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Micropollutants in Wastewater: Fate and Removal Processes

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Abstract

The occurrence of micropollutants (MPs) in various streams of municipal wastewater treatment plants (WWTPs), and their fate and removal processes are discussed. The fate of MPs in WWTPs largely depends on adsorption on suspended particulates, primary and secondary sludge and dissolved organic carbon, and removal occurs due to coagulation-flocculation, and biodegradation. The log K_{ow} (>2.5) and pK_a are the dominant properties of the MPs, and the concentration, organic fraction, and surface charge of suspended particulates dictate the extent of adsorption of MPs. Most of the conventional WWTPs do not remove complex MPs by biodegradation or biotransformation effectively (k_{bio} ≤ 0.0042 L/gss/h), and the removal varies widely for different compounds, as well as for the same substance, due to operational conditions such as aerobic, anaerobic, anoxic, sludge retention time (SRT), pH, redox potential, and temperature. Membrane bioreactor performs better for moderately biodegradable compounds due to the diverse nature of microorganisms as well as greater adaptability due to longer SRT. Ozone and UV-based advanced oxidation processes, membrane filtration can be used for tertiary treatment due to their high rate as well as easy implementation. Various partition coefficients and rate constants values for different MPs are also provided for design and application.

Keywords: micropollutants, wastewater, fate and removal, adsorption, coagulation, biodegradation, membrane filtration, advanced oxidation processes

1. Introduction

The widespread presence of micropollutants (MPs) in aquatic systems is a major concern all across the globe. For example, about 143,000 compounds were registered in European market in 2012; many of which would end up in water systems at some point of their lifecycle. Most of them are not eliminated or biotransformed in traditional wastewater treatment plants, can be persistent in aquatic system or form new chemical species reacting with background humic substances in sunlight, can be bioactive, and can bioaccumulate [1–5]. Although they are present in almost undetectable (low to subparts per billion (ppb)) concentrations, their existence in aquatic systems has been connected to various detrimental effects in organisms such as estrogenicity, mutagenicity, and genotoxicity [6].

While no compound-specific regulation exists anywhere for the removal of MPs in wastewater plants, some regulations are there for the presence in water for compounds such as pesticides, lindane, nonylphenol, and synthetic hormones [7]. The MPs fall into several categories as pharmaceuticals, personal care products (PPCPs), household chemicals, and industrial agents. A comprehensive list of 242 chemicals is provided in EU FP7 Project [8] of which about 70% are pharmaceuticals and personal care products and 30% are industrial agents including perfluoro compounds, pesticides, herbicides, and food additives. Since a significant majority of the MPs in municipal wastewater belong to the class of pharmaceuticals and personal care products (PPCP), fate and removal processes of these compounds are discussed in detail in this chapter.

2. Commonly found PPCP in wastewater effluent and surface water

About 70% of the pharmaceuticals in the wastewater originates from household, 20% comes from livestock farming, 5% is from hospital effluent, and rest 5% comes in runoff from nonparticular sources [9]; however, seasonal and geographical variations typically occur. The fate of MPs in wastewater plant depends on the physical properties such as solubility, octanol-water partition coefficient, and Henry's constant. A list of commonly found pharmaceuticals, personal care products, and biocides and their concentration in wastewater effluent and surface water and physical properties are presented in **Table 1**. The solubility of MPs varies in a wide range of 0.15 mg/L (maprotiline, C₁₀ H₂₃ N, an antidepressant drug) to 588,000 mg/L (acesulfame, C₄H₄KNO₄S, and artificial sweetener), which is also in accordance with their concentration in the effluent.

Type	MP	Application	Average concentration (ng/L) [10, 11]		Solubility* (mg/mL)	log K _{ow} *	pKa*	Henry's constant (atm·m ³ /mole)*
			Surface water	WWTP effluent				
Disinfectants, pharmaceuticals (prescriptions, over-	Atenolol	β-blocker	205	843	0.3	0.16	9.6	1.37 × E-18
	Azithromycin	Antibiotic	12	175	<1 at 25°C	4.02	8.74	5.30 × E-29

Type	MP	Application	Average concentration (ng/L) [10, 11]		Solubility* (mg/mL)	log K_{ow} *	pKa*	Henry's constant (atm-m ³ /mole)*	
			Surface water	WWTP effluent					
the-counter drugs, veterinary drugs) [10]	Bezafibrate	Lipid-lowering drug	24	139	0.00155	3.97	3.83		
	Carbamazepine	Anticonvulsant	13	482	0.152	2.1	15.96	1.08 × 10 ⁻¹⁰	
	Carbamazepin-10, 11-dihydro-10, 11-dihydroxy	Transformation product	490	1551	–	–	–	–	
	Clarithromycin	Antibiotic	30	276	0.00033	3.16	8.99 at 25°C	1.73 × E-29	
	Diatrizoate (amidotrizoic acid)	Contrast medium	206	598	0.107	2.89	2.17	–	
	Diclofenac	Analgesic	65	647	0.00447	4.98	4	4.73 × E-12	
	Erythromycin	Antibiotic	25	42	0.459	2.37	12.44	1.46 × E-29	
	Ethinylestradiol	Synthetic estrogen	5	2	0.00677	3.63	10.33	7.94 × E-12	
	Ibuprofen	Analgesic	35	394	0.0684	3.5	4.85	1.50 × E-07	
	Iomeprol	Contrast medium	275	380	–	–	–	–	
	Iopamidol	Contrast medium	92	377	0.117	1.62	4.15	1.14 × E-25	
	Iopromide	Contrast medium	96	876	0.0238	–2.05	–	1.00 × E-28	
	Mefenamic acids	Analgesic	7	870	0.0137	4.58	3.89	2.57 × E-11	
	Metformin	Antidiabetic	713	10347	1.38	–1.8	12.4	–	
	Metoprolol	β-blocker	20	166	0.402	1.88	14.09	1.40 × E-13	
	Naproxen	Analgesic	37	462	0.0511	3.29	4.19	3.39 × E-10	
	Sotalol	β-blocker	63	435	0.782	0.85	10.07	2.49 × E-14	
	Disinfectants, pharmaceuticals (prescriptions, over-the-counter drugs, veterinary drugs) [11]	Sulfamethoxazole	Antibiotic	26	238	0.459	0.79	6.16	6.42 × E-13
		N4-Acetylsulfamethoxazole	Transformation product	3	67	–	–	–	–
		Trimethoprim	Antibiotic	13	100	0.615	1.26	17.33	2.39 × E-14
Penicillin V		Personal care product	–	28.7	0.454	1.78	3.39	4.42 × E-15	
Irbesartan		Antihypertensives	–	479.5	0.00884	4.51	7.4	–	
Tramadol		Analgesics	–	255.8	0.75	2.71	13.8	1.54 × E-11	
Risperidone		Neuroleptics	–	6.9	0.171	3.27	8.76	–	
	Trihexyphenidyl	Antidementia agents	–	0.2	0.00314	4.93	13.84	4.73 × E-10	
	Venlafaxine	Antidepressant	–	118.9	0.23	2.69	14.42	–	
	Codeine	Morphine derivates	–	70.6	0.577	1.2	13.78	7.58 × E-14	

Type	MP	Application	Average concentration (ng/L) [10, 11]		Solubility* (mg/mL)	log K_{ow} *	pKa*	Henry's constant (atm-m ³ /mole)*
			Surface water	WWTP effluent				
	Fluconazole	Antifungal medication	–	108.2	1.39	0.58	12.71	–
	Diphenhydramine	Antihistamine	–	11.7	0.0752	3.44	8.98	3.70 × E-09
	Repaglinide	Antidiabetic medications	–	3.1	0.00294	5.05	3.68	–
	Flecainide	Antiarrhythmic agents	–	45.5	0.0324	2.98	13.68	5.75 × E-13
	Bisoprolol	β-blockers	–	41.6	0.0707	2.3	14.09	2.89 × E-15
	Alfuzosin	Alpha-blockers	–	2.8	0.282	2.02	14.64	–
	Bupropion	Antidepressant	–	1.0	312	3.6	18.29	–
	Ciprofloxacin	Antibiotics	–	96.3	1.35	0.28	6.09	5.09 × E-19
	Oxazepam	Anxiolytics	–	161.7	0.0881	2.24	10.61	5.53 × E-10
	Carbamazepine	Antiepileptic drugs	–	832.3	0.152	2.45	15.96	1.08 × E-10
	Diclofenac	Analgesics	65	647	0.00447	4.98	4	4.73 × E-12
	Orphenadrine	Antihistamine	–	3.9	0.03	3.77	8.91	4.08 × E-09
	Sulfamethoxazole (VITO)	Antibiotics	–	280.2	0.459	0.89	6.16	–
	Haloperidol	Psychiatric medication	–	32.2	0.00446	4.30	8.66	2.26 × E-14
	Citalopram	Antidepressant	–	33.8	–	–	–	–
	Sulfamethoxazole (JRC)	Antibiotics	–	142.3	0.459	0.89	6.16	–
	Fexofenadine	Antihistamine	–	165.0	0.00266	5.6	4.04	–
	Diltiazem	Antiarrhythmic agents	–	10.7	0.0168	3.09	12.86	8.61 × E-17
	Fluoxetine	Antidepressant	–	2.1	0.0017	4.05	9.8	8.90 × E-08
	Terbutaline	Antiasthmatics	–	1.1	5.84	0.90	8.86	1.65 × E-18
	Clindamycin	Antibiotics	–	70.4	3.1	2.16	12.16	2.89 × E-22
	Telmisartan	Antihypertensives	–	367.5	0.0035	7.7	3.65	–
	Eprosartan	Antihypertensives	–	226.8	0.00866	3.9	3.63	–
	Gemfibrozil	Lipid-lowering drugs	–	137.7	0.0278	3.4	4.42	–
	Zolpidem	Hypnotics	–	1.5	0.0313	3.15	6.2	–
	Hydroxyzine	Antihistamine	–	1.1	0.0914	3.43	15.12	–
	Ketoprofen	Analgesics	–	86.0	0.0213	3.12	4.45	2.12 × E-11
	Ranitidine	Antihistamine	–	68	0.0795	0.27	8.08	3.42 × E-15

Type	MP	Application	Average concentration (ng/L) [10, 11]		Solubility* (mg/mL)	log K_{ow} *	pKa*	Henry's constant (atm-m ³ /mole)*
			Surface water	WWTP effluent				
	Triclosan	Disinfectants	–	74.8	0.00605	5.53	7.9	4.99 × E-09
	Levamisole	Anthelmintics	–	40.6	1.44	1.84	6.98	4.03 × E-10
	Lincomycin	Antibiotics	–	31.2	29.3	0.56	12.37	3.00 × E-23
	Rosuvastatin	Statins	–	31.0	0.0886	1.47	4	–
	Mianserin	Antidepressant	–	1.5	0.232	3.52	6.92	–
	Clofibric acid	Lipid-lowering drugs	–	5.3	0.583	2.57	–4.9	2.19 × E-08
	Iohexol	Radiopaque contrast agents	–	158	0.796	–3.05	11.73	2.66 × E-29
	Memantine	Antidementia agents	–	22.8	0.0455	3.28	10.7	1.47 × E-05
	Sertraline	Antidepressant	–	2.1	0.000145	5.06	9.85	–
	Tiamulin	Antibiotics	–	3.3	–	–	–	–
	Clonazepam	Anticonvulsant	–	1.6	0.0106	2.41	11.89	7.02 × E-13
	Alprazolam	Antidepressant	–	1.3	0.0324	2.12	18.3	9.77 × E-12
	Fenofibrate	Lipid-lowering drugs	–	1.1	0.000707	4.86	–4.9	–
	Sulfadiazine	Antibiotics	–	3.5	0.601	–0.09	6.36	1.58 × E-10
	Tilmicosin	Antibiotics	–	3.1	–	–	–	–
	Cyproheptadine	Chemotherapeutic agents	–	3.9	0.0136	4.69	8.05	9.20 × E-09
Detergents, dishwashing liquids, personal care products (fragrances, cosmetics, sunscreens), and food products [11]	Methylbenzotriazole	Personal care product	–	2900	0.366	2.720	8.55	4.13 × E-07
	Gadolinium	Personal care product	–	115.0	–	–	–	–
	Loperamide	Personal care product	–	29.3	0.00086	4.44	13.96	–
	Buprenorphine	Personal care product	–	3.9	0.0168	4.98	8.31 at 25°C	1.76 × E-17
	Maprotiline	Personal care product	–	0.4	0.00015	4.89	10.54	–
	Duloxetine	Personal care product	–	0.1	0.00296	4.72	9.7	–
	Miconazole	Personal care product	–	0.2	0.000763	5.86	6.77	–
	Chlorpromazine	Personal care product	–	0.1	0.00417	5.18	9.3 at 25°C	3.95 × E-11
	Flutamide	Personal care product	–	0.1	0.00566	3.35	13.17	3.73 × E-10
	DEET, N, N'-diethyltoluamide	Personal care product	–	678.1	0.912	2.80	–	2.08 × E-08
	Caffeine	Food additives	–	191.1	11.0	–0.07	10.4 at 40°C	1.90 × E-19

Type	MP	Application	Average concentration (ng/L) [10, 11]		Solubility* (mg/mL)	log K_{ow} *	pKa*	Henry's constant (atm-m ³ /mole)*
			Surface water	WWTP effluent				
Pesticides [10]	Acesulfame	Food additive	4010	22500	588	-1.33	5.67	-
	Sucralose	Food additive	540	4600	22.7	-1.00	4.2	-
	Diazinon	Insecticide	15	173	0.04	3.81	2.6	1.13 × E-07
	Diethyltoluamide (DEET)	Insecticide	135	593	0.912	2.80		2.08 × E-08
	Dimethoate	Insecticide	22	-	25	0.78		1.05 × E-10
Biocides [10]	MCPA	Insecticides	-	149.9	0.63	3.25	3.13	1.33 × E-09
	Carbaryl	Insecticide	-	1.6	0.11	2.36	10.4	-
	2, 4-D	Herbicide	67	13	0.012	2.81	2.73	1.59 × E-07
	Carbendazim	Fungicide	16	81	0.029	1.52	4.2	2.12 × E-11
	Diuron	Herbicide	54	201	0.042	2.68		5.04 × E-10
	Glyphosate	Herbicide	373	-	12	-3.40	0.8	4.08 × E-19
	Irgarol (cybutryne)	Herbicide	3	30	-	-	-	-
	Isoproturon	Herbicide	315	12	0.065	2.87		1.12 × E-10
	MCPA	Herbicide	40	25	0.63	3.25	3.13	1.33 × E-09
	Mecoprop-p	Herbicide	45	424	0.62	3.13	3.1	1.82 × E-08
	Triclosan	Microbiocide	20	116	0.010	4.76	7.9	4.99 × E-09
	Terbutylazine	Herbicide	-	90.6	0.0085	3.21	2	3.72 × E-08
	Atrazine	Herbicide	-	4.2	0.0347	2.61	1.7	2.36 × E-09
	Terbutylazine-desethyl	Herbicide	-	68.8	-	-	-	-
	Isoproturon	Herbicide	-	10.1	0.065	2.87	-	1.12 × E-10
	Bentazone	Herbicide	-	9.6	0.5	2.34	2.92	2.18 × E-09
	Metolachlor	Herbicide	-	12.4	0.53	3.13	-	9 × E-09
	Dichlorprop	Herbicide	-	9.6	0.35	3.43	3.1	8.68 × E-11
	Simazine	Herbicide	-	26.3	0.0062	2.18	1.62	9.42 × E-10
	Atrazine-desethyl	Herbicide	-	13.8	3.2	1.51	-	1.53 × E-09
Chlortoluron	Herbicide	-	3.2	0.07	2.41	-	-	
Hexazinone	Herbicide	-	0.8	33	1.85	-	2.26 × E-12	
Linuron	Herbicide	-	40.1	0.075	3.20	-	-	

Type	MP	Application	Average concentration (ng/L) [10, 11]		Solubility* (mg/mL)	log K_{ow} *	pKa*	Henry's constant (atm-m ³ /mole)*
			Surface water	WWTP effluent				
	2, 4, 5-T	Herbicide	–	0.3	0.248	3.26	2.88	6.83 × E-09
Hormone active substances (effect on the hormone balance) [10]	Bisphenol A (BPA)	Additive	840	331	0.12	3.32	9.6	1 × E-11
	Estradiol	Natural estrogens	2	3	0.0213	4.01	10.33	3.64 × E-11
	Estrone	Natural estrogens	2	15	0.00394	3.13	10.33	3.8 × E-10
	Nonylphenol	Additive	441	267	0.00635	5.99	10.25	1.1 × E-06
	Perfluorooctane sulfonate (PFOS)	Tenside	–	–	3.1	6.28	0.14	–

“–”: Data are not available in the literature. *Solubility, log K_{ow} , pKa, and Henry's law constant for selected micropollutants are found in <http://www.drugbank.ca/>, <http://chem.sis.nlm.nih.gov/chemidplus/> and <https://pubchem.ncbi.nlm.nih.gov/>.

Table 1. Commonly found MPs in municipal wastewater effluent and surface water.

3. Fate and removal processes of MPs in wastewater

The municipal wastewater treatment plants (WWTP) are designed to remove most of the suspended solids, dissolved organics, and nutrients from the wastewater. WWTPs employ primary, secondary, and occasional tertiary treatment processes to optimally treat the incoming wastewater. In primary treatment, coagulants such as alum, ferric chloride, and polymers and polymeric coagulant aids are used to remove colloidal and suspended particulates. In the process, organics attached with dissolved humic substances and particles can also be removed. In secondary treatment, dissolved organics are removed aerobically by a consortium of microorganisms in suspension. The thickened sludge from both primary and secondary clarifiers is digested anaerobically (biosolids) prior to disposal. In some places, tertiary treatment processes such as activated carbon adsorption, ozonation, or filtration are adopted for final treatment of effluent to remove trace concentration of the organics.

The fate processes for MPs in a typical WWTP include adsorption on suspended particulates, dissolved humic substances, primary and secondary sludge, while the removal processes include coagulation and sedimentation, biodegradation, adsorption, advanced oxidation, and membrane filtration as shown in **Figure 1**. Volatilization of the MPs during any of the treatment steps is negligible due to their very low Henry's constant ($<10^{-5}$ atm-m³/mol) as shown in **Table 1**.

3.1. Fate: adsorption of micropollutants

Adsorption on suspended solids in both primary and secondary treatment units is an important fate process for MPs in wastewater. Adsorption may occur due to the hydrophobic interactions between the aliphatic and aromatic groups of the compounds with the fat and

lipid fractions in primary sludge and the lipophilic cell membrane of the microorganisms in secondary sludge, respectively. Electrostatic interactions also occur between the positively charged groups in the MPs and the negatively charged microorganisms in secondary sludge. Many acidic pharmaceuticals are negatively charged at neutral pH, and their sorption on sludge is negligible.

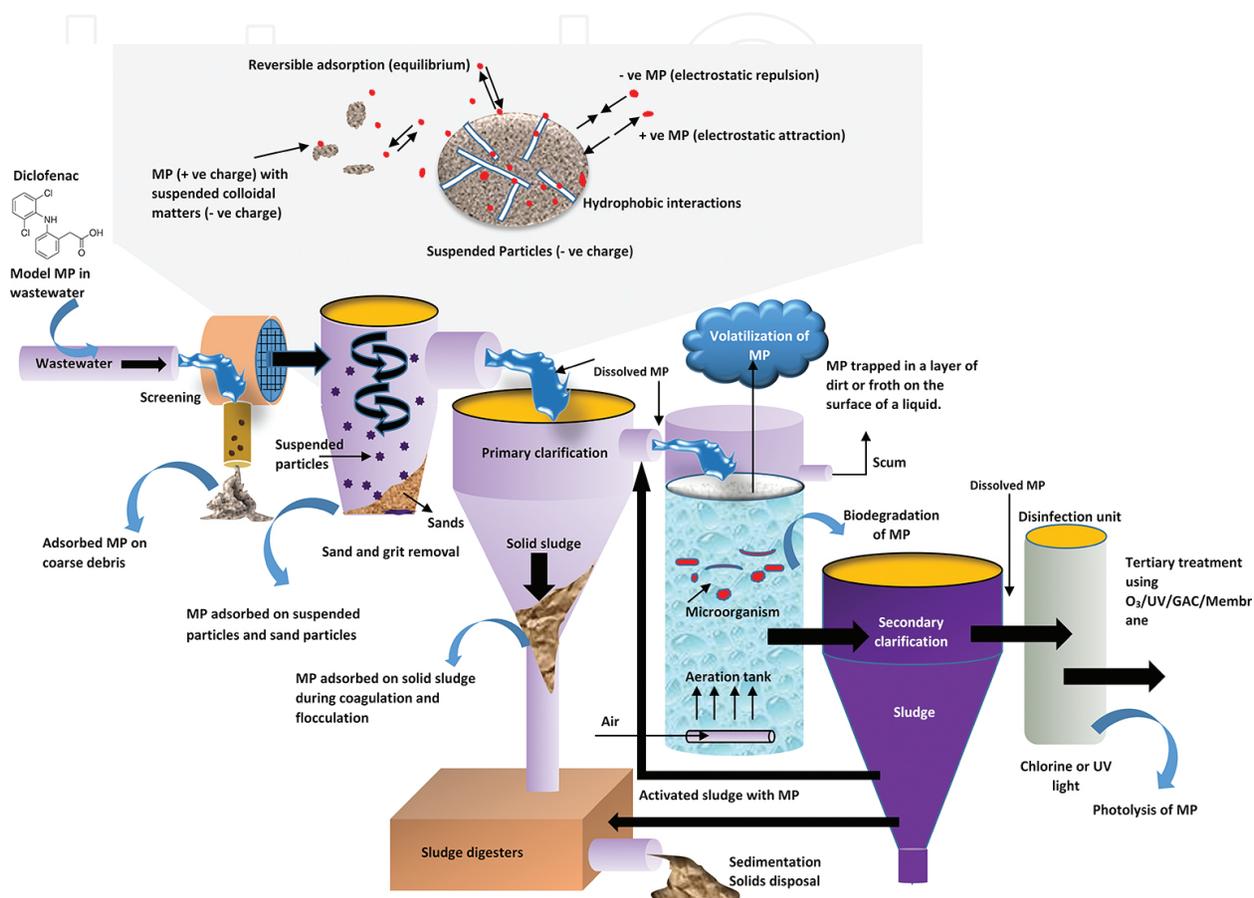


Figure 1. Conceptual model of fate and removal processes of a micropollutant in a typical WWTP.

With a nonpolar core and polar moiety, the properties of pharmaceuticals and antibiotics vary widely, making it difficult to estimate their sorption on sludge. Kinney et al. [12] analyzed nine different biosolids produced by municipal wastewater treatment plants in seven different states in U.S. for 87 different MPs, and the measured concentrations of the contaminants in various sludge were in the range of 64–1811 mg/kg dry weight. Nineteen different pharmaceuticals were detected in these biosolids, representing a wide range of physico-chemical properties, including compounds with low $\log K_{ow}$ and high water solubility values. Adsorption of MPs on biosolids did not exhibit any particular trend, and no correlation was found between organic carbon-normalized MPs concentrations in biosolids with $\log K_{ow}$, suggesting that organic carbon content of the biosolids may not be the only factor controlling MPs adsorption. It is generally expected that compounds with low water solubilities and large $\log K_{ow}$ values will more likely to be present in organic-rich biosolids compared to highly soluble organics; however, this study indicated significant presence of water soluble phar-

maceuticals in all nine biosolids. The 25 MPs detected in all nine biosolids had water solubility ranging from 1.3×10^{-5} to 8.28×10^4 mg/L, and $\log K_{ow}$ from 1.50 to 9.65 indicating complex nature of the process. Other factors, such as the quantity of organics entering the influent stream (which typically varies temporally and spatially), volume of influent, biosolids/water ratio, and sludge retention time (SRT), all affect the distribution of the MPs in different phases. Increasing sludge age had detrimental effect on the adsorption of lindane [13] on activated sludge, adsorption of pentachlorophenol reduced from 40 to 60% at sludge ages below 4 days to less than 10% at sludge ages above 25 days [14].

The concentrations of some of the commonly found MPs in sludge are summarized in **Table 2**.

MP	Type/application	Concentration (mg/kg)	Source	Reference
Triclosan	Personal care product	0.41–46	Sludge (primary, excess activated, anaerobically digested)	Heidler & Halden [15], McAvoy et al. [16]
Triclocarban		4.7–63	Sludge (excess activated, anaerobically digested)	Heidler & Halden [15], Clara et al. [17]
Tonalide		0.4–2.9		
Galaxolide		4.2–21		
Cashmerane		0.022–0.26		
Celestolide		0.023–0.061		
Phantolide		0.010–0.014		
Traesolide		0.29–1.75		
Octocrylene		1.01–1.32		Kupper et al. [18]
Octyl-triazone		2.6–3.04		
Octyl-methoxycinnamate		0.15–1.5		
Pipemidic acid	Antibiotic	0.04–0.27	Sludge (primary, excess activated, dewatered)	Jia et al. [19]
Fleroxacin		0.02–0.09		
Ofloxacin		0.33–7.79		
Enrofloxacin		0.02–0.07		
Lomefloxacin		0.06–1		
Sarafloxacin		0.39–0.13		
Gatifloxacin		0.09–0.42		
Sparfloxacin		0.01–0.04		
Moxifloxacin		0.17–0.56		

MP	Type/application	Concentration (mg/kg)	Source	Reference
Norfloxacin		1.06–7.23	Sludge (primary, excess activated, anaerobically digested, dewatered)	Jia et al. [19], Golet et al. [20]
Ciprofloxacin		0.22–3.1		
Azithromycin		2.5–64	Sludge (excess activated, anaerobically digested)	Gobel et al. [21]
Clarithromycin		0.7–67		
Erythromycin		0.030–0.041	Sludge, Class A & B biosolids	Kinney et al. [12], Ding et al. [22]
Roxythromycin		0.337–1.446	Anaerobically digested dewatered sludge	Nieto et al. [23]
Sulfamethoxazole		0.019–68	Sludge (excess activated, anaerobically digested), biosolids	Gobel et al. [21], Nieto et al. [23], Ding et al. [22]
Sulfapyridine		0.1–28	Sludge (excess activated, anaerobically digested)	Gobel et al. [21]
Sulfamethazine		0.026–0.128	Anaerobically digested dewatered sludge, biosolids	Nieto et al. [23], Ding et al. [22]
Sulfamerazine		0.112–0.669	Biosolids from sewage	Ding et al. [22]
Chlortetracycline		0.069–0.346	sludge	
Oxytetracycline		0.052–0.743		
Demeclocycline		0.036–0.131		
Tetracycline		0.282–1.914		McCellan & Halden [24],
Doxycycline		0.225–0.966		Ding et al. [22]
Trimethoprim		0.017–41	Sludge (excess activated, anaerobically digested)	Gobel et al. [21], Nieto et al. [23]
Clindamycin		nd–0.006	Municipal sludge	Subedi et al. [25]
Lincomycin		0.006–0.174	Municipal sludge, biosolids	Ding et al. [22], Subedi et al. [25]
Tiamulin		nd–0.7	Agricultural Field soil	Schlussener et al. [26]
Tylosin		1.074–1.958	Anaerobically digested dewatered sludge	Nieto et al. [23]
Acetaminophen	Analgesic	0.013–0.419		
Carbamezipine		0.011–0.042		

MP	Type/application	Concentration (mg/kg)	Source	Reference
Diclofenac		nd–0.087		
Ibuprofen		0.024–0.144		
Naproxen		nd–0.057		
Ketoprofen		0.030–0.336	Activated sludge	Radjenovic et al. [27, 28]
Codeine		nd–0.022	Sludge, class A biosolids	Kinney et al. [12]
Metoprolol	β -blocker	nd–0.021	Anaerobically digested dewatered sludge	Nieto et al.[23]
Propranolol		0.026–0.044		Radjenovic et al. [28]
Atenolol		0.007–0.084	Sewage sludge	Radjenovic et al. [28]
Caffeine	Psychoactive drug	0.050–0.074	Anaerobically digested dewatered sludge, biosolids	Nieto et al.[23], Ding et al. [22]
Diltiazem	Antihypertension drug	nd–0.059	Sewage sludge, class A biosolids	Kinney et al. [12]
Fluoxetine	Antidepressant	0.072–1.5		Radjenovic et al. [28]
Paroxetine		0.04–0.62	Sewage sludge	Radjenovic et al. [28]
Gemfibrozil	Lipid lowering drug	0.118–0.420	Sewage sludge, class A biosolids	Kinney et al. [12], Radjenovic et al. [28]
Bezafibrate		nd–0.013	Anaerobically digested dewatered sludge	Nieto et al. [23]
Clofibric acid		0.007–0.01		
Thiabendazole	Antiparasitic drug	nd–5	Sewage sludge, class A biosolids	Kinney et al. [12]
Warfarin	Anticoagulant	nd–0.092		
Cimetidine	Antacid	nd–0.071		
Diphenhydramine	Antihistamine	0.015–7		
Miconazole	Antifungal drug	nd–0.46		
Famotidine	Antacid	0.03–0.050	Sewage sludge	Radjenovic et al. [28]
Loratadine	Antiallergic drug	0.052–0.153		
Hydrochlorothiazide	Diuretic drug	0.011–0.060		
Glibenclamide	Antidiabetic drug	0.013–0.127		

nd- not detected

Table 2. Concentrations of commonly found MPs in sludge.

Although a complex process as described above, the extent of MPs adsorption on sludge is traditionally modeled using linear equilibrium model as

$$C_{\text{ads}} = K_d C_{\text{ss}} C_{\text{dis}} \quad (1)$$

where C_{ads} is the adsorbed concentration of the MP (g/L), C_{ss} is the suspended particulate concentration (g/L), C_{dis} (g/L) is the dissolved concentration, and K_d is the adsorption constant (L/gss), which is also known as the partition coefficient of the compound between the solids and water. K_d has been proposed as a relatively accurate indicator of adsorption [29, 30]; for compounds with a K_d value below 300 L/kg ($\log K_d = 2.48$), the sorption onto secondary sludge is insignificant. Polar compounds typically have higher K_d values in secondary sludge compared to primary sludge. Typical K_d values are presented in **Table 3**. K_d of a compound can be correlated to more fundamental properties such as K_{ow} .

Micropollutants	$\log K_{\text{ow}}^*$	$\log K_d$	$\log K_{\text{oc}}$	Ref [#] .	Micropollutants	$\log K_{\text{ow}}^*$	$\log K_d$	$\log K_{\text{oc}}$	Ref [#] .
Diclofenac	4.98	1.2041	–	b	Estradiol	4.01	2.2304	–	c
Ibuprofen	3.5	0.8513	–	b	Estriol	2.45	1.7324	–	c
DEET	2.18	1.91	2.27	a	Diphenhydramine	3.27	2.5	2.86	a
Clofibric acid	2.57	0.6812	–	b	Estrone	3.13	2.2304	–	c
Ifosfamide	0.86	0.1461	–	b	Ethinylestradiol	3.67	2.4997	–	c
Carbamazepine	2.45	1.95	2.31	a	Fenoprofen	3.1	1.415	–	c
Hydrocodone	2.16	2.03	2.38	a	Fluoxetine	4.05	0.699	–	c
Cyclophosphamide	0.63	0.3802	–	b	Amitriptyline	4.92	2.87	3.21	a
Gemfibrozil	4.77	2.11	2.47	a	Gemfibrozil	3.4	1.2856	–	c
Diazepam	2.82	1.3222	–	b	Hydrocodone	1.2	2.0294	–	c
Diazepam	2.82	2.14	2.53	a	Fluoxetine	4.05	3.08	3.43	a
Ethinylestradiol	3.9	2.5428	–	b	Indomethacine	4.27	1.4472	–	c
Naproxen	3.2	2.16	2.56	a	Ketoprofen	3.12	1.2041	–	C
Perfluorooctanoic acid	6.3	2.3424	–	c	Mefenamic acid	5.12	2.6375	–	C
Diclofenac	4.51	2.18	2.54	a	Methadone	3.93	1.8808	–	C
Perfluorononanoic acid	5.48	3.0934	–	c	Metoprolol	1.88	1.8129	–	C

Micropollutants	log K_{ow}^*	log K_d	log K_{oc}	Ref. [#]	Micropollutants	log K_{ow}^*	log K_d	log K_{oc}	Ref. [#]
Perfluoroundecanoic acid	6.9	3.3581	–	c	Morphine	0.89	1.0792	–	C
Ketoprofen	3.12	2.25	2.64	a	Naproxen	3.18	1	–	C
Bisphenol A	3.32	2.28	2.64	a	Primidone	0.91	1.699	–	C
Amoxicillin	0.87	0.0253	–	c	Propranolol	3.48	2.5353	–	C
Amitriptyline	4.92	2.8698	–	c	Risperidone	2.5	2.73	–	C
Trimethoprim	4.9	2.3	2.65	a	Roxithromycin	1.7	1.7076	–	C
Androstenedione	2.75	2.1271	–	c	Sotalol	0.24	1.2553	–	C
Aspirin	1.19	0.3464	–	c	Sulfadimethoxine	1.63	0.4771	–	C
Ibuprofen	3.97	2.32	2.64	a	Sulfamethazine	0.89	1.301	–	C
Atorvastatin	5.7	1.9685	–	c	Sulfamethoxazole	0.89	1.0414	–	C
Azithromycin	4.02	2.4472	–	c	Sulfapyridine	0.35	0	–	C
Bezafibrate	3.97	1.9395	–	c	Testosterone	3.32	2.1335	–	C
Benzophenone	3.18	2.1335	–	c	Tramadol	2.4	1.6721	–	C
Bisoprolol	1.87	1.6021	–	c	Trimethoprim	0.91	1.4048	–	C
Dilantin	2.47	2.49	2.84	a	Triclosan	4.76	3.59	3.95	A
Celiprolol	2.29	1.9294	–	c	Triclocarban	4.9	4.41	4.76	A
Clarithromycin	3.16	2.415	–	c	Diazepam	2.82	1.301	–	C
Clofibric acid	2.84	0.699	–	c	Diphenhydramine	3.27	2.4997	–	C
Codeine	1.19	1.1461	–	c	Erythromycin	2.37	1.4456	–	C

“–”: Data are not available in the literature. *log K_{ow} for selected MPs are found in <http://www.drugbank.ca/>. [#] log K_d and log K_{oc} values are collected from references (Ref.) as follows: (a) [31], (b) [30], (c) [32].

Table 3. log K_d and log K_{oc} values of some commonly found MPs.

As mentioned before, the sorption to sludge is not significant for compounds with log $K_{ow} < 2.5$, moderate sorption for log K_{ow} between 2.5 and 4, and high sorption for log $K_{ow} > 4.0$ is expected. In absence of experimental data, to relate K_d with K_{ow} , Eqs. (2) and (3) are given by Matter-Muller et al. [33] and Dobbs et al. [34], respectively:

$$\log K_d = 0.67 \times \log K_{ow} + 0.39 \quad (2)$$

$$\log K_d = 0.58 \times \log K_{ow} + 1.14 \quad (3)$$

K_d can also be estimated using Eq. (4) (Fetter [35]) and Eq. (5) (Jones et al. [36]) if the fraction of organic carbon of the solids is known as

$$K_d = f_{oc} \times \frac{10^{0.72 \times \log K_{ow} + 0.49}}{1000} \quad (4)$$

$$K_d = f_{oc} \times 0.41 \times K_{ow} \quad (5)$$

values of K_d and K_{oc} versus K_{ow} for MPs from the literature are plotted in **Figure 2** showing slightly lower linear dependence of K_d and K_{oc} on K_{ow} as compared to Eqs. (2) and (3). In addition, the goodness of fit as indicated by R^2 is in the range of 0.45–0.48, indicating possible influence of other parameters than only K_{oc} or K_{ow} .

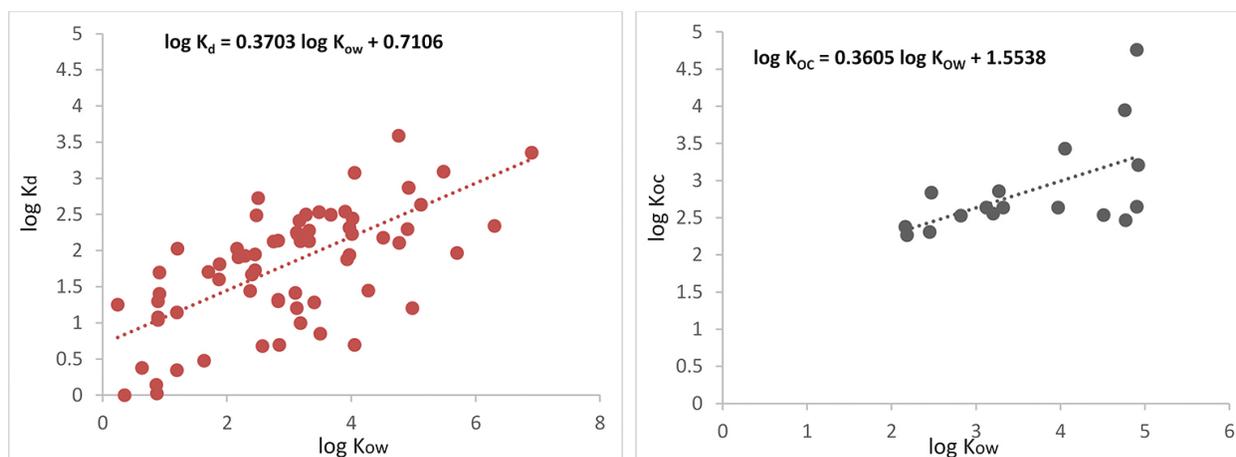


Figure 2. Correlation between $\log K_d$ versus $\log K_{ow}$ and $\log K_{oc}$ versus $\log K_{ow}$ for MPs listed in **Table 3**.

MP adsorption on sludge mostly follow linear isotherm such as Freundlich:

$$q_e = K_f \cdot C_e^{1/n} \quad (6)$$

where q_e = mass adsorbed per unit mass of adsorbent at equilibrium (mg/g)

C_e = concentration of MP in water at equilibrium (mg/L)

$\frac{1}{n}$ = strength of adsorption (dimensionless)

K_f = adsorption capacity at unit concentration (mg/g)(L/mg)^{1/n}

The values of K_f and $1/n$ for MPs on sludge varied from 0.0052 to 4.40 (mg/g) (L/mg)^{1/n} and 0.51 to 1.0076, respectively [37–40]. Larger K_f values indicate higher affinity of adsorption for a particular sludge and closer the value of $1/n$ around 1.0, greater is the indication of comparatively strong adsorption bond. Typically, adsorption equilibrium is achieved within 24 hours with almost 90% removal from dissolved phase occurs in an hour; for example, at 3.6 g/L mixed liquor suspended solids (MLSSs) concentration, 95% of oxytetracycline was removed from water within only 1 hour and the concentration at equilibrium remained unchanged over 24 hours [40].

Colloidal particles are a relatively small fraction of the total waterborne particle mass (<10%) in typical wastewater but possess large surface areas which can enable covalent, electrostatic, and hydrophobic binding of MPs depending on their polarity. The magnitude of sorption depends on the molecular weight distribution and aromatic content of the colloids fraction, which also depends on the sewage composition, strength, and sludge age [41]. Similar to adsorption on suspended particulates, adsorption on colloidal particles can be quantified using a distribution coefficient K_{coc} . Holbrook et al. [41] determined K_{coc} using pyrene as a model MP and colloidal fractions from two biological wastewater plants; sorption coefficients (K_{coc}) for pyrene ranged from 1×10^3 L/kg colloids to 80×10^3 L/kg colloids and were comparable to values obtained in the literature for natural organic matter. Good correlation was obtained between K_{coc} and the aromaticity of the colloidal particles.

3.2. Removal processes

3.2.1. Coagulation and sedimentation of micropollutants

Coagulation-flocculation processes are typically used for improving efficiency of wastewater treatment plants promoting the removal of suspended solids, colloids, and some dissolved organics, which do not settle spontaneously. The coagulation process works by destabilizing the colloids/emulsions using coagulants such as metal salts and/or synthetic organic polymers following any of the mechanisms such as double-layer compression, adsorption and charge neutralization, entrapment of particles in precipitate, adsorption and interparticle bridging. The parameters that affect the performance of coagulation are coagulant dosage, pH, and ionic strength of the solution. Based on the type of coagulant such as aluminum sulfate, ferrous sulfate, and ferric chloride, optimum pH range for coagulation varies between 4.0 and 8.5. In case of polymeric coagulants, the active group (carboxyl, amino group, etc.) present on the polymer influences the change of charge with pH [42].

In general, removal of MPs by coagulation-flocculation processes is not very effective for most of the compounds studied with a few exceptions. Earlier studies on removal of MPs by coagulation were reported for simulated drinking water treatment processes [43–47], and

percent removal of various MPs varied from 15 to 75% using alum and iron salts, and excess lime/soda ash softening. Vieno et al. [46] evaluated the role of dissolved organic matter, mainly the humic substances in the coagulation process. In the presence of dissolved humic matter, diclofenac, ibuprofen, and bezafibrate could be removed by ferric sulfate coagulation. The removal of diclofenac reached a maximum of 77%, while 50% of ibuprofen, and 36% of bezafibrate were removed. Hence, a high amount of high-molecular-weight dissolved organic matter enhanced the removal of ionizable pharmaceuticals. However, contradictory results were reported by Choi et al. [43] where removal of seven tetracycline classes of antibiotic (TAs) from synthetic and river water using coagulation was achieved. TAs were assumed to be removed through the charge neutralization of zwitterionic or negative TAs by cationic Al (III) and sweep coagulation using poly-aluminum chloride (PACl). Aluminum hydroxide precipitates were formed in the presence of sufficient alkalinity, and TAs were removed by being enmeshed into or adsorbed onto the precipitates. It was suggested that the presence of dissolved organic matter, especially the low-molecular-weight fractions, resulted in possible inhibition of MP removal. This was due to preferential removal of the organic matter by the coagulant.

Huerta-Fontela et al. [48] performed coagulation with alum-coagulants, flocculation with a diallyldimethyl ammonium chloride homopolymer (poly-DADMAC), followed by clarification through sand filters. Of the 55 pharmaceutical compounds present, only five compounds (chlordiazepoxide, zolpidem, bromazepam, clopidogrel, and doxazosin) were completely removed, while warfarin, betaxolol, and hydrochlorothiazide accounted for removals higher than 50%. For some pharmaceuticals such as irbesartan, losartan, or carbamazepine epoxide, negligible removals were obtained.

Suarez et al. [49] evaluated the performance of coagulation-flocculation process for the pretreatment of hospital effluent, both in a batch mode and continuous pilot scale. Highest removal efficiency (>90%) was reported for PPCPs such as galaxolide, tonalide, and synthetic musk (ADBI); these are lipophilic compounds, carrying high negative charge, which facilitates their coagulation in the presence of higher fat content in wastewater. Asakura and Matsuto [50] studied the effect of coagulation for treating landfill leachate. Out of the various EDCs, only nonylphenol showed a removal of >90%, whereas diethylhexylphthalate (DEHP) removal was about 70%. Other EDCs such as diethylphthalate (DEP), dibutylphthalate (DBP), butylbenzylphthalate (BBP), 4-t-octylphenol (4tOP), and 4-n-octylphenol (4nOP) showed poor removal (<50%) by coagulation, with the lowest removal of 20% for bisphenol A.

Few studies have reported the removal of MPs due to coagulation and flocculation in wastewater (**Table 4**). Matamoros and Salvadó [51] evaluated several MPs removal in a coagulation/flocculation-lamellar clarifier for treating secondary effluent. The hydrophobicity of the compounds ($\log K_{ow}$) was found to be a major factor in determining the removal efficiency with coagulation-flocculation. The highest removal of 20–50% was observed for the compounds with $\log K_{ow} \geq 4$ at pH 7–8. Since adsorption of MPs on the suspended solids and colloids is the precursor step for their removal during coagulation, the removal efficiency can be tied with the removal efficiency of suspended solids as

$$\% \text{ removal} = \frac{K_d C_{SS}}{1 + K_d C_{SS}} E_{TSS} \quad (7)$$

where E_{TSS} is the efficiency of TSS removal (%) during coagulation.

Carballa et al. [52] observed that during coagulation-flocculation of primary wastewater, lipophilic compounds such as musks were adsorbed in the lipid fractions of the sludge with two different fat concentrations of 60 and 150 mg/L, while acidic compounds such as diclofenac were adsorbed due to electrostatic interaction. Compounds with high sorption properties (galaxolide and tonalide) and diclofenac were significantly removed during coagulation-flocculation with efficiencies around 70%. Compounds with lower K_d values, such as diazepam, carbamazepine, ibuprofen, and naproxen, were reduced to a lesser extent (up to 25%).

Coagulant	Dosage(ppm) with pH	compound	Source	Removal (%)	Reference
Ferric chloride/ aluminum sulfate	25, 50–pH 7	Ibuprofen	Hospital wastewater	12.0 ± 4.8	Suarez et al. [49]
		Diclofenac		21.6 ± 19.4	
		Naproxen		31.8 ± 10.2	
		Carbamazepine		6.3 ± 15.9	
		Sulfamethoxazole		6.0 ± 9.5	
		Tonalide		83.4 ± 14.3	
		Galaxolide		79.2 ± 9.9	
Ferric chloride	100, 200–pH(4, 7, 9)	Bisphenol A	Landfill leachate	20	Asakura and Matsuto [50]
		DEHP		70	
		Nonylphenol		90	
	Not mentioned	Drinking water treatment plant	Sulfamethoxazole	33	Stackelberg et al. [47]
			Acetaminophen	60	
			Cholesterol	45	
			Diazenon	34	
Aluminum sulfate	200–pH 7	Aldrin	Surface water	46	Thuy et al. [53]
	100–pH 7	Bentazon		15	
	78–pH 6.8	Drinking water treatment plant	Estradiol	2	Westerhoff et al. [45]
			Estrone	5	
			Progesterone	6	
			Fluoxetine	15	
			Hydrocodone	24	
			Chlordane	25	
			Benzantracene	26	
			Chrysene	33	
			Erythromycin	33	
			DDT	36	

Coagulant	Dosage(ppm) with pH	compound	Source	Removal (%)	Reference
		Heptachlor		36	
		Aldrin		49	
		Benzofluoranthine		70	
		Benzopyrene		72	
Ferric sulfate	78.5–pH 4.5	Dichlofenac	Lake water with dissolved humic acid	77	Vieno et al. [46]
		Ibuprofen		50	
		Bezafibrate		36	
		Carbamazepine		<10	
		Sulfamethoxazole		<10	
–	–	Celestolide	Secondary effluent from WWTP	50	Matamoros and Salvadó [51]
		Tricholsan		24	
		Octylphenol		50	
		Tonalide		24	
		DMP		19	
		Galaxolide		16	
		Ibuprofen		4	
		Carbamazepine		2	

“–”: Data are not available in the literature. *log K_{ow} for selected MPs are found in <http://www.drugbank.ca/>. # log K_d and log K_{oc} values are collected from references (Ref.) as follows: (a) [31], (b) [30], (c) [32].

Table 4. Removal of MPs by coagulation/flocculation process from various effluents.

3.2.2. Biodegradation of micropollutants in secondary treatment

Most of the conventional municipal WWTPs do not remove complex MPs by biodegradation and/or biotransformation effectively. Observed removal efficiencies vary in a wide range for different compounds, as well as for the same substance, due to operational conditions such as aerobic, anaerobic, anoxic, sludge retention time (SRT), pH, redox potential, and water temperature. Membrane bioreactors (MBRs) seem to be more effective than conventional-activated sludge (CAS) process as MBR process combines biological treatment with membrane filtration (micro and ultrafiltration). In addition, due to higher SRT at MBRs compared to CAS, biodiversity of the microorganisms in MBR is greater than CAS, and opportunity for adaptation of specific microorganisms to the persistent compounds is greater in MBR than in CAS. Removal of 29 antibiotics in a CAS process was reviewed by Verlicchi et al. [54], where removal of compounds such as sulfamethoxazole, ciprofloxacin, roxithromycin, norfloxacin, erythromycin, etc., varied in a wide range of 0 (spiramycin) and 98% (cefaclor) in CAS and between 15 (azithromycin) and 94% (ofloxacin) in MBRs. Only 1 (azithromycin) out of 10 compounds investigated in both systems exhibited higher average removal efficiency in CAS than in MBR. Trinh et al. [55] traced 48 MPs including steroidal hormones, xenoestrogens, pesticides, caffeine, pharmaceuticals, and personal care products (PPCPs) in a MBR with >90% removal for many of the compounds. However, amitriptyline, carbamazepine, diazepam, diclofenac, fluoxetine, gemfibrozil, omeprazole,

sulphamethoxazole, and trimethoprim were only partially removed in MBR with the removal efficiencies of 24–68% [55]. Similar results were obtained in a pilot-scale MBR operated for a Swiss hospital effluent for 1 year [56, 57]. Among the 56 pharmaceuticals, an overall load elimination of all pharmaceuticals and metabolites in the MBR was only 22% due to the presence of persistent iodinated contrast media (almost 80% of the total organic load). Weiss and Reemtsma [58] reported that major advantage of MBR lies for the compounds with moderate removal in CAS; MBR showed no advantages for both well-degradable and recalcitrant compounds. For polar compounds, MBR does not provide significant benefits, because effluent quality is improved only gradually and the most critical components of high aerobic stability remain almost unaltered [58].

Longer SRT as required for nitrogen removal also played an important role in reducing the concentrations of certain MPs [59, 60], and a SRT > 10 days was recommended. Longer SRTs resulted in diverse growth of the microbial community including the growth of nitrifying bacteria. Nitrifying bacteria had shown potential for cometabolic degradation of MPs [61, 62]. However, much longer SRT (49 days) was required for 61% removal of iopromide compared to zero removal in CAS [61]. Mixed bacterial cultures also have proved to be quite effective in removing MPs such as triclosan, BPA, and ibuprofen in river [63, 64] and WWTP [65, 66]. While MPs such as quaternary ammonium compounds are biodegraded as single compound, their biodegradation is inhibited in a mixture using *Pseudomonas* sp. isolated from returned activated sludge [67].

Although an important process variable, hydraulic retention time (HRT) shows varied results for the removal of MPs in WWTP indicating that further research is required on this. A study conducted by Wever et al. [57] reported that decreasing the HRT in a CAS resulted in increasing the concentrations of MPs such as 2, 6 and 1, 6 NDSA; however, it did not affect the percent removal of these compounds in a MBR. In case of pharmaceutical and fragrance compounds, Joss et al. [29] reported that HRT played a very minor role when considering a time period of 0.7 hours for fixed bed reactor, 13 hours for a MBR, and 17 hours for a CAS process.

Solution pH plays a significant role in the removal of MPs as the highly acidic or highly basic solutions affect the solubility of the MPs and also hinder growth of the microbial community [68]. As listed in **Table 1**, MPs exhibit a wide range of pKa values. At pH range of 6–8, as found in most wastewater, many antibiotics and other MPs with pKa values in this range will be ionized. For example, about 40% of pharmaceuticals contain at least one functional group with pKa values in the range of 5–10 [69]. The degree of speciation of such ionizable compounds and their subsequent adsorption and biotransformation will be affected by pH.

The microbial growth and activity, as well as solubility and other physicochemical properties of MPs, are significantly affected by temperature. Temperature variability has been related to deterioration in bulk water quality and system instability; it has also been linked to sludge deflocculation and decreased sludge metabolic activity [70]. Vieno et al. [71] reported that the removal of ibuprofen, diclofenac, benzaifibrate, ketoprofen, and naproxen increased during the summer (average temperature 17°C) and decreased in the winter (average temperature 7°C). However, Lesjean et al. [72] reported that in a conventional WWTP, temperature variation

between 12 and 25°C brought about little or no change to the degradation process of MPs whereas for a MBR the removal rates were greatly affected by the seasonal changes. Hai et al. [70] reported that the removal of most hydrophobic compounds ($\log K_{ow} > 3.2$) in a MBR was stable in the temperature range of 10–35°C, while for less hydrophobic compounds, significant variation occurred in the lower temperature regimes (10–35°C). Lower and more variable removal efficiency at 10°C was observed for certain hydrophilic compounds, which have been reported to be moderately recalcitrant in MBR treatment.

No quantitative relationship between structure and activity can be found for the biological transformation. Overall, it can be concluded that for compounds with a sorption coefficient (K_d) below 300 L/kg, sorption onto secondary sludge is not relevant, and their transformation can consequently be assessed simply by comparing influent and effluent concentrations.

At low dissolved concentration, the kinetics of biodegradation/biotransformation of MPs follow first order as

$$\text{rate} = K_{\text{bio}} C_{\text{ss}} C_{\text{dis}} \quad (8)$$

where K_{bio} is the biodegradation rate constant, C_{ss} is the suspended solids concentration, and C_{dis} is the dissolved concentration of MPs_{ss}. Typically, complex aromatic structure with more than one benzene ring and/or with chlorine and nitro groups are not efficiently biodegraded [32, 73]. The aerobic biodegradation constants of 20 aromatic species using activated sludge were reported, and the kinetic constants were correlated to the structure of the molecules [73]. The normalized first-order rate constants K_{bio} (L/gss/h) using C_{ss} (g/L) were 0.003, 0.02, and 3.80 for 3, 5 dinitrobenzoic acid, 2, 6 dichlorophenol, and benzoic acid, respectively. Pomiesa et al. [32] summarized a list of both aerobic and anaerobic rate constants for 20 pharmaceuticals including antibiotics, and other compounds such as bisphenol A and nonylphenol, and the aerobic K_{bio} (L/gss/h) varied from 0.0025 to 7.08 with carbamazepine being the lowest, and galaxolide (a synthetic fragrance) being the highest biodegradable compound. The difference in rate constants for aerobic and anaerobic conditions is less than 15% for some substances (e.g., celestolide and galaxolide) or can be much higher in some other cases (e.g., >50% for estradiol and roxithromycin). Compounds with $k_{\text{bio}} < 0.0042$ L/gss/h are not removed significantly (<20%), whereas compounds with $k_{\text{bio}} > 0.4$ L/gss/h can be transformed by >90%. Therefore, with the existing biological treatment schemes in municipal wastewater, 90% of the MPs are not removed or biotransformed. Many of the plant data do not distinguish between adsorption and biotransformation due to challenging chemical analyses. In most cases, overall removal is estimated based on the influent and effluent concentrations, and information about the intermediate steps is either missing or not reliable [74]. Other challenges are the fate of metabolites, transformation products of pharmaceuticals, and complex chemistry involving these compounds with background water quality, which are all unknown at this point.

Tertiary treatment of wastewater using various combinations of membrane processes, activated carbon adsorption, and advanced oxidation are being performed or characterized in various jurisdictions with stringent water quality requirements. Above technologies all work well for the removal of trace concentration of organics in lab studies and will be described below.

3.2.3. Activated carbon adsorption

Adsorption as a unit operation using either granular- or powder-activated carbon (GAC and PAC) to remove organics from water metrics is well established. The mechanism of adsorption, relevant parameters, and adsorption models discussed in the section of adsorption on sludge are applicable for GAC and PAC adsorption. In absence of experimental data on adsorption isotherm, a correlation developed by Crittenden et al. [75] combining Polanyi potential theory and linear solvation energy relationships (LSERs) can be used.

Activated carbon adsorption for the removal of MPs has been applied in both secondary and tertiary treatment units. Simultaneous adsorption of sulfamethoxazole and carbamazepine to powdered-activated carbon (PAC) in a membrane bioreactor (MBR) was reported at PAC dosage of 0.1–1 g/L [76–78]. Altmann et al. [77] compared the performance of PAC and ozonation for seven MPs from four different wastewater plants. Typical dosages were about 20 mg/L of PAC and 5–7 mg/L of ozone, respectively, and the performances of both technologies were very much dependent on the type of pollutants. Hydrophobic compounds with $\log K_{ow} > 5$ have much better removal potential by adsorption than polar compounds, with the exceptions of some protonated bases and deprotonated acids. Empty bed contact time (EBCT) for a biological-activated carbon filter for the removal of numerous MPs for three full-scale reclamation plants varied from 9 to 45 min.

3.2.4. Membrane processes

Membrane-based process systems can be classified as direct membrane-based, integrated membrane-based, and combined direct and integrated membrane system. Pressure-driven membrane filtration processes, such as nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), and reverse osmosis (RO), are routinely used for various effluent treatments. While MF and UF are low-pressure processes, NF and RO are high-pressure processes. In tertiary treatment of wastewater for MPs, UF and NF can be effectively used. The removal of MPs by membrane depends on many different factors including characteristics of membrane, MP, aqueous media/solute characteristics, operating conditions, and membrane fouling. The fundamental mechanism of membrane filtration is size exclusion, although adsorption due to hydrophobic interactions, electrostatic repulsion, and adsorption on fouling layer all can play a part [79–82]. Size exclusion mechanism is mostly applicable to noncharged MPs, however, shape of the molecule should also be taken into consideration. Hydrophobic interaction and hydrogen bonding contribute to the adsorption of MPs on the membrane surface. Membrane fouling and the presence of dissolved organic carbon could also increase adsorption by changing the membrane surface characteristics and pore size. For charged MP, electrostatic interaction between the compound and membrane surface gives rise to electrostatic exclusion

for membrane surfaces with like charges. **Figure 3** shows the four mechanisms of MP removal by membrane processes. Membrane-based processes have several advantages such as good adaptability, high removal rate, robustness, and no harmful intermediates are formed. An overview of research at laboratory, pilot and full-scale applications of MPs removal is presented in **Table 5**.

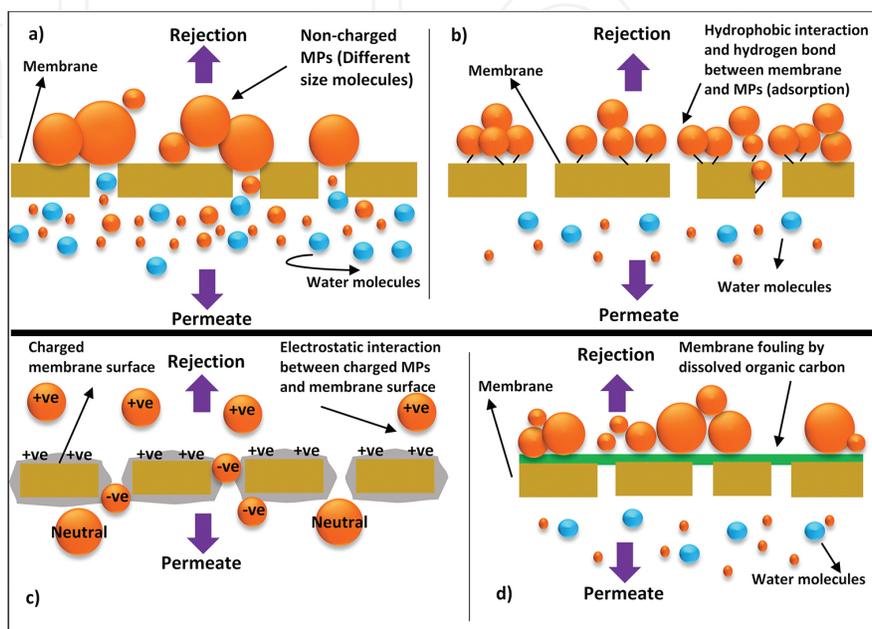


Figure 3. Micropollutants removal mechanism in polymeric membranes. (a) size exclusion, (b) adsorption (hydrophobic interaction), (c) electrostatic repulsion, and (d) adsorption (fouling layer interaction) (concept adopted from Ojajuni et al. [83]).

MPs	% Removal	Remarks	Reference
11 MPs 500 µg/L, (pharmaceuticals and pesticides)	>70%	UF and NF; laboratory scale; secondary effluent	Acero et al. [84]
80 MPs; Metals 18–265 µg/L, VOC 0.65–7.10 µg/L, PAH 0.23–0.67 µg/L, and HVOC 1.45–12.17 µg/L	~40–50% removal for metals	UF; full scale; secondary clarified effluent	Battistoni et al. [85]
Macrolides, roxithromycin (ROX), clarythromycin (CLA), erythromycin (ERY), sulfonamides, and trimethoprim:sulfamethazine (SMZ), sulfamethoxazole (SMX), and trimethoprim (TMP)	45–94%	Full scale UF; raw sewage of WWTP	Sahar et al. [86]
Pharmaceutically active contaminants (PhACs): sulfamethoxazole, carbamazepine, and Ibuprofen (500 µg/L)	50–85%	NF; laboratory scale; spiked synthetic solution	Nghiem et al. [87]
EDCs—estrone, estradiol, and salicin at initial concentration of 1 mg/L	85±4% for estradiol, 65±3% for estrone, 91±1% for salicine	NF; laboratory scale; spiked synthetic solution	Braeken and Van der Bruggen [88]

MPs	% Removal	Remarks	Reference
Pesticide endosulfan (10–100 µg/L)	84–96%	NF; laboratory scale; spiked synthetic solution	De Munari et al. [89]
11 neutral EDCs and PhACs at initial concentration of 100 µg/L	0–91%	RO; laboratory scale; synthetic solution	Kimura et al. [90]
22 EDCs and pharmaceutically active compounds (PhAC)- ~ 1 µg/L	variable removal in NF; >90% removal in RO	Loose and tight NF; RO; bench scale; surface water; effluent of MBR of WWTP	Comerton et al. [91]
PhACs: carbamazepine, diclofenac, and ibuprofen (IBU) 1 concentration 0.025–0.1 µg/L	31–39% removal for carbamazepine; 55–61% removal of ionic diclofenac and ibuprofen	NF; laboratory; drinking water	Vergili [92]
22 compounds representing pharmaceutically active compounds, pesticides, hormones and industrial chemicals; 5 µg/L	80–99%	MBR; laboratory; spiked synthetic municipal wastewater	Hai et al. [70]
bisphenol A (750 µg/L), sulfamethoxazole (750 µg/L)	90% removal for Bisphenol A; 50% for sulphamethoxazole	MBR (submerged); laboratory; secondary effluent spiked	Nghiem et al. [93]
40 organic compounds	above 85% for hydrophobic compounds; less than 20% for the rest	MBR; laboratory; secondary effluent spiked	Tadkaew et al. [80]
Ionisable trace organics :sulfamethoxazole, ibuprofen, ketoprofen, and diclofenac at 2 µg/L	Removal dependent on mixed liquor pH.	MBR (submerged); laboratory; synthetic wastewater	Tadkaew et al. [94]
56 pharmaceuticals, 10 metabolites, and two corrosion inhibitors at concentration from 0.1 µg/L to 2.6 mg/L	Removal varies	MBR; pilot scale; wastewater directly from the hospital sewer collection system	Kovalova et al. [56]
11 emerging contaminants: acetaminophen, metoprolol, caffeine, antipyrine, sulfamethoxazole, flumequine, ketorolac, atrazine, isoproturon, 2-hydroxybiphenyl, and diclofenac(all at 0.5 mg/L)	UF with GAC posttreatment performed better than UF with PAC pretreatment.	UF combined with PAC (pretreatment) and GAC (posttreatment), secondary effluent spiked	Acero et al. [95]
6 antibiotics, 3 pharmaceuticals (ibuprofen, salicylic acid, and diclofenac) and Bisphenol A	>90%	MBR-RO, pilot plant, real wastewater	Sahar et al. [96]
PPCPs; acetaminophen, atenolol, carbamazepine, clopidogrel, diclofenac, dilantin, ibuprofen, iopromide, glimepiride, naproxen, and sulfamethoxazole	Up to 95%	MBR-NF; laboratory; real wastewater	Chon et al. [81]
10 micropollutants detected in wastewater including carbamazepine, ibuprofen, and caffeine	>76.9%	MBR-NF and MBR-RO; pilot plant; real wastewater	Cartagna et al. [97]
9 pharmaceuticals, bezafibrate, carbamazepine, clofibric acid, diclofenac, gemfibrocil, ibuprofen, ketoprofen, naproxen, and fenofibric acid	60–80%	MBR-PAC (submerged); pilot plant; WWTP primary pollutant	Lipp et al. [98]

Table 5. Membrane systems for micropollutants removal in different scales.

3.2.5. Advanced oxidation processes

Advanced oxidation processes (AOPs) using hydroxyl radicals ($\text{OH}\bullet$) are increasingly used for tertiary treatment of municipal wastewater and for water recycling. These processes are fast, nonselective, and effective for recalcitrant compounds. Among numerous combinations of AOPs, UV-, hydrogen peroxide-, and ozone-based processes are easy to implement for tertiary treatment of WWTP effluent. In a comprehensive research, removal efficiency of 220 MPs with postozonation was studied at full scale for a WWTP [1]. Compounds with activated aromatic moieties, amine functions, or double bonds such as sulfamethoxazole, diclofenac, or carbamazepine had second-order rate constants for ozonation $>10^4/\text{M}\cdot\text{s}$ at pH 7 (fast reacting) were eliminated to concentrations below the detection limit for an ozone dose of $0.47 \text{ g O}_3/\text{g DOC}$. Higher ozone dosage of $0.6 \text{ g O}_3/\text{g DOC}$ was needed for more recalcitrant compounds such as atenolol and benzotriazole for $>85\%$. Rahman et al. [99] summarized the second-order ozone and $\text{OH}\bullet$ oxidation constants for commonly found EDCs and pharmaceuticals in pure water, which varied from 0.8 to 7×10^9 and 1.2×10^9 to $9.8 \times 10^9/\text{M}\cdot\text{s}$, respectively. In wastewater, rates will be somewhat lower due to the competition of background organics, suspended particulates, and radical scavengers. However, the effect of background organics competition was found to be minimal for estrone degradation in wastewater by Sarkar et al. [100]. The overall cost of ozonation was found to be lower than that of UV/ H_2O_2 process for estrone degradation, although electrical energy per order was lower for UV/ H_2O_2 . AOPs are effective in a wide range of pH (i.e., 4–11) depending on the type of target compounds; although ozonation is more effective in alkaline pH. In some cases, transformation products that form due to AOPs may be even more toxic compared to parent compounds. For example, intermediates of UV/ H_2O_2 oxidation of bisphenol A exhibited different estrogenic activity depending on the treatment conditions [101]. Whole effluent analysis methods are better for assessing the toxicity of resulting water instead of time- and labor-intensive chemical analyses.

4. Conclusion

Fate and removal processes of micropollutants (MPs) in wastewater treatment are complex, and difficult to assess due to tedious and cost-intensive analyses. However, these processes can be somewhat estimated based on their physical properties such as $\log K_{ow}$, pKa, and solubility. Adsorption on colloidal and suspended particles and subsequent removal in sludge may occur for compounds with $\log K_{ow} > 4.0$. Majority of the MPs are not removed in conventional-activated sludge process, although better removal for some cases occurs in membrane bioreactors due to greater diversity and adaptability of microorganisms. Compounds with biological degradation constant $<0.0042 \text{ L/gss/h}$ are not removed significantly ($<20\%$), whereas compounds with rate constants $>0.4 \text{ L/gss/h}$ can be transformed by $>90\%$. Tertiary treatment of wastewater effluent using activated carbon adsorption, membrane filtration, and advanced oxidation processes are capable of removing MPs with varying degrees of success, although both lab and pilot-scale studies are required to establish their rates of removal. In the case of intermediates or transformation, products are produced during a treatment, whole effluent

analysis using a bioassay is a better method to evaluate the quality of effluent instead of conducting compounds specific chemical analyses.

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