Occurrence and removals of micropollutants in water environment

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ABSTRACT

Micropollutants are often discharged to surface waters through untreated wastewater from sewage treatment plants and wastewater treatment plants. The presence of micropollutants in surface waters is a serious concern because surface water is usually provided to water treatment plants (WTP) to produce drinking water. Many micropollutants can withstand conventional WTP systems and stay in tap water. In particular, pharmaceuticals and endocrine disruptors are examples of micropollutants that are detected at the drinking water, ppb, or even ppb level. A variety of techniques and processes, especially advanced oxidation processes, have been applied to remove micropollutants from water to control drinking water contamination. This paper reviews recent researches on the occurrence and removal of micropollutants in the aquatic environments and during water treatment processes.

Keywords: Adsorption, Advanced oxidation processes (AOPs), Coagulation, Endocrine-disrupting chemicals (EDCs), Pharmaceuticals

1. Introduction

Micropollutants are compounds that are detected in the environment at trace concentrations ranging from μg/L to below ng/L [1]. Micropollutants can be composed of various materials and can contain various compounds such as pesticides, pharmaceuticals, cosmetics, flame retardants, perfumes, waterproofing agents, plasticizers and insulating foams [2]. Pharmaceuticals and personal hygiene products (PPCPs) and endocrine disrupting chemicals (EDCs) are among the most frequently detected anthropogenic contaminants in water.

Micropollutants are ubiquitous, and are often used to improve human life. This makes it difficult to control the source of these compounds in the water environment. Many researches on monitoring contamination by pharmaceuticals and EDCs in a variety of environments, such as surface water, groundwater, drinking water and wastewater, have reported significant levels of micropollutants in the water environment [3-9].

Because conventional processes used in wastewater treatment plants (WWTPs) are not designed to remove micropollutants, these can persist in the treated wastewater effluent. As a result, many of these micropollutants can be present in aquatic environments, including surface waters, and surface waters are a threat to the ecosystem and human health. The occurrence of micropollutants in the aquatic environment is associated with a variety of negative effects including short- and long-term toxicity, EDC and antibiotic resistance in microorganisms [10-12].

To date, regulations have been adopted for small amounts of micro-contaminants in some countries and regions, but WWTPs are not subject to consistent emission guidelines and standards for micropollutants. For example, environmental quality standards for a small number of micropollutants (e.g., nonylphenol, bisphenol-A and diiron) have been regulated by the European Parliament through Directive 2008/105/EC [13]. Nonylphenol and nonylphenol ethoxylates are recognized by the Canadian government as a toxic substance [14]. Other micropollutants, such as pharmaceutical and personal care products (PPCPs) and steroid hormones, are not yet on the list of regulated substances. Further studies on the effects of these micropollutants on human health and ecological health are needed to establish regulatory standards for micropollutants.

Although several review papers have been published regarding the occurrence of micropollutants in different water bodies [15-17], still not enough work has been done to provide a comprehensive summary of the occurrence of micropollutants in aquatic systems or the removal of micropollutants in conventional and advanced water treatment processes. In this review, we summarize recent work on the occurrence and removal of various micropollutants via conventional, as well as advanced, water

treatment processes.

2. Sources and Transport of Micropollutants in the Environment

Micropollutants present in the water environment have diverse origins in which domestic wastewater is a major source of surface water (Fig. 1). Pharmaceuticals are frequently detected in aquatic environments, originating from hospitals, drug stores, and convenience stores; some of these drugs are available without prescription (e.g., acetaminophen, ibuprofen, naproxen and aspirin). Although these pharmaceuticals are produced for human and animal healthcare, they are not metabolized completely in the body [18]. Both residual pharmaceuticals and their metabolites are excreted by humans and animals into wastewater. Waste from the manufacture process and from expired drugs can also be sources of pharmaceuticals.

EDCs such as natural hormones, insecticides, nonylphenol, bisphenol-A, and perfluorooctanesulfonic acids (PFOS) are also important micropollutants. These compounds are released into water from raw materials such as plastic products and flame retardants. They can also be generated directly by humans and animals [19, 20]. These hormone-like activities of EDC compounds have been shown to adversely affect human health [21, 22]. EDCs in human body are excreted in sewage and discharged into aquatic systems such as rivers and lakes. For this reason, sewage effluent is considered a major source of micropollutant contamination.

Physicochemical properties and bioavailability can affect the presence of micropollutants in natural waters. Caliman and Gavrilescu [23] categorized the generation and elimination of micropollutants based on five factors; physicochemical properties, environmental factors, transport and retention, transformation and accumulation. The volatility, water solubility, stability of the chemical structure, and particulate distribution characteristics are additional factors that determine whether micropollutants remain dissolved in water.
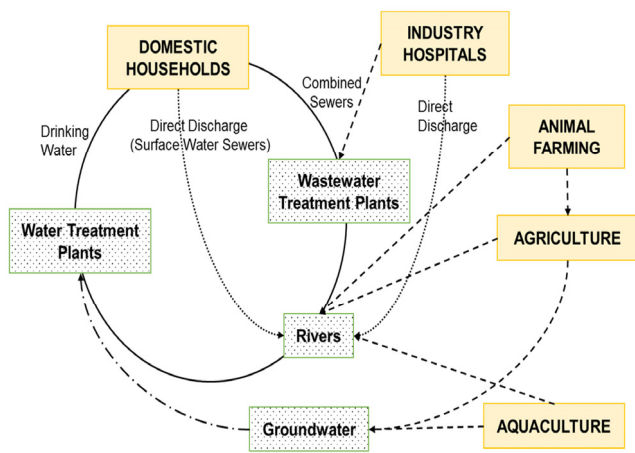
The physical properties of micropollutant can affect the movement of contaminants from one stage to another (e.g., soil-water movement). The mobility of the compounds is determined by transport/retention factors which are dependent on chemical related properties such as acid dissociation constant (pK_a) and octanol-water partition coefficient (K_{ow}). Adsorption, precipitation, complex formation and colloid formation all contribute to the retention of micropollutants in water. Transport mechanisms include advection, dispersion, diffusion and active transport.

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Transformation processes, that is, the decomposition of the parent compound as a byproduct, does not completely prevent the micropollutants from reaching the natural environment. Unless appropriate conversion processes are applied in the wastewater treatment process, it is difficult to control the amount of miropollutants to be emitted and accumulation may occur in the aquatic environment.

3. Occurrence of Micropollutants in Water

The presence of micropollutants in surface water has recently been widely reported. WWTPs can discharge wastewater effluent containing untreated micropollutants directly into rivers, lakes, rivers and reservoirs. Emitted micropollutants can be naturally deposited on sediments or transported to other places due to hydrological impact. These compounds can also be simultaneously converted to by-products by chemical and biological degradation at surface water [24]. However, at least some micro-contaminants are likely to persist and accumulate in surface waters [25].

Table 1 shows the concentrations of micropollutants in surface water, ground water, sewage treatment plant (STP) influents or effluents, WWTP influents or effluents, and hospital effluents. These results indicate that micropollutants have been ubiquitous pollutants in water environment.

In most countries, surface water is the source of drinking water in an area of increasing urban population in general. Therefore, micropollutants in surface waters can enter WTPs, and their presence in drinking water has been reported by several researchers. For example, clofibric acid has been reported at high concentrations (> 165 ng/L) in tap water in Berlin [61]. People can be unconsciously exposed to these micropollutants through tap water used for drinking, cooking and bathing. Therefore, removal of micropollutant by WTP is important for drinking water production. However, the presence of micropollutant present in tap water means that existing water treatment systems can not completely remove micro-contaminants from WTP.

Fig. 1. Sources and pathways of PPCPs in the urban water cycle [22].

Table 1. Distributions of the Micropollutants in Various Water Matrixes

Compounds	Water sample	Country	Concentration (ng/L)	References
acetaminophen	surface water	Serbia	78,170	[26]
	surface water	Korea	5-127	[27]
	surface water	Korea	4.1-7.3	[6]
	ground water	USA	380	[28]
	STP influent	Korea	13,406-56,944	[27]
	STP influent	Spain	24,600-29,000	[29]
	STP effluent	Korea	5-9	[27]
	STP effluent	Korea	1.9-19	[6]
	STP effluent	Spain	32-4,300	[29]
	hospital effluent	Taiwan	62,250	[30]
caffeine	surface water	Germany	65-6,798	[31]
	surface water	Denmark	65-382	[32]
	surface water	China	339	[33]
	surface water	Korea	0-373	[27]
	ground water	Europe	189	[31]
	ground water	USA	290	[34]
	WWTP influent	Greece	17,100-113,200	[35]
	WWTP influent	Taiwan	5,173-17,500	[30]
	WWTP influent	USA	26,567	[36]
	WWTP effluent	Korea	3,600	[37]
	WWTP effluent	Korea	19-873	[27]
	WWTP effluent	Korea	23-776	[6]
	WWTP effluent	Taiwan	19-1,727	[30]
	WWTP effluent	USA	28	[36]
	WWTP effluent	Greece	1,900-13,900	[35]
carbamazepine	surface water	Korea	4.5-61	[6]
	surface water	Korea	< 595	[38]
	surface water	Korea	5-36	[27]
	surface water	USA	6.8	[39]
	STP influent	Korea	5-451	[27]
	STP effluent	Korea	73-729	[6]
	STP effluent	Sweden	1,680	[40]
	STP effluent	Japan	10.8-163	[41]
	hospital effluent	Spain	30-70	[29]
diclofenac	surface water	Korea	8.8-127	[6]
	surface water	China	< 147	[42]
	surface water	Sweden	10-120	[40]
	surface water	UK	20-91	[43]
	STP influent	UK	350-460	[43]
	STP effluent	Korea	8.8-127	[6]
	STP effluent	Sweden	120	[40]
	STP effluent	Spain	200-3,600	[29]
	hospital effluent	Taiwan	328	[30]
ibuprofen	surface water	Korea	11-38	[6]
	surface water	Germany	60-152	[44]
	surface water	Korea	5-414	[38]
	ground water	USA	3,110	[47]
	STP influent	Spain	37-860	[44]
	STP influent	Taiwan	711-17,933	[30]
	STP effluent	Korea	10-137	[6]
	STP effluent	Taiwan	313-3,777	[30]

Compounds	Water sample	Country	Concentration (ng/L)	References
metoprolol	surface water	Spain	90	[12]
	surface water	China	24.8	[48]
	WWTP effluent	Sweden	274	[48]
naproxen	surface water	Sweden	90-250	[40]
	surface water	China	< 118	[42]
	surface water	Germany	70	[44]
	surface water	Korea	20-483	[6]
	STP influent	Sweden	3,650	[40]
	STP influent	Spain	109-455	[44]
	STP influent	Japan	38-230	[41]
	STP effluent	Sweden	250	[40]
	STP effluent	Japan	12-139	[41]
	STP effluent	Belgium	625	[44]
sulfamethoxazole	surface water	Korea	1.7-36	[6]
	surface water	Korea	5-82	[27]
	surface water	USA	150	[45]
	surface water	USA	< 300	[46]
	ground water	USA	1,110	[47]
	STP influent	USA	< 1,000	[46]
	STP influent	Korea	156-984	[27]
	STP effluent	USA	310	[46]
	STP effluent	Korea	3.8-407	[6]
	hospital effluent	Taiwan	1,335	[30]
sulfamethazine	ground water	USA	360	[47]
	STP influent	Korea	132	[49]
	STP effluent	Korea	114	[49]
atrazine	surface water	USA	4.7-3,600	[50]
	surface water	Korea	1.8-18	[51]
	ground water	Europe	8	[52]
	ground water	Switzerland	1-179	[53]
	STP influent	Switzerland	52-59	[53]
	WWTP effluent	Spain	124	[54]
	WWTP effluent	Switzerland	25-34	[53]
bisphenol-A	surface water	USA	81	[50]
	surface water	Korea	4.5-61	[51]
	surface water	Europe	10	[50]
	surface water	Germany	28-68	[31]
	surface water	USA	6,000	[39]
	STP effluent	UK	19.2	[55]
	WWTP effluent	USA	281-3,642	[55]
2,4-D	surface water	China	5.6-6.2	[42]
	ground water	Europe	< 12	[52]
	STP effluent	Spain	33.4	[56]
	STP effluent	Spain	21.4	[56]
triclosan	surface water	USA	9-1,550	[57]
	surface water	USA	4.6-55	[57]
	surface water	USA	3.3-41	[57]
	surface water	USA	8.8-75	[57]
	surface water	USA	10-2,230	[58]
	surface water	USA	10-600	[58]
	surface water	USA	0.45-486	[58]

Compounds	Water sample	Country	Concentration (ng/L)	References
nonylphenol	surface water	USA	800	[45]
	surface water	Korea	23.2-187.6	[59]
	surface water	China	1,900-32,800	[60]
	STP influent	Japan	500-1,100	[41]
	STP effluent	Japan	100-900	[41]

STP: Sewage Treatment Plant; WWTP: Waste Water Treatment Plant

Table 2. Human Toxicological Values of Micropollutants in Drinking Water

Compounds	Toxicological data (taxon, effect)	References
diclofenac	Maximum oral exposure: 4 µg/d, 36 weeks (Pregnant women, Premature closure of the ducts arteriosus or hemodynamic changes Provisional guideline value = 1 µg/L, 24 mon (Rats, Carcinogenetic)	[62]
carbamazepine	Maximum concentration in drinking water: 0.03 µg/L Benchmark quotient: 0.03/1= 0.03	[63]
ibuprofen	Maximum oral exposure = 24 µg/d, 36 weeks (Pregnant women, Premature closure of the ducts arteriosus or hemodynamic changes) Provisional guideline value = 50 µg/L (Diabetic patients, hypoglycemia)	[63]
metoprolol	Maximum concentration in drinking water: 2.1 µg/L Benchmark quotient: 2.1/50 = 0.04	[63]
sulfamethoxazole	Provisional guideline value = 440 µg/L, 60 weeks (Rats, thyroid tumors) Maximum concentration in drinking water: 0.03 µg/L Benchmark quotient: 0.03/440 = 0.00007	[63]

Table 3. Water Quality Standards for the Micropollutants in Environmental Agencies

Compounds	Country	Standards (µg/L)	References
atrazine	International	< 100	[64]
	USA	< 3	[65]
	Canada	<5	[66]
	Australia	< 20	[67]
	Europe	< 0.6*	[68]
2,4-D	International	< 30	[64]
	USA	< 70	[65]
	Canada	< 100	[66]
	Australia	< 30	[67]
diclofenac	Europe	< 0.1*	[69]
nonylphenol	Europe	< 0.3*	[69]
17α-ethinylestradiol	Europe	< 0.000035*	[69]
17β-estradiol	Europe	< 0.0004*	[69]

* This value is the Environmental quality standard (EQS) expressed as an annual average value (i.e., AA-EQS) in inland surface water. Here, "inland surface water" means the rivers and lakes and related artificial or heavily modified water bodies.

4. Human Health Impact of Micropollutants in Water

Pharmaceuticals among micropollutants raised concerns about the effects of unintended exposure to humans and ecosystems. When considering the food chain, these exposures can cause persistent bioaccumulation in the ecosystem. Chronic exposure to the human body can cause potentially unknown health effects. Previous studies reported health risks to humans through chronic pharmaceutical exposure in drinking water (Table 2).

Contamination of micropollutants can have a potentially negative effect on human health. The health effects of trace micropollutants are not clear, but people can increase their negative attitudes towards reused tap water. Because micropollutants are emerging issues in public health, water quality standards and guidelines are needed to provide safe drinking water to people. The criteria for these micropollutants are currently set in a number of countries, such as the United States, Canada, the European Union and Australia, although the levels of water quality standards are currently quite different (Table 3).

5. Removal of Micropollutants in WTPs

Several studies have estimated the removal rate of micropollutants by WTP (Table 4). Gibs et al. [70] evaluated the removal of 113 contaminants during clotting/sedimentation, sand filtration and chlorination. Acetaminophen, diclofenac and sulfamethiazine showed high removal rate (> 95%) after the water treatment process. However, the removal rate was low for micropollutants such as caffeine, carbamazepine, and bisphenol-A. Recently, Nam et al. [71] reported that the removal efficiencies of micropollutants detected in a WTP ranged from 6% to 100%. Diclofenac, acetaminophen, caffeine, carbamazepine, and 2,4-D were effectively removed (> 80%), whereas only small amounts of metoprolol (6%) were removed in the WTP process.

Removal rates of micropollutants are inconsistent among different studies [10, 39, 72]. In particular, caffeine (~42-99%), carbamazepine (~46-99%), atrazine (~53-99%), and bisphenol A (~78-99%) have shown both high and low removal rates by WTPs, because there are often differences among plants in terms of measurement method, and process configuration (Table 4).

Table 4. Removals of Micropollutants in Water Treatment Plants

Compounds	Influent (ng/L)	Effluent (ng/L)	Removal (%)	References
Pharmaceuticals				
acetaminophen	120-150	0-0.3	98	[73]
	163-260	10.7-22	94-98	[74]
	106.1 ± 147.1	5 ± 9.1	95.3	[71]
caffeine	100-190	ND-60	42-99	[73]
	100,000	ND-119	88-99	[10]
	45	ND	99	[6]
	291-526	ND-27.7	93-101	[74]
	36.1 ± 20.8	5.8 ± 7.4	84	[71]
carbamazepine	13	-	99	[12]
	4.1-51	6-18	-46-88	[39]
	4.8	ND	99	[6]
	10.3 ± 9.5	1.7 ± 4.2	84.7	[71]
diclofenac	1.1-1.2	ND	99	[39]
	175-292	ND	98.8-99.2	[74]
	7.8 ± 2.45	ND	100	[71]
ibuprofen	15	ND	99	[6]
	19.6 ± 21	4.3 ± 6	78	[71]
metoprolol	68.7	60	11	[75]
	37.4 ± 34.1	35.18 ± 22.4	6	[71]
naproxen	0.9-32	ND	99	[39]
	99-152	ND	98.8-99.2	[74]
	11.8 ± 12.4	2.7 ± 3.8	78	[71]
sulfamethoxazole	30	ND	99	[73]
	8,000	ND	99	[10]
	57.7-149	ND	98-100	[74]
	7.8 ± 5.4	2.1 ± 1.9	73	[71]
sulfamethazine	113	ND	98-100	[74]
	3.7 ± 2.4	2.31 ± 1.7	38	[71]
Endocrine disrupters				
atrazine	32-870	49-870	-53	[39]
	7	ND	99	[72]
bisphenol-A	6.1-14	25	-78	[39]
	295	5	98.3	[72]
	88 ± 102.8	5 ± 9.1	95.3	[71]
nonylphenol	100-130	93-100	7	[39]
	14.5 ± 52.1	12.6 ± 5.9	70	[71]

ND: Not detected

6. Removal of Micropollutants by Each Water Treatment process

6.1. Coagulation/Sedimentation

Coagulation removes particulate matter, including colloidal and dissolved substances, from water. Chemical coagulation is the main process to remove suspended solids by the addition of coagulants to change the electrostatic state of contaminants [76, 77]. Natural particles, such as clay and natural organic matter (NOM), can be negatively charged to water and electrostatically interact [78]. Natural particles such as clays, and NOM are negatively charged in water, and can therefore interact electrostatically [78]. Small particles and NOM suspended in natural water are too small to precipitate out of surface water. Positively charged metal salts (often aluminum and iron salts) are often used as coagulants. Their efficacy is influenced by pH [76, 79]. The metal salt binds to suspended particles in water via electro-neutralization at pH 5-7 [80-82]. Charge neutralization causes floc formation and these aggregation products bind to each other via van der Waals forces (i.e., sweep flocculation). These mechanisms can separate water and NOM from water.

Several previous studies have evaluated the removal of micropollutants by coagulation, using jar tests among other methods. Table 6 summarizes the removals of micropollutants during coagulation processes. In a study by Matamoros and Salvadó [83], micropollutant removal via coagulation ranged from imperceptible elimi-

nation to 50%, with relatively high removals (20-50%) observed for compounds with a K_{ow} of 4 at pH ~7-8 (e.g., galaxolide, tonalide, and octylphenol). Suárez et al. [84] reported significant reduction (~80%) of musks (e.g., galaxolide and tonalide) during hospital wastewater coagulation treatment. Other micropollutants have shown similar rates of elimination (diclofenac, max. 46%; naproxen, max. 42%; and ibuprofen, max. 23%). Asakura and Matsuto [85] found that biphenol-A could not be removed by coagulation and sedimentation, but that high removal rates for DEHP and nonylphenol (70% and 90%, respectively) were achieved through leachate treatment.

The efficiency of micropollutant removal by coagulation varies depending on conditions such as pH, coagulant type and dose (Table 5). Most micropollutants had low elimination rates (< 50%) by coagulation. However, some studies have reported an electrostatic interaction between coagulants and micropollutants. Hydrophilic micropollutants such as acetaminophen (log K_{ow} = 0.46), sulfamethoxazole (log K_{ow} = 0.68) and sulfamethazine (log K_{ow} = 0.62) can be electrically aggregated with Al^{3+} or Fe^{3+} ions in the coagulants [71, 73]. Especially, due to pKa values (SMZ = 5.7, SMA = 2.6(pK_{a1})/7.7(pK_{a2})), sulfamethoxazole and sulfamethazine exist as negative ions at neutral pH, therefore, these compounds can be effectively coagulated to Al^{3+} ion of PACl (polyalumium chloride) during coagulation process. Antibiotics, such as tetracycline antibiotics (log K_{ow} < -1.37), have been removed at rates of ~43-94% via the coagulation process [86]. These results indicate that electrical aggregation is an important mechanism in the coagulation step.

Table 5. Removal Efficiencies of Some Micropollutants by Coagulation (modified from Luo et al. [87])

Coagulant	Dosage with pH value presented in the parentheses	Compound	Removal (%)	References
FeCl$_3$	25, 50 mg/L (7)	ibuprofen	12.0 ± 4.8	[84]
		diclofenac	21.6 ± 19.4	
		naproxen	21.8 ± 10.2	
		carbamazepine	6.3 ± 15.9	
		sulfamethoxazole	6.0 ± 9.5	
		trimethoprim	32.1 ± 51.1	
		galazxolide	79.2 ± 9.9	
Al$_2$(SO$_4$)$_3$	25 mg/L (7)	diazepam	12.5 ± 18.4	[84]
		sulfamethoxazole	0.9 ± 14.4	
		tonalide	75.8 ± 11.0	
		galazxolide	76.4 ± 5.5	
FeCl$_3$	100, 200 mg/L (4,7,9)	bisphenol-A	20	
		diethylhexylphthalate	70	[85]
		nonylphenol	90	
Al$_2$(SO$_4$)$_3$	200 mg/L (7)	aldrin	46	[88]
	100 mg/L (7)	bentazon	15	
PACl	30 mg/L (7)	sulfamethoxazole	43	[71]
		sulfamethazine	52	
		caffeine	16	
		acetaminophen	17	
		diclofenac	0	
		metoprolol	10	

Other removal mechanisms (e.g., particle adsorption and sunlight photolysis) can be used during the coagulation process to enhance micropollutant removal. Hydrophobic compounds can be adsorbed into suspended particles, and co-removed through coagulation/sedimentation processes [89]. Higher removal efficiencies for acetaminophen (76.6% with the concentrations of 24.7 ± 43.3 ng/L), caffeine (81.2% with the concentrations of 6.7 ± 10.5 ng/L), and diclofenac (100% with the concentration of less than the method detection limit), which are photo-sensitives, have been observed during the WTP coagulation process [71]. This result implies that sunlight photo-degradation can be an additional mechanism for micropollutant removal, because coagulation occurs in the open air; these mechanisms can also act simultaneously.

6.2. Adsorption

Adsorption by activated carbons is commonly used to control the taste and odor of drinking water. Adsorbate and adsorbent interactions in adsorption involve complex surface reactions, hydrophobic interactions at the surface, and adsorption of surfactant or polymers and polyelectrolytes [90].

Several studies on the efficacy of micropollutant removal by adsorption have been done using lab- and pilot-scale experiments (Table 6). Powdered activated carbon (PAC) and granular activated carbon (GAC) have been widely used in adsorption processes, which can be affected by both adsorbate and adsorbent properties [91]. Micropollutant removal has been improved with increased PAC doses, independent of the initial compound concentrations [92]. Batch tests performed by Hernández-Leal et al. [92] demonstrated marked removal (> 94%) of various micropollutants (i.e., with effluent concentrations of 173 ng/L for caffeine and 9 ng/L for buthylparaben) using PAC adsorption, with initial compound concentrations of ~100-1,600 μg/L at a dose of 1.25 g/L and a contact time of 5 min.

Table 6. Removal Efficiencies of Some Micropollutants by Adsorption (modified from Luo et al. [87])

Adsorbent	Dosage	Compound	Removal (%)	References
PAC	8, 23, 43 mg/L	diclofenac	96, 98, 99	[91]
		carbamazepine	98, 99, 100	
		sulfamethoxazole	2, 33, 62	
	100 mg/L	caffeine	> 94	
		bisphenol-A	> 94	[92]
		nonylphenol	> 94	
	5 mg/L	acetaminophen	70-79	[93]
		caffeine	60-62	
		diclofenac	30-57	
		naproxen	52-57	
		sulfamethoxazole	30-37	
		atrazine	55-57	
GAC	Full scale	diclofenac	> 98	[94]
		carbamazepine	23	
		estrone	64	
		17β-estradiol	> 43	
		17α-ethinylestradiol	> 43	
	29 g/70.6 mL bed volume	bisphenol-A	66	
		nonylphenol	84	[92]
		triclosan	95	
	Full scale, empty bed contact time:15 min	diclofenac	~100	[95]
		trimethoprim	90	
		carbamazepine	75	
		caffeine	45	
	1 mg/L	acetaminophen	58	[96]
		caffeine	71.3	
		atrazine	53	
		carbamazepine	69.9	
		diclofenac	25.5	
		ibuprofen	23.3	
		naproxen	46.6	
		sulfamethoxazole	27.1	

PAC: Powdered activated carbon; GAC: Granular activated carbon

Interestingly, sorption coefficients of hydrophilic compounds (i.e., caffeine, acetaminophen, sulfamethoxazole, and sulfamethazine) have been shown to fit a linear isotherm, while hydrophobic compounds (i.e., naproxen, diclofenac, 2,4-D, triclocarban, and atrazine) fit a Freundlich isotherm [79]. In this study, it was found that the removal of hydrophobic pollutants and caffeine was independent of pH changes, but acetaminophen, sulfamethazine, and sulfamethoxazole were adsorbed mainly by electrostatic interaction with PAC; therefore, they were affected by pH. Adsorption removal in surface water samples was decreased; this decrease was significant for hydrophobic compounds. The decline in adsorption capacity in surface water samples was caused by the competitive inhibition of dissolved organic matter (DOM) with micropollutants into PAC. Low temperature (5°C) also decreased the adsorption removal of micropollutants, and affected hydrophobic compounds more than hydrophilic compounds.

As the elimination of trace contaminants depends largely on particle-contaminant interactions, competition for adsorption sites and/or pore blocking (by particle solids) can reduce the removal efficiency of activated carbon [97]. Snyder et al. [93] suggested that a steam-treated GAC could be employed to overcome the drawbacks of GAC, due to its greater absorption capacity. Regular regeneration of GAC also seemed of vital importance to maintain minimal breakthrough of micropollutants. Furthermore, pore shape/size and volumes of activated carbons, as well as carbon type, surface charge of compounds, and operation year, influenced removal performances [27, 96].

6.3. Chlorination

Drinking water purification generally involves antibacterial treatment such as chlorination, ozone treatment (O_3) and ultraviolet (UV-C) to prevent the spread of waterborne diseases. This technique is effective in removing pathogens (> 99%) from WTPs [98-101]. Chlorination is a disinfection process commonly used by WTP in some regions, including Korea.

Chlorination is generally not recognized as an organic contaminant removal process, but it can degrade organic contaminants through the oxidation of free chlorine [101, 102]. Chlorine molecules showed higher reactivity to aromatic pharmaceuticals and higher electrical affinity for certain functional groups of micropollutant. Chlorination is more cost-effective than other technologies (e.g., ozonation and ultraviolet light) because it is easy to perform [104]. However, since degradation by chlorination is too slow (e.g., sulfamethoxazole, acetaminophen, caffeine, and ibuprofen), chlorination is less effective (less than 20%) to remove trace amounts of micropollutants [105, 106]. Production of harmful byproducts (e.g., trihalomethane (THM), haloacetic acid, haloacetonitrile) from drinking water chlorination has been a major concern, and chlorinated disinfection byproducts are considered as emerging contaminants that require elimination by WTPs [107, 108].

6.4. Ozonation

The main reasons for applying ozone to drinking water treatment are disinfection and oxidation (e.g., taste and odor control,

de-coloration, elimination of micropollutants, etc.) or a combination of both [109, 110]. Ozonation can oxidize micropollutants either by a direct reaction with ozone or indirectly after formation of hydroxyl radicals, as follows in Table 7.

Table 7. Ozonation Processes with Micropollutants (modified from von Gunten [109, 110] and Šojić et al. [111])

Ozonation	Reference
directly reaction	[109, 110]
O_3+Contaminants $\rightarrow$ End products	
O_3+Contaminants $\rightarrow$ Contaminants$^{•+}$+$O_3^{•-}$	
indirectly reaction	
$H_2O \rightleftharpoons H^+ + OH^-$	[109, 111]
$O_3 + OH^- \rightarrow HO_2^- + O_2$	
$O_3 + HO_2^- \rightarrow •OH + O_2^{•-} + O_2$	
$O_3 + O2^{•-} \rightarrow O_3^{•-} + O_2$	
Contaminants+•OH $\rightarrow$ Contaminants–H+H_2O	
Contaminants–H+•OH $\rightarrow$ End products	

6.5. Advanced Oxidation Processes (AOPs)

Various AOPs such as UV radiation, UV/Cl₂ and UV/O₃ have been attempted to remove micropollutants (Table 8). This process uses a radical species (e.g., chlorine radical ($^•$Cl), hydroxyl radical ($^•$OH), and ozonide radical ion ($O_3^{•-}$)) to degrade micropollutants by oxidation. The main removal mechanisms of these processes for micropollutants are shown in Table 8.

Table 8. Removal mechanisms of O_3, UV, Cl₂/UV, and UV/O₃ process for micropollutants removals

Processes	References
UV radiation (UV)	
$H_2O+UV\text{-}C \rightarrow {}^•H+{}^•OH$	[38, 112]
Contaminants+$^•$OH $\rightarrow$ Contaminants–H+H_2O	
Contaminants–H+$^•$OH $\rightarrow$ End products	
Chlorination-UV radiation (Cl₂/UV)	
$Cl_2+H_2O \rightarrow HOCl+HCl$	[113, 114]
$HOCl+UV\text{-}C \rightarrow {}^•OH+{}^•Cl$	
Contaminants+$^•$OH $\rightarrow$ End products+H_2O	
Contaminants+$^•$Cl $\rightarrow$ End products+H_2O	
UV radiation-ozonation (UV/O₃)	
$O_3+hv \rightarrow O_2+O^•$	[111, 115]
$O^•+H_2O \rightarrow 2HO^•$	
$O_3+hv+H_2O \rightarrow O_2+H_2O_2$	
$H_2O_2+hv \rightarrow 2HO^•$	
Contaminants+$^•$OH $\rightarrow$ Contaminants–H+H_2O	
Contaminants–H+$^•$OH $\rightarrow$ End products	

Micropollutants are rapidly degraded from parent compounds to byproducts through continuous radical attack. Micropollutants rapidly degrade from parent compounds to their byproducts through continuous radical attacks. A study by Sui et al. [116],

on the efficiency of ozonation for the removal of various micropollutants, showed that carbamazepine, diclofenac, indomethacin, and trimethoprim concentrations were reduced by more than 95% at an applied ozone dose of 5 mg/L. A study conducted by Gerrity et al. [117] focused on the application of O_3/H_2O_2 for removing a suite of micropollutants during water reclamation. This process had considerable removal efficiency (> 90%, with the concentrations of < 0.50 ~ < 25 ng/L in the ozone effluents) for almost all of the target contaminants. Kim et al. [118] investigated the effects of UV (wavelength: 254 nm) -based processes (UV and UV/H_2O_2) to remove 41 micropollutants. While UV alone can only remove only a few compounds at a significant level (> 90%; e.g., ketoprofen, diclofenac and antipyrine), and macrolide has been observed to be ineffective removal (~24-34%). In contrast, the addition of H_2O_2 (7.8 mg/L) in UV significantly improved the efficiency of the process and increased the removal efficiency to 90 for 39 out of 41 compounds.

Oxidation generally does not result in complete mineralization, but in many cases forms a transformed product with much lower biological activity than the parent compound [119-122]. Most organic compounds, including micropollutants, are converted to hydrophilic byproducts with similar or lower molecular weights [123-127]. Richardson et al. [128] reported that most conversion products formed during ozonation have found to contain oxygen in structures such as aldehydes, ketones, and carboxylic acids. In addition to the formation of the conversion products, other unwanted byproducts may be formed, such as bromate, which is a potential human carcinogen formed during the ozonation of the bromide-containing water by a complex mechanism involving both ozone and hydroxyl radicals [109, 110]. N-nitrosodimethylamine (NDMA) formation also has been reported during drinking-water ozonation [129, 130].

UV/H_2O_2 oxidation is a promising drinking water production technology for the reduction of a wide range of organic pollutants and undesirable natural organic constituents [131-133]. Recent studies have reported that UV/H_2O_2 can increase the formation of controlled trihalomethanes (THMs) and haloacetic acid (HAA) under certain conditions [134, 135], whereas medium-pressure UV at high fluence (as in AOPs) could destroy some NDMA precursors [136]. Chu et al. [137] investigated changes in haloacetamide formation and speciation attributed to UV, H_2O_2 or UV/H_2O_2, followed by the application of free chlorine to quench any excess hydrogen peroxide and to provide residual disinfection. The results showed that H_2O_2 preoxidation alone resulted in diiodoacetamide formation in two iodide-containing waters and increased bromine utilization.

It has recently been reported that a combination of disinfectants with AOP can be used to remove contaminant micropollutants. Šojić et al. [111] showed that 84% of metoprolol was degraded using the UV/O_3 reaction. Recently, Nam et al. [114] have shown that the UV/Cl_2 process is effective in treating methoproprol by generating OH and Cl radicals. After the filtration step in WTPs, the UV/chlorination process can be used not only for disinfection purposes but also for the removal of micropollutants.

7. Conclusions

Micropollutants are discharged to surface water from untreated STP and WWTP wastewaters. Some micropollutants enter WTPs after being discharged into surface waters. Conventional WTP processes such as coagulation, precipitation, chlorination and adsorption can remove trace amounts of micropollutants. However, the removal efficiency varies depending on the physicochemical properties of the micropollutants. Alternatively, AOP can be applied to improve removal of micropollutants in WTPs. Although advanced treatment techniques have proven to be promising alternatives for the removal of micropollutants, there are two problems associated with the application; high operating costs and the formation of undesirable by-products. Thus, a comprehensive understanding of the fate and toxicity of microorganisms and their byproducts in surface water and drinking water is essential to effectively predict effects of micropollutants on the receiving environment.

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