scale RO facilities, target EDCs and pharmaceuticals and personal care products (PPCPs) were efficiently rejected to below detection limit except for caffeine, still detected in the permeates. The study performed by Al-Rifai et al. [35] in one Australian wastewater recycling scheme proved the ability of RO to remove trace organic contaminants including 11 PhACs from various therapeutic categories and nonylphenol and bisphenol A, two nonsteroidal estrogenic compounds. Al-Rifai et al. [45] monitored the removal of these same microcontaminants in a full-scale water recycling plant in Queensland, Australia. The RO membrane process contributed efficiently to the removal of all the microcontaminants except bisphenol A. In contrast to the last two cited studies, nonylphenol presented the worst removal (83%) within different EDCs studied during a pilot-scale sewage treatment equipped with RO [46]. A study analyzing the removal of different PhACs, hormones, and industrial products in a WWTP in Tel Aviv (Israel) revealed that high total removal rates (>93%) were achieved by the both configurations assessed at pilot plant scale (MBR/RO and CAS–UF/RO) [31]. Snyder et al. [36] studied several pilot- and full-scale RO systems monitoring the removals of a large amount of EDCs and PPCPs. RO systems removed nearly all target analytes to below or very near the method reported limit. However, trace levels of some contaminants were still detectable in RO permeates (i.e., the PhACs meprobamate, gemfibrozil, naproxen, sulfamethoxazole, loperamide, and the personal care products TCEP, DEET, and galaxolide). They also observed that the second pass in a

double-pass RO was able to remove compounds that were not entirely removed during the first pass.

2.2 Ozonation

2.2.1 Main Concepts and Bases of Ozonation

Ozonation is a mature technology, and the reactions involved in the process are well known. There are two main reaction pathways for microcontaminant elimination by ozone. Ozone can react directly with organic contaminants through an ozone molecular reaction. This reaction is slow and selective. On the other hand, in alkaline waters, ozone can also react with water or other substances, forming the highly oxidant hydroxyl radicals $\text{HO}\cdot$.

Due to its instability and quick reactivity, ozone must be generated on-site using air or high-purity oxygen. Normally, the gas generated contains between 1% and 3% of ozone by weight if initial gas is air and between 8% and 12% if pure oxygen was fed. Ozonation units in WWTPs for secondary effluent disinfection are injecting doses in the range of 3–30 mg ozone L^{-1} .

After the generation, since the concentration of ozone is very low, it is important to ensure a good contact between the gas and the water to ensure a good distribution of ozone and avoid over-concentrations of ozone which can lead to the formation of hazardous by-products.

Furthermore, ozonation presents a reasonable cost of 0.16 € m^{-3} [47] compared to other tertiary treatments.

2.2.2 Full-Scale Application

Due to the several ozonation units already operating in different WWTPs, there are already some studies about the effectiveness of ozonation to eliminate microcontaminants at full scale. Also several studies can be found at pilot plant level. As an example of the use of ozonation at full scale, Table 1 summarizes some details of some works cited in this chapter. In the listed references, ozonation units usually are placed after the secondary treatment, and they come before some sand or carbon filter.

Microcontaminant Removal

The effects of ozonation after biological treatment for microcontaminant removal have been widely studied. Similar results are found if microcontaminants are gathered according to their affinity to react with ozone. There is a first group of compounds which are easily removed below detection limits with an average dose

Table 1 Works at full scale/pilot plant scale about the microcontaminant removal listed for ozonation technology

Authors	WWTP location	Flow rate (m ³ day ⁻¹)	Equivalent population	Advanced treatment	Microcontaminant: monitored/before adv. treatment/after adv. treatment	O ₃ dose	Residence time (min)
Hollander (2009)	Regensdorf (Switzerland)	5,550	25,000	Ozonation + sand filter	220/55/11	0.4–1.2 g O ₃ ; g DOC	4–10
Margot (2013)	Lausanne (Switzerland)	95,000	220,000 ^a	Ozonation + sand filter	120/70	2–13 mg O ₃ L ⁻¹	20–60
Rosal (2007)	Alcalá de Henares (Spain)		3,000	Ozonation (lab plant)	72/54/12	2.4–16 mg O ₃ L ⁻¹	
Nakada (2007)	Tokyo	170,000	460,000	Sand filter + ozonation	29/24/19	3 mg O ₃ L ⁻¹	27
Reungoat (2010)	South Caboolture (Australia)	8,000	40,000	Ozonation + BAC	85/54/4	0.5 mg O ₃ ; mgDOC	15 (O ₃) 18 (BAC)
Reungoat (2011)	Three plants at Australia: Caboolture Landsborough Gerringong	8,000/ 2,000/ 900	40,000 10,000 11,000	Ozonation + BAC	41/21/11	0.2–0.8 mg O ₃ ; mgDOC	BAC: 9–45

^aOzonation studied a pilot plant to treat a maximum flow rate of 100 L s⁻¹ (13,000 PE)

of ozone ($0.8 \text{ g O}_3 \text{ g}^{-1} \text{DOC}$). Normally, those compounds present second-order rate constants $>10^4 \text{ M}^{-1} \text{s}^{-1}$ (regarding to the direct reaction with O_3) such as compounds with aromatic rings, double bonds, or amine moieties, with a high affinity for direct reaction with ozone [6]. There is a second group of compounds with low affinity for O_3 (second-order rate constants $<10^4 \text{ M}^{-1} \text{s}^{-1}$) but with high affinity for the strong and unselective hydroxyl radical. An average removal around 60% was achieved for these substances. $\text{HO}\cdot$ radical exposure to microcontaminants varies with the EfOM composition (it is sensitive to the addition of coagulants), presence of $\text{HO}\cdot$ scavengers (such as carbonate), and pH. Finally, there is a third group which includes those microcontaminants with low affinity to O_3 direct reaction and also to $\text{HO}\cdot$. They formed the group of recalcitrant compounds with low removal (below 40%): atrazine, iothalamic acids, atenolol, diatrizoate, iopromide, mecoprop, benzotriazole, 5-methylbenzotriazole, sucralose, DEET, diazinon, galaxolidone, benzothiazole, microcontaminants with amide groups in general, etc [47, 48].

Regarding to specific removal data, Hollender et al. [6] found that, of the 55 microcontaminants identified after the secondary clarifier, only 11 were detected after the ozonation, using a moderate dose of $0.62 \text{ g O}_3 \text{ g}^{-1} \text{DOC}$. Margot et al. [47] found that the number of microcontaminants with a concentration above 100 ng L^{-1} was reduced from 52 compounds in the effluent of the biologically treated wastewater to 30 compounds after the ozonation with an average ozone dose. Thirteen (13) substances were removed over 90%. Nakada et al. [49] monitored 24 pharmaceutically active compounds. The combination of ozonation and sand filtration with activated sludge treatment led to an efficient removal ($>80\%$) of most of the target compounds, mainly due to the ozonation step. Rosal et al. [50] found that 31 of the 54 microcontaminants detected at influent of the ozonation were below the detection limit using a moderate dose of $6.2 \text{ mg O}_3 \text{ L}^{-1}$. Reungoat et al. [51] studied the removal of microcontaminants in a reclamation plant. After the main ozonation ($0.5 \text{ mg O}_3 \text{ mg DOC}^{-1}$), 26 of the 54 microcontaminants initially detected were below the detection limits. Among the others, 9 showed a reduction higher than 90%, 13 higher than 70%, and only iopromide and gabapentin were reduced by 55%. Later, the study was extended, and Reungoat et al. [52] investigated the fate of 41 microcontaminants in three full-scale WWTPs using ozonation followed by biological activated carbon (BAC) as advanced tertiary treatment. Twenty-one (21) compounds were found at the influent of the ozonation. Half of them presented a removal higher than 80% after the ozonation. The percentage of removal of the microcontaminants at the different WWTPs was very similar.

The persistent compounds required extended exposure to $\text{HO}\cdot$ to achieve significant concentration reductions. Thus, in some of the studies, more extreme conditions were tested, and ozone dose was increased to high values. At the highest ozone dose tested by Hollender et al. [6], $1.4 \text{ g O}_3 \text{ g}^{-1} \text{DOC}$, only two X-ray contrast media still detected the originally 11 recalcitrant compounds. At even stronger O_3 dose conditions ($17.6 \text{ mg O}_3 \text{ L}^{-1}$, equivalent to $2.6 \text{ g O}_3 \text{ g}^{-1} \text{DOC}$), Margot et al. [47] found that even the most resistant microcontaminants were highly removed, with an average elimination of 80%. However, at these O_3 concentrations,

cost is much higher, and the generation of bromate is more feasible and so usually is discarded.

Generation of By-Products

One of the main problems faced by ozonation is the generation of some unintended, toxic by-products. For example, when bromide-containing wastewater is ozonized, bromate, a genotoxic carcinogen [53], can be generated. Thus, bromate was recently included in stringent drinking water standards. Both the European Union and the United States Environmental Protection Agency (EPA) established a maximum contaminant level of $10 \mu\text{g L}^{-1}$. Normally, bromide concentrations in wastewater are low enough to be below that threshold, but further research about how to minimize their presence is required. More recently, the observation that ozonation results in direct nitrosamine formation [6] indicates a new focus of attention which must be investigated. Nitrosamines are highly toxic, especially to the liver, and are suspected human carcinogens [54]. Recent investigations point to specific precursors of nitrosamines as degradation products of fungicides and even bromide catalysis [55].

Hollender et al. [6] studied the generation of both undesired by-products, and for the highest dose of ozone tested, $1.4 \text{ g O}_3 \text{ g}^{-1} \text{ DOC}$, the bromate concentration was never found to exceed $7.5 \mu\text{g L}^{-1}$, lower than the $10 \mu\text{g L}^{-1}$ threshold fixed by EPA or European regulations. The authors also monitored eight nitrosamines, being *N*-Nitrosodimethylamine (NDMA) the most predominant, with concentration up to 21 ng L^{-1} . They found that the amount of NDMA generated during ozonation was only a function of the composition of the influent coming from the clarifier. Only 25% of NDMA was removed with the highest ozone dose. Margot et al. [47] also studied the formation of bromate. Before ozonation, bromate concentration was below the detection limit. After ozonation ($0.8 \text{ g O}_3 \text{ g}^{-1} \text{ DOC}$), the concentration grew up to $3.7 \mu\text{g L}^{-1}$, again below the drinking water standard of $10 \mu\text{g L}^{-1}$. The authors found that the formation of bromate was dependent on the ozone dose applied, exceeding the drinking water standard for an ozone dose above $1.4 \text{ mg O}_3 \text{ mg}^{-1} \text{ DOC}$. As it can be seen, for the same dose of ozone, different amounts of bromate were measured. This proves the importance of a continuous monitoring of the bromate concentration to be sure that water standards are not overcome since it is affected by the characteristics of the influent.

Due to the process-related formation of reactive transformation products, it is recommended to install a stage with biological activity (e.g., sand filter) after ozonation of the wastewater so that these products can fully biodegrade. For example, sand filter can retain 50% of NDMA generated during ozonation. Biological sand filtration proves as an economic, useful complement to ozonation for elimination of by-products biologically degradable and removal of suspended solids and phosphate [6, 47, 50]. Unfortunately, bromate concentration is not reduced during the sand filtration, and therefore a high ozone dose should be avoided to ensure low bromate concentrations in the effluent [47].

Ecotoxicity of Ozonation Processes

Since the harmful by-products generated by ozone are a concern for the use of this technology, the use of a battery of bioassays as complementary tools to chemical analysis can provide valuable additional information on the water quality and the process efficiency. Furthermore, the bioassays allow taking into account the presence of non-identified compounds, formed transformation products, and/or mixture effects. Generally, bioassays carried out in different studies show that ozonation decreases the toxicity of waters. At average ozone doses, it can be concluded that the mixture of degradation products formed has an overall less harmful potential than the mixture of parent compounds [47, 51, 52].

Reungoat et al. [52] found that more than 87% reduction of estrogenicity was observed in the ozonation stage of all the three reclamation plants studied. Even at the lowest dose of 0.2–0.3 mg O₃ mg⁻¹ DOC, high removal of estrogenicity was achieved. Nonspecific toxicity, measured with Microtox test, was reduced around 30–40% showing that new by-products generated during ozonation were less toxic to Microtox test than the former ones. In another study [51], authors carried out more specific measurements after a treatment train composed by ozonation + BAC. Authors carried out different bioassays to measure specific toxic actions: Ah receptor response (removal of 62% of dioxin and dioxin-like activity), genotoxicity effects (removal of >93%), neurotoxicity effects (removal of >90%), and phyto-toxicity effects (removal of 75%). If only ozonation step is considered, the specific toxicity values of the listed bioassays notably decreased. For example, estrogenicity effects present 90% of removal after the main ozonation. Margot et al. [47] did a similar study but with different bioassays, arriving to similar conclusions. They monitored the photosynthesis inhibition (removal of 82%), the algae growth inhibition (75%), and estrogenic activity (89%). Finally, they also found that ozonation clearly reduced the fish early-life stage toxicity of the effluent.

In spite of the good perspectives for ozonation presented in most of the literature, there are also some works which warn about the necessity of further research to consider ozonation a totally safe technology. Actually, some studies show an increase of toxicity of wastewater effluent due to the formation of toxic by-products during the ozonation stage [56–58]. Petala et al. [56] found that ozonation of secondary effluents with high doses of ozone may increase the toxic potential (Microtox test) or mutagenic activity (Ames test) of the stream. Mutagenic activity was usually reduced when ozone dose and contact time were increased. Magdeburg et al. [57] monitored the toxicity of a secondary effluent with in vivo test battery before and after ozonation and sand filtration. Authors used one aquatic plant and five invertebrate species. They found that ozonation induced an increase of toxicity for three of the tested systems, assuming the generation of adverse by-products. After sand filtration, toxicity levels were reduced up to the levels at the outlet of the secondary effluent or even lower. A similar study was carried out by Stalter et al. [58]. They evaluated the variation of toxicity after a conventional secondary treatment followed by an ozonation + sand filter unit, by means of the fish early-life stage toxicity test. They found that ozonation decreases

the estrogenic activity. However, authors also showed that ozonation produced a development retardation in fishes, probably due to the generation of toxic by-products. That negative effect disappeared after sand filtration, proving that the by-products are easily degradable or adsorbable.

According to the overall results, it may be assumed that usually the outlet flow presented a lower toxicity than the inlet. However, since there are also some studies which warn about the generation of toxic by-products, further research is required to know the operation parameters that make ozonation a safe technology. The controversy that use of ozone presents is clear. The necessity of a proper design of the ozone reactor and a careful study of the operation parameters as contact time seem obvious [47].

Disinfection and Other Contaminants Removal by Ozonation

With regard to other parameters, ozonation proves to be an excellent tool for disinfection purposes. Ozonation is able to disinfect the effluent greatly, with removal of coliphage virus below the detection limit (5 UFP ml^{-1}) (>95% removal) and a reduction over 97% in the concentration of fecal bacteria; this level is below the European standard for good bathing water quality [47].

If other contaminants (DOC, phosphorous, NO_3^-) are monitored, ozonation is not very effective against them. For example, DOC removal is normally very small in an ozonation unit, proving that it is difficult for ozonation to achieve the complete mineralization of microcontaminants. Ratios of 10% of DOC removal can be found in literature [51, 52]. Thus, if required, it is convenient adding a complementary step after ozonation to decrease those parameters.

2.3 Adsorption

2.3.1 Main Concepts and Basis of Adsorption with Activated Carbon

Adsorption is a technology widely used in wastewater treatment, and several types of materials have been tested as absorbents. However, although there are a large variety of adsorbents in the market, most of the adsorption units in WWTPs use activated carbon due to economic reasons. Activated carbon is generated by a pyrolysis process at 700°C . After the pyrolysis process, the obtained chair is “activated” being exposed to oxidizing gases as steam or CO_2 at high temperatures ($800\text{--}900^\circ\text{C}$). There are different types of activated carbon according to the pore sizes and the particle size, with a different adsorption capacity. The two types of activated carbon more frequently used are powdered and granulated activated carbon.

Powdered activated carbon (PAC): It refers to particles with a diameter less than 0.074 mm and an apparent density between 300 and 700 g L^{-1} . PAC presents a

large surface to volume ratio with a small diffusion distance. PAC is usually fed directly to other process units in the treatment process. Since both DOM and microcontaminants adsorb onto the activated carbon, the PAC stage is best located after extensive biological treatment in order to minimize competition and the PAC consumption. PAC also offers the advantage of being used seasonally when risk of microcontaminants may be greater (e.g., low-flow events) [36].

When loaded with microcontaminants, PACs should be disposed, but recirculation of the spent PAC to the biological treatment before its elimination can additionally improve the global microcontaminant removal efficiency without impacting the quality of the biological treatment [47]. This configuration enhances microcontaminant removal by 10–50% comparison with the application without recycling [59].

Granulated activated carbon (GAC): It has a diameter greater than 0.1 mm and an apparent density between 400 and 500 g L⁻¹. The higher diameter and lower head loss allow it to be used in dedicated vessels. As with PAC, residence time is the major factor that affects the yield of the process. GAC usually is loaded in the contactor (frequently a fixed bed reactor), and the wastewater passes through it. Adsorption capacity is reduced with operation time, so it is very important to plan periodically regenerations, especially to avoid desorption and releasing of hazardous components to the effluent [17].

There is also a variation of GAC called *biological activated carbon (BAC)*. BAC is a type of GAC with a biofilm in the surface which adds biological activity to the GAC properties. The major advantage of the BAC system is that the recalcitrant organic matter removed from water is firstly adsorbed into the macropores, where it is detained long enough to promote its slow biodegradation by attached bacteria, also leading usually to continuous bioregeneration of the GAC [60].

2.3.2 Full-Scale Application of Adsorption Process for Wastewater Treatment

Adsorption is considered as a good option for the removal of microcontaminants due to the wide amount of compounds that can be retained. The rate of adsorption of the microcontaminants to the activated carbon and the contact time will be key parameters for the final contaminant removal achieved. The first one is the function of the properties of both adsorbate (K_{OW} , pKa, molecular size, aromaticity versus aliphaticity, and presence of specific functional groups) and adsorbent (surface area, pore size and texture, surface chemistry, and mineral matter content) [40]. The contact time is fixed with the design of the unit. In PAC systems, 1–3 h contact time is normally provided compared to contact times of typically less than 30 min in GAC where the effluent is passed through a packed bed. The presence of competing solutes for the adsorption sites, as dissolved organic carbon (DOC), is also important when microcontaminant removal is pursued [47, 59].

Activated carbon has been widely used in WWTP as PAC, GAC, or BAC form. Therefore, there are a number of studies which have applied these technologies to

Table 2 Works at full scale/pilot plant scale about the microcontaminant removal listed for adsorption technologies

Authors	WWTP location	Flow rate (m ³ day ⁻¹)	Equivalent population	Advanced treatment	Microcontaminants: monitored/detected before adv treatment/detected after adv. treatment	PAC/GAC concentration	Residence time (min)
Boehler (2012)	Kloten/Opfikon (Switzerland)	–	60,000	PAC	38/37/26	10–20 g PAC m ³	
Snyder (2007)	Facility 1	–		PAC	–/14/1	–	–
	Facility 2	–			–/21/18		
Grover (2010)	Swindon (UK)	–	155,000	GAC	14/8/4	–	–
Sang (2007)	Seven plants at South Korea	–	–	GAC	26/14/0	–	–
Margot (2013)	Lausanne (Switzerland)	95,000	220,000 ^a	GAC + sand filter/GAC + UF	120/70	3–5 GAC g L ⁻¹	40–170 water/2–17 days GAC
Reungoat (2010)	South Caboolture (Australia)	8,000	40,000	Ozonation +BAC	85/54/4	0.5 mg O ₃ ; mgDOC	15 min (O ₃) 18 min (BAC)
Reungoat (2011)	Three plants at Australia:			Ozonation + BAC	41/21/11	0.2–0.8 mg O ₃ ; mgDOC,	BAC: 9–45 min
	Caboolture	8,000/	40,000				
	Landsborough	2,000/	10,000				
	Gerringsong	900	11,000				

^aGAC studied at a pilot plant at a maximum flow of 10–15 L s⁻¹ (ca. 1,700 PE)

microcontaminant removal at real WWTPs. Table 2 shows the characteristic of the WWTPs of some of the most complete works listed in this chapter focusing on the use of adsorption as microcontaminant removal technology.

Microcontaminant Removal

As it is expected, better removal of microcontaminants is achieved for higher doses of activated carbon and longer retention time. Also, electrostatic and hydrophobic interactions seem to play an important role in the adsorption process. Positively charged substances usually present a very high removal, independently of their hydrophobicity. PAC usually is charged negatively due to the layer formed by EfOM over the surface of the carbon particle, mainly attracting positively charged compounds. With regard to hydrophobic interactions, Rogers et al. [61] provided a general rule of thumb for applying octanol–water partition coefficient (K_{OW}) to the estimation of adsorption: $\log K_{OW} < 2.5$ indicates low sorption potential, $2.5 < \log K_{OW} < 4$ indicates medium sorption potential, and $\log K_{OW} > 4$ indicates high sorption potential. Thus, the most hydrophilic compounds are eliminated to a lesser extent [47].

Margot et al. [47] carried out an extensive study and monitored 70 compounds present at the inlet of the PAC slurry reactor with a moderate concentration (10–20 mg PAC L⁻¹). Authors found that 32% of microcontaminants presented a very good affinity for PAC and more than 90% was removed. Almost all were either positively charged (five substances) or neutral (seven substances) at the pH of the wastewater, covering a broad range of hydrophobicity ($\log D_{ow}$ ¹ from -1.3 to 3.7). Around 38% of analyzed microcontaminants presented a medium affinity for PAC and had, on average, between 70% and 90% removal, including six neutral and six negatively charged compounds. Thirty percent of monitored microcontaminants composed of neutral or negatively charged compounds (including all the hydrophilic contrast media) showed poor or very variable affinity for PAC with an average removal between 11% and 66%. A higher PAC dose of 60 mg L⁻¹ was tested during one campaign, leading to more than 90% removal for those substances with a low PAC affinity.

Better results were reported by Boehler et al. [59]. They monitored 19 microcontaminants before and after adding PAC in a WWTP, and at least 80% of each microcontaminant was removed by the PAC with a dose of 15 g PAC m⁻³. Also DOC was greatly reduced, with an elimination of around 45%. It was also proved that the performance of PAC in eliminating microcontaminants depends upon PAC dose and contact time, the molecular structure and behavior of the targeted compound, as well as the water/wastewater composition. Grover et al. [62] studied the effect of installing a GAC unit at the effluent of an urban WWTP at Swindon (UK).

¹ Log D_{OW} is a corrected form of the octanol–water partition coefficient ($\log K_{ow}$) determined for nonionic substances, to account for the molecule dissociation or protonation at pH 7.

Authors monitored three representative EDCs and five detected PhACs. Two EDCs were below detection limit after the GAC unit, and 64% of the third one was removed. With regard to the PhACs, concentrations were substantially reduced in post-GAC effluents. On average, the additional removal of PhACs by GAC was between 17% for propranolol and >98% for indomethacin. Also estrogenic potency of the effluent was estimated by means of E2 equivalence factor (EEQ). It was found that EEQ was reduced from 2.2 to 14.6 ng L⁻¹ before GAC to <0.5 ng L⁻¹ after GAC, proving that the final effect of the water had notably decreased. In South Korea, Sang et al. [39] studied the elimination of different chemicals during drinking water and wastewater treatment processes at full- and pilot-scale by GAC technology in seven WWTPs and drinking water plants. Sang et al. [39] monitored 26 microcontaminants (PhACs, hormones, antibiotics, personal care products, flame retardant). The authors found that the conventional water treatment processes (e.g., coagulation and sand filtration) tested were inefficient. However, the monitored microcontaminants were removed below detection limits, thanks to the GAC step.

Another important factor when using activated carbon refers to the remaining adsorption capacity at a given moment. If adsorption capacity is exhausted, the activated carbon can only perform a biological degradation, but for those microcontaminants which have escaped from traditional biological reactor, removal may be very poor. Thus, exhausted activated carbon reactors (several BACs perform on this way) can be useful to remove biodegradable by-products generated by prior advanced treatments but not to eliminate microcontaminants. For example, Snyder et al. [36] studied the performance of two full-scale GAC installations installed in water plants for removing 29 microcontaminants including PhACs, personal care products, pesticides, steroids, fragrances, and antimicrobials. The first installation uses on-site GAC regeneration to ensure the activated carbon was capable of adsorbing organic compounds. Authors found that all the microcontaminants monitored were below detection limit except atrazine, but with a removal higher than 90%. On the other hand, the second installation does not replace regularly the GAC, and it was exhausted. On this case, the GAC column shows a very poor removal of the organic microcontaminants monitored. However, Reungoat et al. [52] studied the effect of three BAC units installed in WWTP after ozonation units with different results. They monitored 21 microcontaminants before and after the BAC unit. Authors found that BAC units could further remove all the remaining microcontaminants. Fifteen microcontaminants presented removals higher than 80%.

It is also interesting to underline that human PhAC metabolites usually are much less removed by activated carbon than the original compound. Indeed, the liver or kidney transforms the pharmaceutical drugs to more polar and hydrophilic compounds, so they can be easily eliminated through the urine or bile, but then there is a weaker tendency to be absorbed by activated carbon [63].

Ecotoxicity of Activated Carbon Processes

Since no by-products are generated by adsorption process, an improvement in the indicators of the bioassays is expected after the activated carbon treatment, as it is proved experimentally. Margot et al. [47] carried out an ecotoxicological evaluation of PAC use. Around 85% of toxicity was removed by PAC reactor. Photosynthesis inhibition was strongly reduced (87%) as well as algae growth inhibition (84% of removal) and estrogenic activity (88% of removal). Furthermore, PAC significantly decreased the toxicity of the WWTP effluent on the development of rainbow trout embryos for all end points measured: the overall survival of the fish, the hatching success, the swim up, the individual development (weight and size), and the induction of estrogenic effects. In the same line of results, Reungoat et al. [52] carried out a nonspecific toxicity test (bioluminescence inhibition test with *V. fischeri*) before and after different BAC units in three different WWTPs. Authors measured a removal between 13% and 54% of nonspecific toxicity. The units were installed after an ozonation unit which achieve a removal of 30–40% of toxicity. Overall, the combination of ozonation and BAC filtration could achieve removals of 50% for DOC and more than 90% for a wide range of microcontaminants as well as a reduction of 70% of nonspecific toxicity and more than 95% of estrogenicity. Thus, BAC process proved to be an excellent complement to ozonation step.

Microcontaminant Removal by Adsorption

Regarding DOC elimination, activated carbon can show a good performance. For BAC reactor, DOC removals up to 48% have been reported [52]. Similar values of DOC removal were found in PAC+UF units. PAC shows a good performance for phosphorus, NH_4 , and BOD_5 removal and a complete removal of TSS, intestinal bacteria, and coliphages [47].

Finally, activated carbon proved to be technically feasible at large scale in municipal WWTP. For example, PAC presents a reasonable cost of 0.18 € m^{-3} [47], very similar to ozonation.

2.4 Advanced Oxidation Processes (AOPs)

The AOPs covered in this section are UV/ H_2O_2 , photo-Fenton, heterogeneous photocatalysis, and $\text{O}_3/\text{H}_2\text{O}_2$.

2.4.1 General Disadvantages of AOPs

The main disadvantages of AOPs are their high chemical requirement and/or the energy consumption, which are reflected in high operating costs. Regarding the use of H_2O_2 , there are significant limitations associated with its use. For example, the additional costs and complexities associated with chemical storage, handling, and injection may limit its attractiveness, and the residual H_2O_2 must also be quenched in some applications prior to environmental discharge.

Similarly to the use of ozone, AOPs (except in cases under very drastic oxidation conditions) do not commonly result in complete mineralization of microcontaminants. Therefore, the major concern is the formation of oxidation by-products (or transformation products) from microcontaminants. To further reduce parent compounds and oxidation by-products, biological post-filtration (sand filtration or activated carbon filtration) can be considered.

2.4.2 Water Reclamation: Full- and Pilot-Scale Application

The UV/ H_2O_2 full-scale process installed after a RO membrane in a water reuse facility studied by Snyder et al. [36] showed significant degradation of the four target microcontaminants still present in the permeate of the RO. De la Cruz et al. [64] reported very high removals for 22 selected microcontaminants (15 PhACs, 2 X-ray contrast media, 1 corrosion inhibitor, and 4 biocides/pesticides) in an effluent from a municipal WWTP using a UV/ H_2O_2 pilot-scale process (cylindrical reactor chamber of 37 L equipped with five lamps of 150W each emitting at 254 nm). They carried out experiments at different flow rates and H_2O_2 concentrations and concluded that a concentration of 50 mg H_2O_2 /L and a residence time of 10s provided the most economical setting and the best microcontaminant elimination (global degradation >88%). However, they reported a global degradation of only 26% working at much lower flow rate with UV alone. Only two (diclofenac and ketoprofen) microcontaminants reached more than 80% degradation. Sang et al. [39] determined that a UV pilot-scale treatment applied after RO and NF processes did not contribute significantly to microcontaminant removal. Another bench-scale UV/ H_2O_2 process study performed by Kim et al. [65] showed that 90% removal efficiency was reached in 39 of the 42 PhACs found in a WWTP secondary effluent. The UV dose (254 nm) was 923 mJ/cm², and the contact time and H_2O_2 concentration were 5 min and 7.8 mg/L, respectively. They found that only few PhACs (especially ketoprofen, diclofenac, and antipyrine) were significantly removed by UV radiation alone. The removal efficiencies of macrolide antibiotics such as clarithromycin, erythromycin, and azithromycin resulted very low even by the introduction of UV doses 20 times higher than common disinfection doses and contact times of 15 min. Good removal of microcontaminants cannot be expected by the UV processes alone and let alone at the radiation doses applied for disinfection of treated water in WWTPs (40–140 mJ/cm²). The addition of H_2O_2

to the UV processes reduces drastically the UV energy required for the effective PhAC removal.

Snyder et al. [66] studied the degradation of steroids, PhACs, pesticides, and industrial chemicals by ozonation at pilot scale. TCEP, musk ketone, and meprobamate were not well removed. They concluded that the addition of H_2O_2 caused little benefit and even in some cases decreased the efficiency of O_3 . Ozone with addition of H_2O_2 was assayed in at pilot scale in a water reclamation plant for removing several steroid hormones and PPCPs. Results showed considerable removal efficiency (N90%) for almost all of the target contaminants, except TCEP (13%), TCPP (26%), atrazine (69%), meprobamate (80%), and ibuprofen (83%) [67, 68].

Chi et al. [69] assessed the performance of a heterogeneous Fenton's pilot-scale process to remove different EDCs and PPCPs from three different municipal WWTP secondary effluents. The system incorporated a modified polyacrylonitrile catalyst which allowed to decompose >90% of the EDCs and >40% of PPCPs using 200 mg/L of H_2O_2 in 3 h residence time working at natural pH. According to them, the system showed great potential in the removal of low levels of PPCPs and EDCs when compared to homogeneous Fenton's, photo-Fenton's, electro-Fenton's, and photocatalysis on TiO_2 . Solar photo-Fenton and solar TiO_2 photocatalysis were studied at pilot scale as tertiary treatments for the remediation of 66 microcontaminants present in municipal WWTP effluents by Prieto-Rodríguez et al. [70]. Photo-Fenton (pH 2.8) achieved 90% of microcontaminant elimination in short reaction times using 5 mg Fe^{2+} /L and 60 mg H_2O_2 /L. It also proved to substantially eliminate the degradation products. However, solar photocatalysis with TiO_2 resulted very inefficient in terms of treatment time and accumulative energy compared to solar photo-Fenton. They highlighted the potential of solar photo-Fenton as tertiary treatment in municipal WWTPs, with estimated treatment costs in the range of $<0.4 \text{ €/m}^3$, which is very competitive compared with more mature processes.

2.4.3 Treatment of Retentates

Because there is an urgent need for environmentally friendly management options for RO brines, diverse technologies for the treatment of RO brines have been investigated. Although more conventional treatments have been studied for this purpose (coagulation/flocculation, activated carbon adsorption, ozonation, electrochemical oxidation, river bank filtration among others), AOPs appear to be appropriate for the treatment of these waste streams that are highly concentrated in recalcitrant microcontaminants [34]. Authors evaluated the efficiency of UV/ H_2O_2 for mitigation of 11 PhACs present in RO brines of a wastewater reclamation facility. Although high oxidant doses were necessary to ensure the complete removal of all the monitored microcontaminants, authors conclude that UV/ H_2O_2 process appeared to be a promising and efficient tool for treating these concentrates. There is still a lack of studies and information about the efficiency of

AOPs in removing microcontaminants from these complex matrices and improving the quality of the effluents.

2.5 Overall Comparison

In Table 3, a comprehensive comparison among the different technologies is presented. Although each individual microcontaminant can behave differently with each technology, if an overall comparison is made, it is found that the highest rejection of microcontaminant is presented by RO or NF, although they also present some drawback as the generation of a waste stream. Activated carbon presents an efficacy for microcontaminant removal very similar to ozonation. AOPs show a good potential for microcontaminant removal but the technology is less tested at full-scale level.

3 Overall Conclusions

In this chapter, four technologies for eliminating the microcontaminants present in the effluents of WWTPs have been reviewed: adsorption, membranes, AOPs, and ozonation. The choice has been done since they are well known, already used in existing WWTP. Therefore, its specific utilization for the removal of microcontaminants may be done easily. All treatments prove to be feasible at large scale and for long-term operation in real WWTP conditions. However, given the wide range of properties exhibited by microcontaminants, there is no single treatment process that provides an absolute barrier to all chemicals. To minimize their presence in treated water, a sequence of diverse treatment processes seems suitable. However, other considerations must be taken into account to ensure the viability of the solution since the most restrictive technologies are economically expensive and energetically demanding. Therefore, it is necessary to carry out more research to improve and make them more efficient.

Finally, the main conclusions for each technology are listed below.

3.1 Membrane Filtration

The use of MF or UF membranes alone is not sufficient for microcontaminant removal. Therefore, the combination with other membrane processes (i.e., NF or RO) is essential for enhanced elimination of microcontaminants. All analyzed data indicate that NF and RO could be considered as a powerful tool to mitigate the presence of most of microcontaminants present in municipal wastewaters.

Table 3 Comparison of different technologies focused on microcontaminant removals

Technology	Pros	Cons	Compounds easily removed	Compounds hardly removed
Ozonation	Does not generate a waste stream	Potential generation of hazardous by-products	Microcontaminants with electron-rich moieties: aromatic rings, double bonds, or amine moieties	Microcontaminants with low affinity to O ₃ direct reaction and also to HO·: atrazine, iothalamic acids, carbamazepine, diatrizoate, iopromide, mecoprop, benzotriazole,
	Excellent disinfectant	Ozone is toxic and explosive. Safety measures required	Microcontaminants with second-order rate constants > 10 ⁴ M ⁻¹ s ⁻¹ (direct reaction with O ₃)	5-methylbenzotriazole, sucralose, DEET, diazinon, galaxolide, benzothiazole, amide functional groups
	Oxidate microcontaminants; no further treatments needed	Installation requires qualified personnel	Hydrophobic or positively charged microcontaminants	
	Good performance in bioassay test	Poor removal of DOC		
	High removal of some specific compounds	Efficiency affected negatively by the presence of EfOM; prior removal required		
Adsorption (activated carbon)	Adsorbs a wide variety of contaminants	AC does not destroy contaminants	Hydrophilic (k _{ow} > 4) or negatively charged microcontaminants	Hydrophobic (k _{ow} < 2.5) or positively charged microcontaminants
	Easy operation	Microcontaminants can be released to effluent if AC is not regenerated		Gabapentin, diatrizoate, iothalamic acid, Irgarol, propylparanol, DEET
	Good performance in bioassay test	Efficiency affected negatively by the presence of EfOM; prior removal required		High molecular or colloidal compounds
	BAC offers adsorption and biodegradation	Periodic regeneration required		
	PAC can be used seasonally, when required			
	Good removal of DOC			

Membranes (RO/NF)	Reduced labor requirements, can be automated easily	RO and NF do not destroy contaminant	Hydrophobic, ionic compounds	Hydrophilic, nonionic, and low molecular weight compounds Variable and poor rejection with “loose” NF for several compounds Worse rejection in RO studies: hormones, salicylic acid, naphthalene, ibuprofen, DEHP, BDPEs, caffeine, bisphenol A, nonylphenol, meprobamate, gemfibrozil, naproxen, sulfamethoxazole, iopromide, TCEP, DEET, galaxolide
	Most inorganic and organic constituents and microorganisms are removed (especially with RO)	Disposal of concentrate		
		Desorption of sorbed chemicals from membrane		
		High investment required		
		High energy consumption		
AOP	Does not generate a waste stream Non-selectivity of HO Rapid reaction rates Easily automated and controlled	Membrane fouling	Most of target compounds due to the non-selectivity of HO.	
		Periodic membrane replacement required		
		Performance declines over time		
		Potential generation of hazardous by-products		
		Chemical and/or energy consumption		
		Installation requires qualified personnel		
		Subsequent quenching required if a strong oxidant is used		
		Complex chemistry must be tailored to specific application		

There is some controversy about how membrane selectivity affects the efficiency of membranes in microcontaminant removal. In general, it seems that there is a tendency for an expected decrease in microcontaminant rejection with decreasing membrane selectivity. However, some authors consider that conductivity rejection does not appear to be a reliable indicator to assess the removal efficiency of microcontaminants by NF/RO membranes.

In general, microcontaminant removal efficiency would follow the next order: RO > “tight” NF > “loose” NF. However, different comparative works [22, 39, 43, 71] concluded that, although the retention of microcontaminants by NF is lower than that obtained by RO, the latter has demonstrated only marginally increased rejection in comparison with NF.

There are different points of view about the appropriateness of NF or RO to mitigate the microcontaminant problem. According to some studies, it would be questionable, unless desalination is a requirement, that the use of RO is preferable than the use of NF. Its higher operational costs incurred from higher pressure operation would not justify the additional purification achieved in comparison with NF. Other studies remark that not even the RO can serve as an absolute barrier to microcontaminants. Therefore, additional treatment processes should be considered to be incorporated aside the RO to ensure complete removal of such substances. In addition, an important point to be taken into account is that NF and RO require significant amounts of energy, which may lead indirectly to greater environmental risks than the presence of minute concentrations of organic contaminants. Thus, careful consideration must be given to the actual costs and benefits of these processes simply for the removal of microcontaminants [36].

It is also important to consider brine disposal associated with RO and NF membranes. The rejected compounds are merely concentrated in brine streams which must be disposed of properly since brine would be expected to have much greater toxicity than the influent water.

3.2 Adsorption

Adsorption with activated carbon has proved to be an efficient tool for removal of microcontaminants. Since it adsorbs a wide variety of compounds, EfOM competes strongly for the active site, decreasing the adsorption rate of microcontaminants. Thus, it is convenient to install the activated carbon unit as a tertiary treatment after an operation which reduces organic matter. Activated carbon adsorbs easily hydrophobic and positively charged compounds although other interactions as hydrogen bond formation and pi–pi interaction between microcontaminants and the activated carbon surface seem to be important. Since there is no transformation of the compounds, no hazardous by-products are expected. Thus, bioassays reviewed show a less toxic effluent after the adsorption treatment. Finally, use of PAC as tertiary treatment and the reuse of it in the biological reactor (a kind of counter-current system) show efficiencies 10–50% higher. PAC can also be added seasonally

to face peaks of contamination. GAC is not so flexible but requires a smaller residence time.

3.3 Ozonation

Ozone is a useful technology for microcontaminant removal. In most of the studies reviewed, it achieves great results with removal over 80% for several of compounds analyzed. However, the rate of removal proves to be very dependent on the type of contaminant. Ozone is efficient in the oxidation of compounds with electron-rich moieties, which react directly with ozone. A second group of compounds less efficiently removed includes those compounds which react with radical HO \cdot . Finally, there is a group of recalcitrant compounds which present a low reactivity with molecular ozone or hydroxyl radical.

The main concern when using ozone for wastewater treatment is the generation of hazardous by-products as bromate, nitrosamines, or other unknown species which can increase toxicity of the effluent. At normal operation conditions, those compounds seem to be generated in very small amounts, below the recommended thresholds proposed by recognized official organisms. To minimize this risk, it is very important to assure a good contact between gas and liquid. It is also advisable to install a barrier unit after the ozonation process. For example, a sand filter has proved to be very effective on those scenarios where ozonation produced an increase on toxicity or to eliminate nitrosamines.

3.4 Advanced Oxidation Processes

The efficiency of AOPs for organic contaminant removal has been well proven at laboratory scale. The non-selectivity of these AOPs is a great advantage and guaranty. Nobody doubts about the potential of AOPs to degrade microcontaminants. However, more studies at pilot and full scale are needed in order to determine the optimal operational conditions and elaborate consistent and reliable cost evaluations.

References

1. du Pisani PL (2006) Direct reclamation of potable water at Windhoek's Goreangab reclamation plant. *Desalination* 188(1–3):79–88. doi:[10.1016/j.desal.2005.04.104](https://doi.org/10.1016/j.desal.2005.04.104)
2. Asano T, Cotruvo JA (2004) Groundwater recharge with reclaimed municipal wastewater: health and regulatory considerations. *Water Res* 38(8):1941–1951. doi:[10.1016/j.watres.2004.01.023](https://doi.org/10.1016/j.watres.2004.01.023)
3. Ogoshi M, Suzuki Y, Asano T (2001) Water reuse in Japan. *Water Sci Technol* 43(10):17–23

4. Ogoshi M, Suzuki Y, Asano T (2000) Non potable urban water reuse: a case of Japanese water recycling. *Water* 21:27–30
5. Global Water Intelligence (GWI) (2010) New revenue stream springs up. Water reuse market set for explosive growth. Municipal water reuse markets 2010, Media Analytics Limited, Oxford
6. Hollender J, Zimmermann SG, Koepke S, Krauss M, McArdell CS, Ort C, Singer H, von Gunten U, Siegrist H (2009) Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration. *Environ Sci Technol* 43(20):7862–7869
7. Martín J, Camacho-Muñoz D, Santos JL, Aparicio I, Alonso E (2012) Occurrence of pharmaceutical compounds in wastewater and sludge from wastewater treatment plants: removal and ecotoxicological impact of wastewater discharges and sludge disposal. *J Hazard Mater* 239–240:40–47. doi:[10.1016/j.jhazmat.2012.04.068](https://doi.org/10.1016/j.jhazmat.2012.04.068)
8. Carballa M, Omil F, Lema JM, Llombart M, García-Jares C, Rodríguez I, Gómez M, Ternes T (2004) Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. *Water Res* 38(12):2918–2926. doi:[10.1016/j.watres.2004.03.029](https://doi.org/10.1016/j.watres.2004.03.029)
9. Carballa M, Omil F, Lema JM (2005) Removal of cosmetic ingredients and pharmaceuticals in sewage primary treatment. *Water Res* 39(19):4790–4796. doi:[10.1016/j.watres.2005.09.018](https://doi.org/10.1016/j.watres.2005.09.018)
10. Suárez S, Carballa M, Omil F, Lema J (2008) How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? *Rev Environ Sci Biotechnol* 7(2): 125–138. doi:[10.1007/s11157-008-9130-2](https://doi.org/10.1007/s11157-008-9130-2)
11. Calderón-Preciado D, Matamoros V, Bayona JM (2011) Occurrence and potential crop uptake of emerging contaminants and related compounds in an agricultural irrigation network. *Sci Total Environ* 412–413:14–19. doi:[10.1016/j.scitotenv.2011.09.057](https://doi.org/10.1016/j.scitotenv.2011.09.057)
12. Calderón-Preciado D, Jiménez-Cartagena C, Matamoros V, Bayona JM (2011) Screening of 47 organic microcontaminants in agricultural irrigation waters and their soil loading. *Water Res* 45(1):221–231. doi:[10.1016/j.watres.2010.07.050](https://doi.org/10.1016/j.watres.2010.07.050)
13. Jones-Lepp TL, Sanchez CA, Moy T, Kazemi R (2010) Method development and application to determine potential plant uptake of antibiotics and other drugs in irrigated crop production systems. *J Agric Food Chem* 58(22):11568–11573. doi:[10.1021/jf1028152](https://doi.org/10.1021/jf1028152)
14. Bouwer H (2000) Groundwater problems caused by irrigation with sewage effluent. *J Environ Health* 63(3):17
15. Oulton RL, Kohn T, Cwiertny DM (2010) Pharmaceuticals and personal care products in effluent matrices: a survey of transformation and removal during wastewater treatment and implications for wastewater management. *J Environ Monit* 12(11):1956–1978. doi:[10.1039/c0em00068j](https://doi.org/10.1039/c0em00068j)
16. Environmental Protection Agency (2012) Guidelines for water reuse
17. Ying G-G, Kookana RS, Waite T, Australian Water Conservation, Australian Water Association (2004) Endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in reclaimed water in Australia. Australian Water Conservation and Reuse Research Program
18. Drewes JE, Reinhard M, Fox P (2003) Comparing microfiltration-reverse osmosis and soil-aquifer treatment for indirect potable reuse of water. *Water Res* 37(15):3612–3621. doi:[10.1016/S0043-1354\(03\)00230-6](https://doi.org/10.1016/S0043-1354(03)00230-6)
19. Ngo H, Guo W, Vigneswaran S (2012) Membrane processes for water reclamation and reuse. *Membr Technol Environ Appl* pp 239–275. doi:[10.1061/9780784412275](https://doi.org/10.1061/9780784412275)
20. Bixio D, Theuye C, De Koning J, Joksimovic D, Savic D, Wintgens T, Melin T (2006) Wastewater reuse in Europe. *Desalination* 187(1):89–101
21. Drewes JE, Bellona C, Oedekoven M, Xu P, Kim T-U, Amy G (2005) Rejection of wastewater-derived micropollutants in high-pressure membrane applications leading to indirect potable reuse. *Environ Prog* 24(4):400–409. doi:[10.1002/ep.10110](https://doi.org/10.1002/ep.10110)

22. Khan SJ, Wintgens T, Sherman P, Zaricky J, Schäfer AI (2004) Removal of hormones and pharmaceuticals in the advanced water recycling demonstration plant in Queensland, Australia. *Water Sci Technol* 50(5):15–22
23. Nghiem LD, Coleman PJ (2008) NF/RO filtration of the hydrophobic ionogenic compound triclosan: transport mechanisms and the influence of membrane fouling. *Sep Purif Technol* 62(3):709–716
24. Comerton AM, Andrews RC, Bagley DM, Hao C (2008) The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound and water matrix properties. *J Membr Sci* 313(1):323–335
25. Agenson KO, Urase T (2007) Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications. *Sep Purif Technol* 55(2):147–156
26. Xu P, Drewes JE, Kim T-U, Bellona C, Amy G (2006) Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications. *J Membr Sci* 279(1):165–175
27. Nghiem LD, Hawkes S (2007) Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): mechanisms and role of membrane pore size. *Sep Purif Technol* 57(1):176–184
28. Plakas K, Karabelas A, Wintgens T, Melin T (2006) A study of selected herbicides retention by nanofiltration membranes—the role of organic fouling. *J Membr Sci* 284(1):291–300
29. Sadmani A, Andrews RC, Bagley DM (2014) Nanofiltration of pharmaceutically active and endocrine disrupting compounds as a function of compound interactions with DOM fractions and cations in natural water. *Sep Purif Technol* 122:462–471
30. Yangali-Quintanilla V, Maeng SK, Fujioka T, Kennedy M, Li Z, Amy G (2011) Nanofiltration vs. reverse osmosis for the removal of emerging organic contaminants in water reuse. *Desalin Water Treat* 34(1–3):50–56
31. Sahar E, David I, Gelman Y, Chikurel H, Aharoni A, Messalem R, Brenner A (2011) The use of RO to remove emerging micropollutants following CAS/UF or MBR treatment of municipal wastewater. *Desalination* 273(1):142–147
32. Yoon Y, Westerhoff P, Snyder SA, Wert EC (2006) Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. *J Membr Sci* 270(1):88–100
33. Cho J, Amy G, Pellegrino J (2000) Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane. *J Membr Sci* 164(1):89–110
34. Justo A, González O, Aceña J, Pérez S, Barceló D, Sans C, Esplugas S (2013) Pharmaceuticals and organic pollution mitigation in reclamation osmosis brines by UV/H₂O₂ and ozone. *J Hazard Mater* 263:268–274. doi:[10.1016/j.jhazmat.2013.05.030](https://doi.org/10.1016/j.jhazmat.2013.05.030)
35. Al-Rifai JH, Gabelish CL, Schäfer AI (2007) Occurrence of pharmaceutically active and non-steroidal estrogenic compounds in three different wastewater recycling schemes in Australia. *Chemosphere* 69(5):803–815
36. Snyder SA, Adham S, Redding AM, Cannon FS, DeCarolis J, Oppenheimer J, Wert EC, Yoon Y (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* 202(1):156–181
37. Drewes J, Heberer T, Reddersen K (2002) Fate of pharmaceuticals during indirect potable reuse. *Water Sci Technol* 46(3):73–80
38. Trinh T, Van Den Akker B, Stuetz R, Coleman H, Le-Clech P, Khan S (2012) Removal of trace organic chemical contaminants by a membrane bioreactor. *Water Sci Technol* 66(9):1856–1863
39. Kim SD, Cho J, Kim IS, Vanderford BJ, Snyder SA (2007) Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Res* 41(5):1013–1021

40. Kovalova L, Siegrist H, Singer H, Wittmer A, McArdell CS (2012) Hospital wastewater treatment by membrane bioreactor: performance and efficiency for organic micropollutant elimination. *Environ Sci Technol* 46(3):1536–1545
41. Alturki AA, Tadkaew N, McDonald JA, Khan SJ, Price WE, Nghiem LD (2010) Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse applications. *J Membr Sci* 365:206–215. doi:[10.1016/j.memsci.2010.09.008](https://doi.org/10.1016/j.memsci.2010.09.008)
42. Košutić K, Dolar D, Ašperger D, Kunst B (2007) Removal of antibiotics from a model wastewater by RO/NF membranes. *Sep Purif Technol* 53(3):244–249
43. Garcia N, Moreno J, Cartmell E, Rodriguez-Roda I, Judd S (2013) The application of microfiltration-reverse osmosis/nanofiltration to trace organics removal for municipal wastewater reuse. *Environ Technol* 34(24):3183–3189
44. Sui Q, Huang J, Deng S, Yu G, Fan Q (2010) Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. *Water Res* 44(2): 417–426
45. Al-Rifai JH, Khabbaz H, Schäfer AI (2011) Removal of pharmaceuticals and endocrine disrupting compounds in a water recycling process using reverse osmosis systems. *Sep Purif Technol* 77(1):60–67. doi:[10.1016/j.seppur.2010.11.020](https://doi.org/10.1016/j.seppur.2010.11.020)
46. Lee J, Lee BC, Ra JS, Cho J, Kim IS, Chang NI, Kim HK, Kim SD (2008) Comparison of the removal efficiency of endocrine disrupting compounds in pilot scale sewage treatment processes. *Chemosphere* 71(8):1582–1592. doi:[10.1016/j.chemosphere.2007.11.021](https://doi.org/10.1016/j.chemosphere.2007.11.021)
47. Margot J, Kienle C, Magnet A, Weil M, Rossi L, de Alencastro LF, Abegglen C, Thonney D, Chèvre N, Schärer M (2013) Treatment of micropollutants in municipal wastewater: ozone or powdered activated carbon? *Sci Total Environ* 461:480–498
48. Reungoat J, Escher B, Macova M, Argaud F, Gernjak W, Keller J (2012) Ozonation and biological activated carbon filtration of wastewater treatment plant effluents. *Water Res* 46(3): 863–872
49. Nakada N, Shinohara H, Murata A, Kiri K, Managaki S, Sato N, Takada H (2007) Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. *Water Res* 41(19):4373–4382
50. Rosal R, Rodríguez A, Perdigón-Melón JA, Petre A, García-Calvo E, Gómez MJ, Agüera A, Fernández-Alba AR (2010) Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. *Water Res* 44(2):578–588
51. Reungoat J, Macova M, Escher B, Carswell S, Mueller J, Keller J (2010) Removal of micropollutants and reduction of biological activity in a full scale reclamation plant using ozonation and activated carbon filtration. *Water Res* 44(2):625–637
52. Reungoat J, Escher B, Macova M, Keller J (2011) Biofiltration of wastewater treatment plant effluent: effective removal of pharmaceuticals and personal care products and reduction of toxicity. *Water Res* 45(9):2751–2762
53. Kurokawa Y, Maekawa A, Takahashi M, Hayashi Y (1990) Toxicity and carcinogenicity of potassium bromate—a new renal carcinogen. *Environ Health Perspect* 87:309
54. Krauss M, Longrée P, Dorusch F, Ort C, Hollender J (2009) Occurrence and removal of N-nitrosamines in wastewater treatment plants. *Water Res* 43(17):4381–4391
55. von Gunten U, Salhi E, Schmidt CK, Arnold WA (2010) Kinetics and mechanisms of N-nitrosodimethylamine formation upon ozonation of N, N-dimethylsulfamide-containing waters: bromide catalysis. *Environ Sci Technol* 44(15):5762–5768
56. Petala M, Samaras P, Zouboulis A, Kungolos A, Sakellariopoulos G (2008) Influence of ozonation on the in vitro mutagenic and toxic potential of secondary effluents. *Water Res* 42(20):4929–4940
57. Magdeburg A, Stalter D, Oehlmann J (2012) Whole effluent toxicity assessment at a wastewater treatment plant upgraded with a full-scale post-ozonation using aquatic key species. *Chemosphere* 88(8):1008–1014

58. Stalter D, Magdeburg A, Weil M, Knacker T, Oehlmann J (2010) Toxication or detoxication? In vivo toxicity assessment of ozonation as advanced wastewater treatment with the rainbow trout. *Water Res* 44(2):439–448
59. Boehler M, Zwickenspflug B, Hollender J, Ternes T, Joss A, Siegrist H (2012) Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon. *Water Sci Technol* 66(10):2115–2121
60. Kalkan C, Yapsakli K, Mertoglu B, Tufan D, Saatci A (2011) Evaluation of biological activated carbon (BAC) process in wastewater treatment secondary effluent for reclamation purposes. *Desalination* 265(1):266–273
61. Rogers HR (1996) Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *Sci Total Environ* 185(1):3–26
62. Grover D, Zhou J, Frickers P, Readman J (2011) Improved removal of estrogenic and pharmaceutical compounds in sewage effluent by full scale granular activated carbon: impact on receiving river water. *J Hazard Mater* 185(2):1005–1011
63. Ikehata K, Jodeiri Naghashkar N, Gamal El-Din M (2006) Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: a review. *Ozone Sci Eng* 28(6): 353–414
64. De la Cruz N, Esquius L, Grandjean D, Magnet A, Tungler A, de Alencastro LF, Pulgarín C (2013) Degradation of emergent contaminants by UV, UV/H₂O₂ and neutral photo-Fenton at pilot scale in a domestic wastewater treatment plant. *Water Res* 47(15):5836–5845. doi:[10.1016/j.watres.2013.07.005](https://doi.org/10.1016/j.watres.2013.07.005)
65. Kim I, Yamashita N, Tanaka H (2009) Performance of UV and UV/H₂O₂ processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. *J Hazard Mater* 166(2–3):1134–1140. doi:[10.1016/j.jhazmat.2008.12.020](https://doi.org/10.1016/j.jhazmat.2008.12.020)
66. Snyder SA, Wert EC, Rexing DJ, Zegers RE, Drury DD (2006) Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone Sci Eng* 28(6): 445–460. doi:[10.1080/01919510601039726](https://doi.org/10.1080/01919510601039726)
67. Gerrity D, Snyder S (2011) Review of ozone for water reuse applications: toxicity, regulations, and trace organic contaminant oxidation. *Ozone Sci Eng* 33(4):253–266
68. Gerrity D, Gamage S, Holady JC, Mawhinney DB, Quiñones O, Trenholm RA, Snyder SA (2011) Pilot-scale evaluation of ozone and biological activated carbon for trace organic contaminant mitigation and disinfection. *Water Res* 45(5):2155–2165. doi:[10.1016/j.watres.2010.12.031](https://doi.org/10.1016/j.watres.2010.12.031)
69. Chi GT, Churchley J, Huddersman KD (2013) Pilot-Scale removal of trace steroid hormones and pharmaceuticals and personal care products from municipal wastewater using a heterogeneous Fenton's catalytic process. *Int J Chem Eng*. doi:[10.1155/2013/760915](https://doi.org/10.1155/2013/760915)
70. Prieto-Rodríguez L, Oller I, Klammerth N, Agüera A, Rodríguez E, Malato S (2013) Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents. *Water Res* 47(4):1521–1528
71. Bellona C, Heil D, Yu C, Fu P, Drewes J (2012) The pros and cons of using nanofiltration in lieu of reverse osmosis for indirect potable reuse applications. *Sep Purif Technol* 85:69–76. doi:[10.1016/j.seppur.2011.09.046](https://doi.org/10.1016/j.seppur.2011.09.046)

Advanced Treatment Technologies for Urban
Wastewater Reuse

Fatta-Kassinos, D.; Dionysiou, D.D.; Kümmerer, K. (Eds.)

2016, XIV, 305 p. 111 illus., 27 illus. in color., Hardcover

ISBN: 978-3-319-23885-2