Scientific Research Publishing

Journal of Water Resource and Protection, 2017, 9, 411-431
http://www.scirp.org/journal/jwarp
ISSN Online: 1945-3108
ISSN Print: 1945-3094

Micropollutant Removal from Water by Membrane and Advanced Oxidation Processes—A Review

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How to cite this paper: Silva, L.L.S., Moreira, C.G., Curzio, B.A. and da Fonseca, F.V. (2017) Micropollutant Removal from Water by Membrane and Advanced Oxidation Processes—A Review. *Journal of Water Resource and Protection*, **9**, 411-431.
https://doi.org/10.4236/jwarp.2017.95027

Received: August 15, 2016
Accepted: April 14, 2017
Published: April 17, 2017

Abstract

Micropollutants are defined as contaminants found in trace concentrations in water bodies that are persistent and bioactive, meaning they are not completely biodegradable and cannot be removed by conventional water treatment methods. Because of these aspects, their detection and removal pose a challenge to the scientific community. Among them are endocrine disruptors, drugs, agricultural chemicals, personal grooming products, industrial additives and others. These micropollutants are the cause for global concern, because their presence in water supply systems is suspected of causing health problems in humans and animals. To develop efficient techniques to remove them, it is fundamental to understand their physico-chemical properties and the available treatment types and conditions. Membrane separation processes (MSPs) and advanced oxidation processes (AOPs) are the focus of this literature review, as potential treatment methods to remove micropollutants. The former process stands out for high rejection rates (above 90%) of various micropollutants, but it generates a concentrated secondary waste stream. In turn, the latter process can remove micropollutants without generating secondary wastes, and can also be applied and combined with other treatment methods.

Keywords

Micropollutants, MSP, AOP

1. Introduction

In recent decades, the presence of many substances in water bodies that can harm human and animal health has caused the growing concern. Among these substances are emerging micropollutants, present in both industrial and household wastewater in vestigial quantities, with concentrations ranging in scale from

$\mu g \cdot L^{-1}$ and $ng \cdot L^{-1}$. Some of these compounds known as Endocrine Disrupters (ED) are considered exogenous agents that interfere with the synthesis, secretion, transport, binding and action or elimination of natural hormones in the body which are responsible for maintenance, reproduction, development, and/or behavior organisms [1]. Among the sources of these substances are pharmaceutical products, personal grooming products, steroid hormones, industrial chemicals, pesticides and many other substances.

Many researchers have investigated the effect of these substances in water bodies, observing harmful effects on humans and animals, such as endocrine system anomalies, cancer, reduction of sperm quantity and endometriosis, among others [2] [3]. Furthermore, micropollutants can act synergistically with other substances, aggravating the negative effects [4].

Strategic programs for the development of detection protocols and regulatory laws that include the ED as the imminent risk to the health of animals and humans have been proposed, including "Two-tier Endocrine Disruptor Screening" (EDSP-USEPA), "Strategic Programs on Endocrine Disruptors" (SPEED—Japan Environment Agency), and "21 Joint Working Group on Endocrine Disrupters Testing and Assessment" (EDTA-OECD) [5].

The presence of micropollutants in aquatic environments has also been associated with the development of resistance to antibiotics by microorganisms. However, because of their low concentrations and wide diversity of types, the methods to detect and analyze micropollutants are not always precise, posing a challenge to wastewater treatment facilities [6] [7]. **Figure 1** shows the route of environmental contamination by micropollutants. Sorption in sediments of rivers,

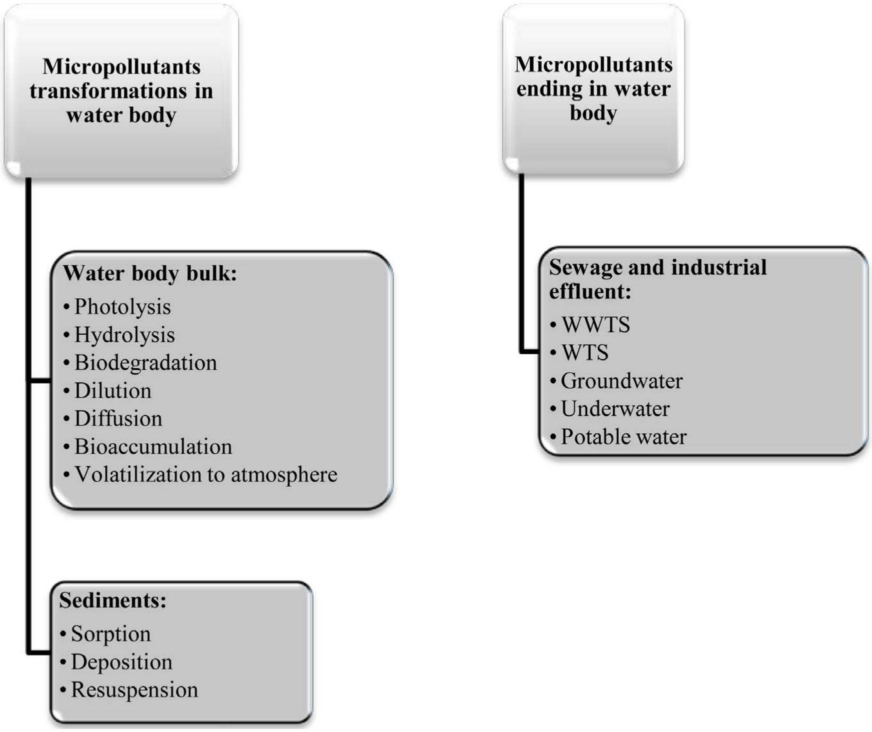

Figure 1. Environmental contamination route by micropollutants.

bioaccumulation and biomagnification can be considered; there are many works that relate these phenomenon [8] [9]. Despite the difficulty of degradation, several reactions can occur in the natural environment, such as photolysis (breakdown of substances by presence of sunlight), biodegradation (the presence of organic wastes favors proliferation of microorganisms) and hydrolysis (highly polar molecules). These reactions can generate active substances or biologically inactive, e.g. the natural estrogens are excreted by human body in idle and when incorporated into the environment so go to form active, may cause deleterious effects to biota around [2] [8]. Another phenomenon that must also be considered is the volatilization compound to the atmosphere.

The technologies used by water treatment stations (WTS) and wastewater treatment stations (WWTS) are generally not effective in removing these micropollutants, because many are hard to separate and/or resistant to degradation. Compounding this problem, no monitoring is conducted for the majority of these contaminants, which are typically only present in trace levels [10].

Therefore, it is necessary to develop new technologies for removing micropollutants, to prevent their bioaccumulation and the consequent aggravation of the deleterious effects on human and animal health. Recently, membrane separation processes (MSP) and advanced oxidation processes (AOP) are becoming consolidated as effective technologies to remove micropollutants.

The application of MSP, with nanofiltration (NF) and reverse osmosis (RO) membranes is growing among tertiary treatment methods, especially for use by wastewater/sewage treatment plants. The high purity of the treated water is due to the ability of these membranes to separate salts (RO) and organic compounds with low molecular weight (NF).

The AOP, especially those involving ultraviolet radiation, hydrogen peroxide and/or ozone, have been widely studied and found to be highly efficient in removing micropollutants. The main advantage of this process is the possibility of complete mineralization of the organic matter without generating secondary wastes and sludge.

2. Membrane Separation Process

Membranes are known as selective barriers that separate two phases and restrict the transport of various chemicals [11]. The most important property of membranes is their ability to control the rate of permeation of different species [12].

The separation mechanism depends on the type of membrane, the presence of pores and morphology or structure. There are three forms of separation: size exclusion (MF and UF), rejection by difference in solubility and diffusivity (RO) and separation by charge difference between species (Electrodialysis membranes). Especially for NF membranes, occur three mechanisms, because these membranes have dense and porous parts, as well as charges on their surface [13].

According to Baker [12], the mechanism of transport through RO membranes is called the solution-diffusion model. In this model, solutes permeate the membrane by dissolving in the membrane material and diffusing down a concentration gradient. Separation occurs because of the difference in solubility and mobility of different solutes in the membrane.

The removal of micropollutants by MSP has been amply investigated, especially RO and NF membranes, which can retain dissolved salts and solutes, being adequate for the majority of micropollutants that have molecular weight in the range of 200 - 400 Da [14] [15]. When comparing the removal efficiency of RO and NF membranes, the former can retain a larger number of micropollutants, because their pores are smaller [14]. However, NF membranes have other specific features that favor their use, such as retention efficiency very near that of RO membranes, the possibility of working with greater flows and/or lower pressures, lower fouling rates and lower cost [16] [17] [18].

Table 1 lists the publications that have assessed the removal of micropollutants by MSP in different aquatic matrixes.

Factors such as membrane properties, physico-chemical characteristics of the substances targeted for removal, transport mechanism and matrix effect should be taken into consideration when evaluating MSP [14] [19].

The membrane's selectivity can be related to several mechanisms: size exclusion, electrostatic repulsion, adsorption, diffusion, solute-solute interaction and fouling. Simon *et al.* [20] assessed the adsorption of ibuprofen by NF and RO membranes and found that this phenomenon is directly linked to the electrostatic repulsion between the pollutant and membrane and the solution's pH. In other words, reducing the pH to values below the pKa (acid dissociation constant) of ibuprofen weakens the electrostatic repulsion, because the membrane becomes positively charged, facilitating the adsorption of ibuprofen inside the membrane, which has a negative surface charge. Shanmugana than *et al.* [21] found higher removal rates (97%) of ionic compounds than nonionic ones (82%) by NF and RO membranes. Therefore, the diffusion phenomenon degrades the membrane's efficiency in removing substances by adsorption.

According to Sahar *et al.* [22], the drug diclofenac was removed by RO membranes (negative surface charge) at rates above 95%, due to the electrostatic repulsion between the membrane and this micropollutant. In another study, the same effect was observed when analyzing diclofenac and other drugs as well as personal grooming products whose charges are negative when in solution, such as ibuprofen, glimepiride, naxoprene and sulfametoxazole [19]. The removal efficiency diminished considerably for micropollutants having neutral or positive charges. For example, the removal was near 100% fornaxoprene, versus 20% for acetaminophen (neutral) and 60% for athenolol (positive) [23].

In the case of adsorption, Gur-Reznik *et al.* [24] found that for some substances with low hydrophobicity and high pKa, such as carbamazepine and diatrizoate, the adsorption by NF and RO membranes is negligible, so the effective mechanism in this case is size exclusion. Linares *et al.* [25] confirmed this possibility, indicating that hydrophilic compounds with neutral charges are only weakly adsorbed when fouling is not present. Cartagena *et al.* [17] reported the same phenomenon, confirming that in this case the higher the value of LogKow (octanol-water partition coefficient), the better the removal rates are.

Table 1. Micropollutant removal from different matrixes by distinct membrane separation processes.

Reference	Matrix	Membrane type	Operation conditions	Micropollutants	Removal
[15]	Secondary treatment effluent	RO (polyamide)	flow 1.3 $m^3 \cdot h^{-1}$, 75% - 80% recovery, 0.4 - 0.6 bar	chloramphenicol, trimethoprim, bezafibrate, clofibric acid, gemfibrozil, diclofenac, indomethacine, ketoprofen, etc.	50 - 90
		MF/UF ZeeWeed1000 (PVDF)	flux 0.023 $m^3 \cdot m^{-2} \cdot h^{-1}$, 80.000 $m^3 \cdot d^{-1}$		
[17]	MBR (FS) effluent// MBR (HF) effluent	RO, BW30-4040 (polyamide)	15% recovery, 7.5 bar, permeate flow 7.2 $m^3 \cdot h^{-1}$	acetaminophen, ibuprofen, caffeine, nicotine, carbamazepine, diclofenac, triclosan, 4-octylphenol, 4-t-octylphenol, bisphenol A	50 - 100
		NF, NF90-4040 (polyamide)	15% recovery, 5.5 bar, permeate flow 7.2 $m^3 \cdot h^{-1}$		
		MBR	hollow fiber		
[18]	Second treatment effluent, ultrapure water	NF, NFX (polyamine)	cross-flow, flat sheet, 75% recovery, 2 - 10 bar	norfloxacin, ofloxacina, azithromycin, roxithromycin	>98
[19]	WWTP effluent	NF, NE40, NE70 e NE90 (polyamide)	3·5 bar, retention flow 0.030 $m^3 \cdot h^{-1}$, 6 - 10.9 $\mu m \cdot s^{-1}$	acetaminophen, atenolol, carbamazepine, clopidogrel, diclofenac, dilantin, ibuprofen, iopromide, glimepiride, naxopren, sulfamethoxazole	15 - 98
		MBR polyvinylidene	hollow fiber		
[20]	Synthetic water/NaOCl	NF, TFC-SR2, NF-270, NF90	-	sulfamethoxazole, carbamazepine, ibuprofen	5 - 100
		RO, BW30	permeate flux 0.054 $m^3 \cdot m^{-2} \cdot h^{-1}$; pH 4 - 10		
[21]	Second treatment effluent	NF, NTR 729HF (polyvinylalcohol/polyamide)	flat sheet, permeate flux 0.0485 $m^3 \cdot m^{-2} \cdot h^{-1}$, 4 bar	atenolol, caffeine, carbamazepine, diclofenac, gemfibrozil, naproxen, sulfamethoxazole, triclosan, trimethoprim	99
[22]	Primary treatment effluent	RO, TW30-2540 e BW30-400	80% - 90% recovery, flow 22 - 45 $m^3 \cdot h^{-1}$, 8.7 - 12 bar	Salycilic acid, ibupropheno, bisphenol A, diclofenac, cholesterol, sulfamethoxazole, sulfamethazine, trimethoprim, erythromycin, clarithromycina, roxithromycin	93 - 99
		MBR, UF, ZeeWeed-1000 e ZeeWeed-500	flux 0.01 - 0.047 $m^3 \cdot m^{-2} \cdot h^{-1}$, 0.06 - 0.24 bar		
[23]	Primary treatment effluent	RO, TR70-4021 (polyamide)	10 bar, flow 0.18 $m^3 \cdot h^{-1}$	codeine, carbamazepine, diazepam, ranitidine, azithromycin, clarithromycin, erithromycin, sulfamethoxazole, etc.	99
		MBR	retention time 12.5 h		
[24]	MBR effluent	NF, NF90 e NF270	5 bar	carbamazepine e diatrizoate	41 - 100
		RO, XLE, BW30 e SW3O	7 - 55 bar, concentrateflow 0.18 - 0.24 $m^3 \cdot h^{-1}$, permeateflow 0.00004 - 0.0001 $m^3 \cdot h^{-1}$		

Continued

[25]	Secondary treatment effluent	RO (polyamide)	flat sheet, 15 bar, permeate flow 0.000096 $m^3 \cdot h^{-1}$, concentrate flow 0.0048 $m^3 \cdot h^{-1}$, flux 0.007 $m^3 \cdot m^{-2} \cdot h^{-1}$, 2% recovery	1,4-dioxin, acetaminophen, metronidazole, phenazone, caffeine, bisphenol A, carbamazepine, 17α-ethinylestradiol, ibuprofen, naxopren, fenoprofen, gemfibrozil, ketoprofen	40 - 100
		FO (poly methyl methacrylate)	flat sheet, recirculation flow 0.003 $m^3 \cdot h^{-1}$		
[26]	WWTP effluent	RO, RE8040-FL (polyamide)	72.6% recovery, permeate flow 3.42 $m^3 \cdot h^{-1}$	atenolol, carbamazepine, caffeine, diclofenac, dilatin, florfenicol, sulfamethoxazole	19 - 99
		UF, P75R (PVDF)	permeate flow 9.46 $m^3 \cdot h^{-1}$		
[27]	Synthetic water		NF, NF-200 e NF-90 (polyamide), flat sheet, 2 and 8% recovery, 2.76 and 4.82 bar, permeate fluxes 0.00018 - 0.0012 $m^3 \cdot m^{-2} \cdot h^{-1}$	caffeine, sulfamethoxazole, acetaminophen, carbamazepine, naxopren, ibuprofen, metronidazole, estrone, 17β-estradiol, bisphenol A, nonylphenol, atrazine	21 - 99
[28]	Secondary treatment effluent	RO	73% recovery, permeate flow 50 $m^3 \cdot h^{-1}$	EDTA, nonylphenol, estrone, 17β-estraiol, 17α-ethinylestradiol, tributyltin, naphthalene, ibuprofen, ofloxacin, oxytretacyc, erythromycin, propanolol, fluoxetine, etc.	15 - 99
		MF	86% recovery, permeate flux 68.33 $m^3 \cdot h^{-1}$, inlet flow 79.58 $m^3 \cdot h^{-1}$		
		RO, HR-4040 e LE-4040	-		
	MBR effluent	NF, NF270-4040	12 - 15% recovery, permeate flow 0.40 - 0.46 $m^3 \cdot h^{-1}$, 5 - 11.8 bar		
[29]	Activated Sludge effluent	MBR	hollow fiber	azithromycin, erythromycin, ofloxacin, sulfamethoxazole, trimethoprim, acetaminophen, diclofenac, ibuprofen, etc.	70 - 100
		RO, ULP-4040 (polyamide)	65% recovery, permeate flux 0.034 $m^3 \cdot m^{-2} \cdot h^{-1}$		
		MF, HF-66-43-PM500	hollow fiber, permeate flux 0.323 $m^3 \cdot m^{-2} \cdot h^{-1}$		
[30]	Synthetic water; natural water/UF/Resin/ Coagulation	RO, BM30-400 (polyamide)	15.5 bar, permeate flux 0.039 - 0.05 $m^3 \cdot m^{-2} \cdot h^{-1}$	acetaminophen, atrazine, bisphenol A, caffeine, carbamazepine, cotinine, DEET, 17α-ethinylestradiol, gemfibrozil, ibuprofen, lopressor, progesterone, propylparaben, sulfamethoxazole, triclosan, trimethoprim	69 - 100
		UF, PVDF	flux 0.08 $m^3 \cdot m^{-2} \cdot h^{-1}$		
[31]	MBR effluent	RO (polyamide)	21% recovery, 7 bar, flux 0.012 $m^3 \cdot m^{-2} \cdot h^{-1}$	amoxicillin, atenolol, caffeine, carbamazepine, dilantin, iopromide, etc.	95 - 100
[32]	Synthetic water, Ontário lake/resin/cation	NF, NE4040-70 (polyamide)	50% recovery, 3.45 - 4.14 bar, permeate flow 0.00061 - 0.00085 $m^3 \cdot h^{-1}$, flux 0.039 - 0.055 $m^3 . \cdot m^{-2} \cdot h^{-1}$, concentrate flow 0.0018 - 0.0025 $m^3 \cdot h^{-1}$	acetaminophen, bisphenol A, carbamazepine, clofibric acid, diethylbestrol, estrone, 17β-estradiol, estriol, sulfamethoxazole	20 - 95
[33]	Drinking water Synthetic water	NF, Desal 5DK	10 bar, 100% recovery, 6 h	atrazine, isoproturon, diuron, alachlor, chlorfenvinphos	95 - 99
[34]	Groundwater Surface water	NF, Desal 5DK	10 bar, flux 0.0047 $m^3 \cdot m^{-2} \cdot h^{-1}$	atrazine, alachlor, pentachlorophenol, estrone, 17β-estraiol, 17α-ethinylestradiol, estriol, progesterone	92 - 100

Reverse Osmosis (RO); Microfiltration (MF); Ultrafiltration (UF); Nanofiltration (NF); Polyvinylidene Fluoride (PVDF); Membrane Bioreactor (MBR); Flat Sheet (FS); Hollow fiber (HF); Forward Osmosis (FO); Sodium hypochlorite (NaOCl); Wastewater Treatment Plant (WWTP).

In contrast, Chon *et al.* [26] analyzed removal of sulfametoxazole (hydrophilic) and found that this adsorption should be considered, since even though this substance has a negative charge, when in solution the membrane removal efficiency is low. Further according to them, micropollutants that have neutral charges but high hydrophobicity are easier to remove when using NF membranes, which have negative surface charge.

Therefore micropollutants can be classified into groups according to their pKa and LogKow values: neutral hydrophilic, neutral hydrophobic, ionic hydrophilic and ionic hydrophobic [26]. In this respect, for a hydrophilic membrane and a substance with negative charge, the fouling phenomenon helps to retain neutral hydrophobic substances (because the adsorbed layer on the membrane surface serves as an additional barrier) and ionic hydrophilic ones (due to electrostatic repulsion), as well as facilitating adsorption of neutral hydrophilic substances [25].

Different types of materials are used to produce membranes, but polymers are most commonly used for removal of micropollutants from wastewaters and sewage, because these membranes are less expensive, are versatile regarding conformation and have high separation performance [12] [14] [35] [36] [37].

For removal of micropollutants, the majority of researchers have used membranes made of materials specifically chosen to remove determined substances, such as polyamide membranes (**Figure 1**). These membranes have a negative charge when in contact with substances having neutral pH, thus enhancing their retention of negatively charged compounds. Other types of membranes are also used for different objectives, such as those made of cellulose acetate, which are frequently used to treat effluents with high concentration of chlorine, reaching salt removal rates of 99.5% in desalination applications [12]. However, according to Klüpfel and Frimmel [38], RO membranes produced with cellulose acetate do not have satisfactory performance in removing metamitron, clofibric acid, atrazine and terbutaline.

In order to improve the effectiveness of polyethersulfone (PES) membranes for mi-cropollutant removal, Kaminska *et al.* [39] inserted "small amounts of single walled carbon nanotubes" in this membrane, which increased the adsorption of bisphenol A and nonylphenol. But, the authors warn about that increase of the pressure can diminish the removal, probably because the porosity of the membrane and the convection through it.

Some authors have investigated the removal of micropollutants by MSP on industrial scale. Sui *et al.* [15] analyzed the removal of 14 compounds at four WTS located in Beijing, China. According to them, all were detected in the inflows to the stations, with the most abundant being caffeine (3.4 - 6.6 $\mu g \cdot L^{-1}$) and DEET (0.6 - 1.2 $\mu g \cdot L^{-1}$). However, they also observed that the station having a tertiary treatment system composed of MF and NF membranes achieved removal rates above 90% for the majority of the compounds analyzed. The only compounds that were poorly removed, were caffeine (50% - 80%) and mefenamic acid (0% - 50%).

Investigating the same types of membranes, Al-Rifai *et al.* [40] analyzed the removal of 13 micropollutants at a WTS. The substances with the highest concentrations in the inflow were salicylic acid, ibuprofen and bisphenol-A (6.3 - 38.5 $\mu g \cdot L^{-1}$). Despite these high incoming concentrations, only the last was not removed effectively, showing concentrations in the permeate of 20 - 464 $ng \cdot L^{-1}$.

Garcia *et al.* [28] assessed the removal of 20 micropollutants at a WTS equipped with tertiary treatment with MF and RO membranes in sequence, finding that only ibuprofen and nonylphenol were not efficiently removed (<30%), in contrast to the other substances (>75%). Therefore, they decided to study the removal of the two former substances in a pilot plant having a membrane bioreactor (MBR) system followed by a MSP system, alternating with NF and RO membranes. The authors observed removal rates of 99%. They concluded that the deterioration state of the membranes directly affects the removal of micropollutants.

The study of new processes on pilot scale provides important information, enabling the prevention of possible operating risks and extrapolation of costs to industrial scale [16] [36]. In this sense, various studies have investigated the treatment of effluents on this scale, with a growing number devoted specifically to removal of micropollutants (**Figure 1**).

Dolar *et al.* [23] investigated the removal of several micropollutants by reverse osmosis after passage through a MBR and observed that all the target compounds were below the limit of quantification. Likewise, Cartagena *et al.* [17] obtained high removal rates (>99%) of various classes of micropollutants in the permeates from NF and RO membranes. Corroborating these two studies, Rodriguez-Mozaz *et al.* [29] attained concentrations below 16 $ng \cdot L^{-1}$ in a combined system of UF and RO membranes. According to the authors, the use of a MSP to remove micropollutants can be strongly recommended, because unlike AOPs, there is no formation of byproducts and the process also serves as a barrier to possible microorganisms coming from the previous biological system.

However, Sahar *et al.* [22] compared the removal of 11 micropollutants by RO after passage through two types of system: MBR and CAS-UF (a hybrid system of conventional activated sludge and ultrafiltration). The authors concluded that despite the high removal rates (>93%), vestiges of the compounds analyzed were found in the permeate (28 - 223 $ng \cdot L^{-1}$) as a result of adsorption on the membrane. This suggests that the employment of RO is not effective, so other processes like adsorption in activated carbon and AOPs should be examined.

3. Advanced Oxidation Process

AOP are characterized by the generation of hydroxyl radical (HO•), nonselective oxidant with high reaction potential (Eo = 2.8 V), able to degrade even the most complex organic structures. These processes can be divided into homogeneous (catalyst and substrate or only substrate forming a single phase) and heterogeneous (catalyst and substrate forming two or more phases, with the catalyst generally being a solid). In turn, the generation of hydroxyl radicals can occur in the presence or absence of ultraviolet radiation [41]. When the reaction is complete, the hydroxyl radicals degrade the organic molecules into CO_2, H_2O and inorganic ions [4] [42]. **Figure 2** presents the most used and investigated AOP.

According Kommineni *et al.* [43], in the advanced oxidative processes, two oxidation stages are involved: (1) formation of strong oxidants and (2) the oxidizing reaction of these with organic contaminants in water. After the formation of HO•, two types of initial reactions are proposed, abstraction of the hydrogen atom, *i.e.* alkanes or alcohols, to form water or HO• adding in olefins or aromatics for the opening of the rings [44].

Many studies have been conducted of the removal of micropollutants from wastewaters by advanced oxidation processes. **Table 2** lists these papers.

Ozonation is a process widely applied to treat wastewaters containing recalcitrant organic matter. This occurs due to the high oxidation power of ozone (2.07 V), which acts directly on the pollutant molecules, transforming or eliminating them. It can also be combined with UV radiation and/or H_2O_2 treatment, increasing the oxidation potential. Ozone's mechanism of action involves direct reactions (ozonolysis) or indirect ones (generation of hydroxyl radicals) and its effectiveness is related to the pH of the sample [45] [46].

Some micropollutants have been studied for treatment by ozonation and AOP, presenting a removal percentage for bisphenol-A ranging from 60% to 100% by O_3 and 52% to 85% by S_2O_8-/UV-C and H_2O_2/UV-C (**Table 2**). Others have been found to be highly resistant, such as bezafibrate, with a removal rate of only 14% by O_3 [15].

Choi *et al.* [47] performed bench and pilot scale tests with river water to remove bisphenol-A by ozonation. The initial bisphenol-A concentration in the water varied from 543 to 844 $ng{\cdot}L^{-1}$. The authors tested different O_3 doses (1 - 10 $mg{\cdot}L^{-1}$), with alkaline pH, and after contact for 7 minutes obtained removal rates of 60% to 100%. In turn, Gerrity *et al.* [48] used a combination of O_3 and H_2O_2 with initial concentrations of 5 $mg{\cdot}L^{-1}$ and 3.5 $mg{\cdot}L^{-1}$, respectively, at pH 6.9. After contact time of 5 minutes and bisphenol-A concentration of 43 $ng{\cdot}L^{-1}$, they found removal rates greater than 78%.

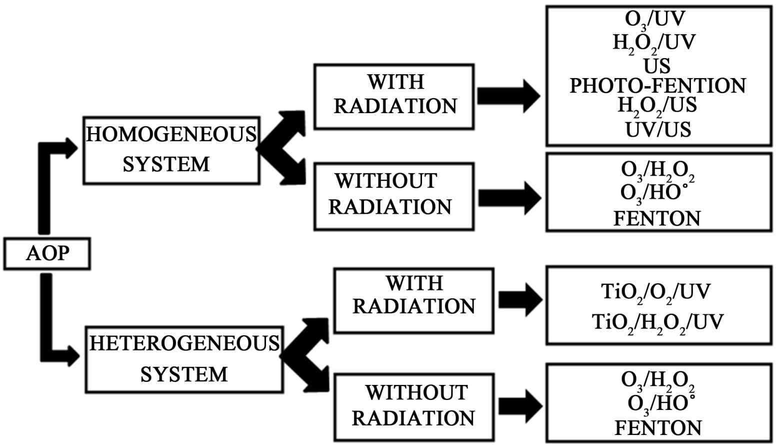

Figure 2. The most popular AOP.

Table 2. Micropollutant removal from different matrixes by distinct membrane separation processes.

Reference	Matrix	POA	Conditions	Micropollutant	Removal (%)
[15]	WTS effluent after ultrafiltration	O_3	$[O_3] = 5\ mg·L^{-1}$; pH 6.5 - 8.0; 15 min	clofibric acid, mefenamic acid, bezafibrate, caffeine, carbamazepine, diclofenac, gemfibrozil, indomethacine, metoprolol, DEET, trimethoprim	0 - >90
[42]	River water	O_3	$[O_3] = 1 - 10\ mg·L^{-1}$; pH 8.2 - 8.5; 7 min	bisphenol-A	60 - 100
[43]	Secondary treatment effluent	O_3/H_2O_2	$[O_3] = 5\ mg·L^{-1}$; $[H_2O_2] = 3.5\ mg·L^{-1}$; pH 6.9; 5 min	atenolol, atorvastatin, atrazine, benzophenone, bisphenol-a, caffeine, carbamazepine, diazepam, diclofenac, estradiol, estrone, ethynylestradiol, progesterone, testosterone, naxopren, ibuprofen, triclosan, trimethoprim, etc.	13 - >99
[45]	Secondary treatment effluent	O_3	$[O_3] = 3\ mg·L^{-1}$; pH 2.0; 27 min	thymol, triclosan, ibuprofen, naproxen, ketoprofen, fenoprofen, mefenamic acid, propylphenazone, crotamiton, carbamazepine, diethyltoluamide, etc.	>80
[47]	Synthetic water	UV; UV/H_2O_2; O_3; O_3/H_2O_2; O_3/UV; $O_3/UV/H_2O_2$	$[O_3] = 0.33 - 1.31\ mg·L^{-1}$; $[H_2O_2] = 20 - 60\ mg·L^{-1}$; pH 6.5; 15 - 75 min	estrone	100
[48]	Synthetic water	O_3/TiO_2/UV-A	$[O_3] = 10\ mg·L^{-1}$; $[TiO_2] = 1500\ mg·L^{-1}$; pH 5.0; λ = 313 nm; 30 min;	diclofenac	100
[49]	Synthetic water	Electro-fenton	$[Fe^{3+}] = 0.1$ mM; $[Cu^{2+}] = 4$ mM; pH 3.0; 22 min	atrazine	100
[50]	Synthetic water	UV/H_2O_2; $UV/S_2O_8^{2-}$; UV/HSO_5^-	$[H_2O_2] = 20 - 190$ uM; $\left[S_2O_8^{2-}\right] = 0 - 100$ uM; $\left[HSO_5^-\right] = 0 - 100$ uM; pH 3.0 - 11.0	atrazine	100
[51]	Secondary treatment effluent	UV/H_2O_2	$[H_2O_2] = 4 - 16\ mg·L^{-1}$; UV dose = $24.48 - 122.4\ kJ·m^{-2}$; 60 - 600 min	17β-estradiol, 17α-esthinylestradiol and estriol	91% - 100%
[52]	Distilled water	TiO_2/UV TiO_2/H_2O_2/UV UV	-	Tylosin	>98
[53]	Tap water and surface water	TiO_2/UV-C	$[TiO_2] = 500$ and $750\ mg·L^{-1}$; UV-C radiation: $1.04 - 2.08\ W·L^{-1}$; 180 - 300 min	diclofenac	56 - 100
[54]	Secondary treatment effluent	TiO_2/UV HSO_5^-/Fe^{2+}/UV	$[TiO_2] = 50 - 2000\ mg·L^{-1}$; [Fe] = 0.1 mM; $[HSO_5^-] = 0.025 - 0.5$ mM	Sulfamethoxazole, diclofenac, carbamazepine, clothianidin, mesotrione and bifenthrin	100
[55]	Synthetic water	$MW/UV/H_2O_2$	$[H_2O_2] = 0 - 500\ mg·L^{-1}$; pH 5.0 - 7.0; λ = 200 - 320 nm; 20 min	atrazine	100
[56]	Secondary treatment effluent	UV; UV/H_2O_2; Fe^{2+}/H_2O_2; $Fe^{2+}/H_2O_2/UV$; $Fe^{2+}/H_2O_2/UV_{290}$	$[H_2O_2] = 0 - 50\ mg·L^{-1}$; $[Fe^{2+}] = 0 - 5\ mg·L^{-1}$; pH 7.0 - 7.42; λ = 254 - 290 nm; 10 - 90 min	atenolol, atrazine, azithromycin, bezafibrate, benzotriazole, carbamazepine, ciprofloxacin, clarithromycin, diclofenac, diuron, gemfibrozil, ibuprofen, ketoprofen, iopamidol, metformin, methylbenzotriazole, metoprolol, etc.	0 - 100

Continued

[57]	Synthetic water	Fenton	$[Fe^{6+}] = 2.52\ mol \cdot L^{-1}$; pH 7.0; 10 min	bisphenol A	97.5
[58]	Synthetic water	O_3	$[O_3] = 8.3 - 15\ mg \cdot L^{-1}$; pH 8.4; 15 - 45 min	hexylcinnamic aldehyde, benzophenone-3, bisphenol-a, butylparaben, caffeine, ethylparaben, galaxolide, 4-methylbenzylidene-camphor, methylparaben, nonylphenol, propylparaben, tonalide, triclosan	95 - >99
[59]	Sewage	O_3/US	$[O_3] = 7 - 12\ mg \cdot L^{-1}$; US = 0% - 100%; 1 - 13 min	acetaminophen, bezafibrate, ciprofloxacin, clarithromycin, diclofenac, gemfibrozil, ibuprofen, naproxen, ofloxacin, salicylic acid, sulfamethazine, sulfametoxazole, venlafaxine, furosemida, carbamazepine, benzoilecgonine, etc.	90 - 100
[60]	WWTS effluent	UV/H_2O_2	$[H_2O_2] = 7.8\ mg \cdot L^{-1}$; 5 min	antipyrine, diclofenac, ketoprofen, isopropylantipyrine, indomethacine, fenoprofen, naproxen, mefenamic acid, ethenzamide, acetaminophen, disopyramide, atenolol, propanolol, metoprolol, chlortetracycline, norfloxacin, sulfamethoxazole, etc.	60 - 100
[61]	Synthetic water	O_3	$[O_3] = 6$ mmol; pH 3; 25 min	bisphenol A	87 - 99.5
[62]	Synthetic water and WWTP effluent	UV/H_2O_2; UV/$S_2O_8^{2-}$	$\left[S_2O_8^{2-}\right] = [H_2O_2] = 4$ mM; pH 6.0	ibuprofen	92.2
[63]	Synthetic water	H_2O_2/UV; Fe^{3+}/UV; Fe^{2+}/H_2O_2; Fe^{3+}/H_2O_2	$[Fe^{3+}] = 0.06 - 0.5$ mM; $[Fe^{2+}] = 0.28$ mM; $[H_2O_2] = 0.14 - 5$ mM; pH 3.0; 0.66 - 6.66 min	atrazine	90
[64]	Synthetic water	O_3	$[O_3] = 14 - 20$ uM; [pCBA] = 0.25 - 0.34 uM; pH 9.0	nonylphenol, octylphenol	85
[65]	River water	O_3/UV	$[O_3] = 45\ mg \cdot L^{-1}$; pH 7.0; 30 min	diethyl phthalate	100
[66]	Synthetic water	$S_2O_8^{2-}$/UV-C ; H_2O_2/UV-C	$\left[S_2O_8^{2-}\right] = 2.5$ mM; $[H_2O_2] = 2.5$ mM; pH 6.5; 120 min	bisphenol A	52 - 85
[67]	Synthetic water and Effluent	O_3; UV/H_2O_2	$[O_3] = 5\ mg \cdot L^{-1}$; $[H_2O_2] = 1000\ mg \cdot L^{-1}$; pH 7.0 - 8.5; 60 min	bisphenol a, ciprofloxacin, metoprolol, sulfamethoxazole	100
[68]	Synthetic water	US	$\left[HCO_3^{-}\right] = 0 - 10$ mM; 2 kW (20 kHz); pH 7; 0; 20 min; 20˚C	estradiol, estrone, estriol, ethynylestradiol	10 - 70

Water Treatment Stations (WTS); Wastewater Treatment Stations (WWTS); Wastewater Treatment Plant (WWTP); Ozone (O_3); Hydrogen peroxide (H_2O_2); Ultraviolet (UV); Ultraviolet cancer (UV-C); Ultraviolet age (UV-A); Titanium dioxide (TiO_2); Iron ion II (Fe^{2+}); Iron ion III (Fe^{3+}); Iron ion VI (Fe^{6+}); Copper ion II (Cu^{2+}); Persulfate ion ($S_2O_8^{2-}$); Peroxomonosulfate ion (HSO_5^{1-}); Microwave (MW); Ultrasound (US); p-chlorobenzoic acid (pCBA).

Lee *et al.* [49] studied the removal of 25 drugs in hospital effluent by ozonation. They observed that the removal percentages of these compounds at pH of 7 and 8 depended on the initial ozone dose and that the addition of H_2O_2 enhanced the reaction efficiency, due to the generation of hydroxyl radicals. Nevertheless, they also observed that when the $gO_3/gDOC$ ratio was below the organic matter quickly consumed the ozone and the addition of H_2O_2 did not increase the degradation of these compounds.

Nakada *et al.* [50] investigated the efficiency or removing 24 pharmaceutical compounds by ozonation in samples from a sewage treatment plant in Japan. They observed that the efficiency of ozonation was related to the chemical structure of the compound, because the action mechanism of ozone is favored in the presence of double bonds, C=C or aromatic chains with donor electrons. However, they did not observe the same results in compounds containing an amide group. Nearly all the compounds were efficiently removed (>80%) with combination of the two processes, the only exceptions being carbamazepine and diethyltoluamide.

Hydrogen peroxide and ultraviolet radiation are used to degrade some micropollutant in water and wastewater. The formation of HO• by UV/H_2O_2 process occurs according to the reactions 1, 2 and 3 [51].

$$H_2O_2 \xrightarrow{hv} 2\cdot OH. \tag{1}$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+. \tag{2}$$

$$HO_2^- \xrightarrow{hv} \cdot OH + O^-. \tag{3}$$

Sarkar *et al.* [69] carried out laboratory tests for removal of 5 $mg\cdot L^{-1}$ of estrone from water by different AOP, namely UV, UV/H_2O_2, O_3, O_3/H_2O_2, O_3/UV and $O_3/UV/H_2O_2$. Under almost all the conditions tested, it was possible to remove 100% of the estrone from the water.

Aguinaco *et al.* [70] conducted tests to remove diclofenac with ultrapure water in an acid medium by $O_3/TiO_2/UVA$, with initial O_3 and TiO_2 concentrations of 10 $mg\cdot L^{-1}$ and 1.5 $g\cdot L^{-1}$, respectively, wavelength of 313 nm and contact time of 30 min, achieving 100% removal. In turn, Sui *et al.* [15] performed tests to treat the effluent from a WWTS after ultrafiltration containing from 100 to 1000 $ng\cdot L^{-1}$ of the micropollutant in question. With 5 $mg\cdot L^{-1}$ of O_3, pH 6.5 - 8.0 and contact time of 15 min, the removal percentage was higher than 90%.

Balci *et al.* [71] studied the Electro-Fenton process and concluded that 0.1 mM of Fe^{3+} with 4 mM of Cu^{2+} was the most effective catalytic system in this process. Khan *et al.* [72] assessed the degradation of atrazine. They observed that the $UV/S_2O_8^{2-}$ process accelerates the degradation of this micropollutant in the presence of the radical sulfate ($k = 2.59 \times 109\ M^{-1}\cdot s^{-1}$) and the radical hydroxyl ($k = 2.25 \times 109\ M^{-1}\cdot s^{-1}$).

Silva *et al.* [73] investigating the removal of 17β-estradiol, 17α-ethinylestradiol and estriol by AOP and RO process observed that the H_2O_2/UV (4 $mg\cdot L^{-1}$ H_2O_2 and 122.4 $kJ\cdot m^{-2}$) eliminated the presence of the two first estrogens and 91% of estriol. The authors concluded that AOP was effective although the membrane process, which couldn't remove estrogens tested.

WTS are among the leading sources of emerging contaminants, because they receive all the effluents from generating sources, such as residences, hospitals and factories. Many of these contaminants are not removed by conventional processes, making it necessary to use tertiary treatment methods, which can be used alone or in combination, such as nanofiltration, reverse osmosis, advanced oxidation processes and/or ozonation, solar photo-Fenton, among others [18] [37] [74] [75] [76] [77] [78]. The use of AOP has been widely studied in synthetic water and surface water in order to evaluate the efficiency of removal as well as the detection of degradation products and the kinetics involved [79] [80] [81] [82] [83]. However, there are few studies that discuss the removal of micropollutants present in sewage, as well as the endocrine disruptors.

Thus, many studies can achieve removals up to 99 % of estrogens in WTS effluents, but it is necessary to study the best relation of the variants (like UV doses, H_2O_2 concentration, O_3 doses and catalysts concentration) to avoid competitive reactions that diminish the efficiency of the UV/H_2O_2 process [75] [81] [82].

4. Integrated Processes

WWTS are one of the main sources of emerging contaminants in the environment, as they receive effluents from differences sources such as residences, hospitals, industries, etc. Many of these contaminants are not removed by conventional processes or only one technique (as have been shown in **Table 1** and **Table 2**). So, it's make necessary the use of integrated processes that could reach high levels of quality of the treated water. Several works studied integrated process to remove micropollutant from water, such as nanofiltration, reverse osmosis, AOP, ozone, activated carbon (AC), membrane bioreactor (MBR), among others (**Table 3**). These articles have investigated the use of integrated tertiary treatments with a main objective being reduction of energy costs while at the same time achieving satisfactory contaminant removal rates [76].

Another use of integrated processes is the treatment of concentrate stream generated from membrane process. In these works, the concentrated pollutants was treated by AOP [18] [75] [83] or ozone as pre-treatment for membranes [84].

Schaar *et al.* [85] observed in a WWTS in Austria that the installation of a pilot-scale ozonation facility (0.6 O_3g/gDOC) after biological treatment resulted in removal of most micropollutants, such as carbamazepine and diclofenac.

Laoufi *et al.* [86] studied the photodegradation of tylosin, a veterinary antibiotic, using a photoreactor containing TiO_2. The antibiotic was completely removed after 7 hours of illumination; the best degradation was obtained at pH 3. More than 98% of tylosin has been oxidized after an irradiation time of 7 hours at the optimum position of UV light.

The combined photocatalytic membrane reactor and TiO_2 nanoparticles was evaluated by Plakas *et al.* [87] to degradation of the pharmaceutical diclofenac. The authors achieved diclofenac removal between 56% and 100%, whereas 52% TOC removal was recorded.

Table 3. Integrated processes for microlpollutant removal.

Reference	Integrated processes	Rejection/Removal of several micropollutants
[17]	MBR - >NF MBR - >RO	50% - 99.9% 57.1% - 99.9%
[18]	NF - >UV NF - >O_3 NF - >UV/O_3	≈49% (30 min) ≈99% (10 - 20 min) 85% - 99% (5 min)
[19]	MBR - >NF	15% - 99%
[21]	GAC/MF GAC/MF - >NF	54.6% - 89.1% >99%
[22]	MBR - >RO AS - >UF - >RO	93.2% - 99.6%
[26]	Coagulation - >DF - >UF - >RO	90% - 99%
[28]	MF - >RO MBR - >RO MBR - >NF	15% - 95% 95% - 99% 95% - 99%
[29]	AS - >MF - >RO AS - >UV - >Cl	100% 48% - 100%
[32]	UF - >NF IER - >NF	39% - 90% 20% - 85%
[34]	UV_{254} - >NF	40% - 100%
[76]	MF - >RO - >UV + H_2O_2	99%
[87]	TiO_2 nanoparticles - >UF	50% - 100%
[83]	MF - >RO - >GAC/MF	80% - 99%
[84]	O_3 - >NF	100%

Granular Activated Carbon (GAC); Microfiltration (MF); Nanofiltration (NF); Ultraviolet (UV); Ozone (O_3); Titanium dioxide (TiO_2); Ultrafiltration (UF); Ion Exchange Resins (IER); Membrane Bioreactor (MBR); Disk Filtration (DF); Reverse Osmosis (RO); Activated Sludge (AS); Chlorination (Cl); Ultrafiltration (UF).

Advanced oxidation system using solar irradiation/peroxymonosulfate (PMS)/Fe^{2+} to degrade many organic micropollutants was studied by Ahmed *et al.* [88] and compared with the UV/TiO_2 oxidative system. The authors showed that the PMS/Fe(II)/UV-Vis advanced oxidation system has better kinetic performances over TiO_2/UV-Vis system for six organic micropollutants removal in WWTP effluents mainly due to the higher selectivity in reactivity of $SO_4\bullet^-$ with respect to HO• in organic matrices. A molar ratio PMS:Fe(II) of 2:1 was found to be optimum for a full mineralization of investigated compounds in 30 min.

5. Discussion and Conclusion

This review summarized the findings of many works in the literature that had investigated Membrane and AOP to remove micropollutants from various wastewater sources.

Several studies have associated the presence of micropollutants in water/wastewater and the adverse effects in the environment. It is known that the most organic micropollutants are persistent and show the difficult degradation. The low concentrations that they are detected, are also present in surface water in concentrations of ng·L^{-1}; the complete removal is hard to achieve.

Membrane processes, in particular nanofiltration and reverse osmosis, have been reported as promising technologies for the removal of micropollutants in water. The works reviewed in this paper showed satisfactory results and high removal efficiency values for many classes of micropollutants such as pharmaceuticals, personal care products, hormones and pesticides. Because of the affinity of some micropollutants with the membrane's surface, some authors have associated separation process with pollutant adsorption phenomena on the membrane. However, this phenomenon can reduce the removal efficiency by occurrence of a diffusive process and subsequent desorption of micropollutant at permeate. In some studies, it was found that the best micropollutant removal efficiency occurs at pH values above the pKa of the compound, for reasons of electrical repulsion with the membrane. It was also found that the removal of micropollutants membrane could be related to the size of the molecules by the exclusion phenomenon.

AOP has been studied for degradation of several classes of micropollutants, especially because they have advantages such as the mineralization capacity and no generation of a concentrated stream. However, it is observed that although there is the effective micropollutant degradation, the formation of by-products could lead to an increase in antagonistic effects such as toxicity and estrogenic activity. The best operation conditions for complete mineralization of micropollutant and degradation kinetics which has been the key to the AOP are effective in the treatment of water and wastewater. From AOP systems, the most important point related by several authors is the best relation of the variants that have to be applied to achieve high removals and avoid unnecessary waste with reactants. Also, depending on the micropollutants and the type of matrix, a sequence of advanced treatments' processes has to be considered.

Acknowledgements

The authors want to thank CAPES for research founding, which made this project possible.

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