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REMOVAL OF EMERGING CONTAMINANTS AND ENDOCRINE DISRUPTING COMPOUNDS FROM WASTEWATER IN THE ASPECT OF WATER PROTECTION

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Abstract

The paper presents the selected compounds classified as "emerging contaminants" ECs as well as endocrine active or endocrine disrupting (EAC/EDC). It has been shown that the removal efficiency of these compounds during conventional wastewater treatment varies, but usually, it is insufficient for adequate protection of effluents' receivers. Because of this, pollution of the receiving waters by these compounds systematically increases. It is therefore essential to plan and to implement into practice other processes that allow for highly effective degradation or separation of these pollutants. Research studies confirm that the use of advanced chemical oxidation processes (AOPs) and AOPs coupled with photodegradation allow for the effective degradation of these xenobiotics. Membrane processes, coagulation, and sorption ensure the separation of these pollutants from the water phase. An increase in the removal of these compounds could be also achieved by using integrated processes. The development of such processes is at this stage of knowledge the priority issue in water quality protection. The aim of this literature review is to outline the scale of the problem of continuously increasing the number of pollutants in the water environment as a result of discharging WWTPs effluents. It is essential in the aspect of the development of the strategy of comprehensive actions aimed at the protection of water resources according to the sustainable development principle.

Keywords*: Emerging contaminants, Endocrine disrupting compounds, Pharmaceutics, Hormones, PAHs, Dioxins, Pesticides, Personal care products*

Introduction

Nowadays, the development of chemical analytics allows us to determine many micro-pollutants, often found in trace concentrations (micro-, nano- or picograms in a unit of volume or mass) in surface and underground waters. Among them, persistent organic pollutants (POPs) so-called "emerging contaminants" can be distinguished. The groups are not separate and some relationships are exchanged in both groups. It should be pointed out that some of them have carcinogenic, mutagenic, and teratogenic properties as well as toxic effects on organisms. Therefore, the presence in natural waters should be constantly monitored. The POPs group includes primarily such compounds as: organic halogenated compounds (polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and compounds labeled as adsorbed on activated carbon organic halides (AOX), biologically active ingredients in pesticides, herbicides

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and other plant protection products), DEHP ethyloxophthalates, NPE nonylphenols and their ethoxylates, and some surfactants (linear LAS alkyl sulfonates). Three groups of these compounds (PCDD/F, PCB) and nine single chlorine derivatives have been classified as persistent organic compounds in the Stockholm Convention of 2001 [1], and the others were added to this list during the implementation of this convention in various European countries, including in Poland. In the group of emerging contaminants, often called endocrinal active (EAC), except of halogenated derivatives and PAHs, pharmaceuticals and metabolites of these compounds could be found as they occur in the cells of organisms, natural and synthetic hormones, personal protection products (PCP), flame retardants, corrosion inhibitors and many other compounds added to dyes, glues or deicing components [2]. One of the main sources of water pollution with the abovementioned compounds are municipal wastewater, industrial outflows, runoff from agricultural fields, and landfill leachate. Due to the diversity of these relationships, current legislation does not cover many of them; there is also no obligation to control these compounds in the abovementioned outflows [3-5]. Taking into account the fact that surface waters are often a source of water supply for urban agglomerations, developing effective methods for their removal or degradation in wastewater is a priority, which also coincides with the assumptions of sustainable development. It is also associated with what has been repeatedly demonstrated in toxicological studies that many of the abovementioned organic micro-contaminants have carcinogenic, mutagenic and teratogenic effects on test organisms and potentially for humans [6-10].

Organic micropollutants are not effectively removed during conventional wastewater treatment. Wastewater treatment processes are designed to remove mainly macropollutants, including organic carbon, nitrogen and phosphorus compounds, suspended solids, etc. In municipal wastewater treatment plants many processes can contribute to micropollutants removal from the liquid phase. Thy are among others adsorption on suspended matter (including sludge particles), biodegradation, photodegradation or volatilization. Effectiveness of these processes may vary a lot depending on physicochemical properties of the individual micropollutant e.g. logKow, water solubility, Henry's constant, polarity, and the characteristics of wastewater, e.g. presence of detergents, pH or temperature. Data presented by various authors indicate that it is extremely difficult to estimate the effectiveness of micropollutants removal during wastewater treatment in conventional treatment plants. It can be in a wide range not only when we compare various compounds, but also for the same chemicals under different conditions, eg. nonylophenols are expected to be removed by over 90% during coagulation whereas in the case of bisphenol A the observed removal efficiency is less than 20% [11]. Such compound as diclofenac was in different studies, and in various wastewater treatment plants, removed in varying degree, from less than 10, to more than 70% [12]. Because of the variety of organic micropollutants, diversification in removal rates and physicochemical properties of wastewater, as well as confirmed presence of the micropollutants in effluents, third stage of wastewater treatment is recommended. There is a need to design and implement additional processes.

The purpose of this work is to outline the scale of the problem of the constantly increasing amount of organic micro-pollutants in the aquatic environment resulting from their introduction with wastewater. This is important in the aspect of developing a comprehensive strategy for the protection of water resources. Is should be emphasized that this approach especially fits in the principle of sustainable development. The persistent organic pollutants can be present in the environment for a very long time, they can accumulate in living organisms as well as in deposits, can via mutagenic effects, affect reproductive processes and as a result, despite their low concentrations, significantly change the environment in the way which makes it difficult to allow the next generations to meet their needs. By reducing pollution with the organic pollutants, we provide our opportunity to live in the environment of adequate quality,

what is the most important point of sustainable development. Protection against deterioration of the environment pays a key role in conservation of the nature.

Effectiveness of ECs and EDC removal in conventional wastewater treatment plants

As indicated by the results of the research described in the literature and own studies, the author's and co-author's micro-pollutants present in raw wastewater are determined in amounts from nano- to several milligrams per the unit volume [13-21]. The content of micro-pollutants in raw wastewater depends on the type and share of industrial wastewater in the total amount of municipal wastewater and the type of active compound. In most cases, in conventional wastewater treatment plants, individual compounds are not sufficiently removed, that is why they are also identified in treated wastewater [4, 15, 21-31]. The group of compounds belonging to "emerging contaminants" is wide and not uniform in terms of properties, therefore also the concentration ranges in raw wastewater are very wide: from zero to several hundred micrograms per liter. Based on the literature data, Tran and co-authors wrote the results regarding the removal efficiency of 60 different compounds classified as "emerging contaminants" in treatment plants in Europe, Asia, and North America [30]. The concentration changes in wastewater treatment plants of selected compounds classified as antibiotics, antifungal/antimicrobial agents, nonsteroidal anti-inflammatory drugs (NSAIDs), anticonvulsants/antidepressants, artificial sweeteners, beta-adrenoceptor blocking agents, lipid regulating drugs, steroidal hormones, X-ray contrast media, UV filters, stimulants, anti-itching drugs, insecticides and plasticizers [32]. The highest concentration, reaching 164μg/L, was noted for salicylic acid from the group of nonsteroidal anti-inflammatory drugs. The concentration of caffeine (up to 113μg/L) included in the stimulants group was also high. There were large differences in EC concentrations in raw wastewater originating from different wastewater treatment plants and in different geographical regions. This is probably due to differences in land use, climatic conditions, population density and analytical methodology, as well as the method of testing the treatment plant. The described research carried out by various authors confirms the diverse effectiveness of their removal in the process of sorption and biodegradation (from 0 to 100%). The differences occur not only in EC concentrations in raw wastewater, but there are also large differences in the effectiveness of removing these compounds among countries, as well as treatment plants within the same country. It was found that conventional wastewater treatment plants based on the activated sludge process or MBR systems do not provide satisfactory EC removal. This is especially true for persistent compounds such as: antibiotics, anticonvulsants, and beta-blockers [5, 30]. Micro-contaminant concentrations in treated wastewater are usually lower than those in raw wastewater, but the reverse is the case. The decrease in concentrations is mainly due to sorption on suspended particles and activated sludge flocs and ultimately to accumulation in sewage sludge. A small number of micro-pollutants are biodegradable. Sorption efficiency and accumulation in sewage sludge depends on the properties of individual compounds, concentration, type of process (sedimentation, biological processes), process conditions, and the presence of other compounds. The efficiency of removal of the described compounds in biochemical processes depends, in addition to the abovementioned, also on the type of population and the enzymatic capacity of microorganisms for metabolic or co-metabolic transformations occurring in xenobiotics wastewater and the toxicity of pollutants towards the microflora involved in the biological treatment process. The reason for the determination of higher concentrations at the outflow from the treatment plant may be the result of improper sampling (e.g. temporary, one-time) during which the time of wastewater retention in individual treatment plant equipment was not taken into consideration. Also in the heterogeneous mixture of wastewater, changes and interactions occur between pollutants with or without microorganisms that have not been sufficiently recognized and identified yet [30]. The removal efficiency of individual compounds

in various technological systems is also varied and ranges from 0 to 100% [28, 31-36]. For example, Torret's research indicates that in raw wastewater collected from two Italian wastewater treatment plants, PAH concentrations did not exceed 4μg/L [14], and in Mezzanotte studies 9.3μg/L, respectively. The removal efficiency of these compounds in the municipal wastewater treatment plant reached 97% [13]. According to Qiao and co-authors, low-molecular compounds are removed in the process of volatilization under aerobic conditions and they are mineralized and adsorbed under anaerobic conditions, while high-molecular compounds are largely sorbed on sewage sludge particles [15]. Earlier author's research on PAHs showed that the total concentration of these compounds in the raw wastewater flowing into the municipal wastewater treatment plant in one of the cities of southern Poland may reach 7.0μg/L. Taking into account the retention of wastewater in individual devices, it was demonstrated that the efficiency of removing these compounds from wastewater did not exceed 80%. Taking into account carcinogenic compounds, it was found that the estimated annual load of these compounds introduced into the receiver can be 14-30kg depending on the season [2]. Studies on the efficiency of EC removal in Polish treatment plants are limited. Data from the Krakow wastewater treatment plant indicate that the effectiveness of removing the investigated pharmaceuticals from the group of non-steroids and antibacterial agents was in the range of 89-96%. However, bactericides, on the example of Triclosan, were removed only to an extent not exceeding 45%, and the degree of removal of diclofenac and bezafibrate was even smaller. In treated wastewater of the municipal wastewater treatment plant in Zabrze, the concentration of pharmaceutical residues was relatively high and reached the value of 8.4μg/L [27]. Research results published in the literature are varied and often difficult to compare due to the wide range of analyzed compounds, heterogeneous analytical methodology, and the specificity of wastewater collected from real facilities. Despite the extensive literature on the subject, researchers focus mainly on treated wastewater in the context of additional processes to treat them and determine the impact on the aquatic environment of residues and metabolites of these compounds. Determination of the level of micro-contaminants in raw municipal and industrial wastewater is performed much less frequently.

Removal of EC and EDC from wastewater in physical-chemical processes

As was formerly mentioned, studies described in the literature indicate that the efficiency of removing individual organic micro-pollutants is varied (from 0-100%). It has been shown that it depends on the type of compound, initial concentration, its properties (e.g. solubility, octanol-water partition coefficient), the presence of other compounds and the type of process (physical, chemical, biological) and the conditions of its conduct (pH, temperature, oxidation-reduction potential value). The literature on the removal of organic micro-pollutants is wide and includes various active compounds (including the above-mentioned ones), and research is carried out for various media (water solutions, surface waters, underground waters, prepared waters, rainwater, domestic and industrial wastewater, landfill leachate, soil remediation). Various methods are used in the investigations, that are conducted under various process conditions and the studies are carried out using model solutions or real wastewater, in laboratory conditions, semi-technical or full scale [29, 36-41]. Due to the protection of waters, the degree of removal of organic pollutants belonging to the EC is insufficient, therefore it is necessary to apply additional processes to the treatment plant circulation. Sedimentation, flotation, coagulation, sorption, and membrane separation are mentioned among the physical processes. Chemical methods, on the other hand, include advanced oxidation processes (AOP), including the classic Fenton process and its modifications (like-Fenton processes) as well as photochemical and catalytic processes. Other methods are sonodegradation, the use of ultrasound, or gamma radiation. In recent years there has been a development of hybrid (integrated) methods, which include combinations of the abovementioned physical-chemical

and biological methods. Examples of devices for integrated processes are MBR (Membrane bioreactor) and MBBR (Moving Bed Biofilm Reactor) reactors [26, 31, 40-43]. It should be emphasized that the degradation of micro contaminants is only possible in chemical, photochemical and biological processes. In other processes, only pollutants are separated from the wastewater and accumulated in sewage sludge or retained on membranes or in concentrate. Although in-depth oxidation processes lead to the decomposition of organic micro-pollutants, the process parameters should be selected to ensure complete decomposition (mineralization) of these xenobiotics. Otherwise, intermediate products formed that may be more toxic than basic compounds [44, 45]. In biological processes, complete or partial decomposition of organic contaminants can be obtained, but the conversions are conditioned by the presence of appropriate microorganisms capable of producing enzymes that cause metabolic or co-metabolic changes of individual compounds. In this case, the efficiency of biochemical changes is also dependent on process parameters such as the value of the oxidation-reduction potential, the presence of an easily available carbon source and nutrients for microorganisms [28, 31, 39]. Table 1 shows the efficiency of removing selected EC and EDC from wastewater in the coagulation process.

Table 1. Effectiveness of removal of selected micro-contaminants in the coagulation process [5, 31, 46-49]

Coagulating agent	Compound	Efficiency of removal (%)	Coagulating agent	Compound	Efficiency of removal (%)
Aluminum Sulfate $Al_2(SO_4)_3$	Aldrin	46	Iron III chloride / Aluminum Sulfate $FeCl_3/Al_2(SO_4)_3$	Ibuprofen	7.2-16.8
	Bentazone	15		Diclofenac	22 -70
	Mecoprop	80		Naproxen	22-42
				Sulfametaxosole	0-15
	16 PAHs	30 - 94		Carbamazepine	0-22
				Tonalide	69-97
				Galaxolide	70-89
Aluminum chloride $AlCl_3$	Di(2-ethylohexylene) phthalate DEHP, Diethyl phthalate DEP, Di-n-butyl phthalate DBP	32-50	n.m	Ibuprofen	4
				Carbamazepine	2
				Tonalide	24
				Galaxolide	16
				Triclosan	24
				Octylophenol	50
Iron III chloride $FeCl_3$	Bisphenol A	20	Aluminum salts pre-hydrolysed	16 PAHs	47
	Nonylophenol	90			
	Phtalates DEHP	70			

n.m. – not mentioned

Selected results confirm the diverse coagulation efficiency in removing organic micro-pollutants. This effectiveness depends on the properties of the chemical compound and process parameters, the type of coagulant, and its dose. As a result of the coagulation process, it is possible to achieve a reduction in pollutants belonging to the EC to varying degrees. It depends on the type of compound (its structure), type, and dose of coagulant and process parameters. For example, the efficiency of phthalate removal did not exceed 50% after using aluminum salts, while 70% - after using iron (III) salts. While pharmaceuticals - it reached 70% [46]. Earlier co-author studies concerned the course of changes in PAH concentrations in water treatment processes in real conditions. These studies showed that the efficiency of decommissioning 16 PAHs in the coagulation process using pre-hydrolyzed aluminum salts did not exceed 47% [50]. In the process of coagulation of industrial wastewater, it was shown that the efficiency of removal of these compounds depended on the properties of hydrocarbons and so low-molecular were removed less than high-molecular. In the case of the latter, characterized by relatively high octanol-water partition coefficients, the removal efficiency reached 94% [49]. Table 2 shows the efficiency of removal of selected micro-pollutants in the process of adsorption on granulated (in the form of a bed) and dusty activated carbon added to the solution.

Table 2. Effectiveness of removal of selected micro-contaminants in the adsorption process [31, 37, 51-53]

Adsorbent	Compound	Removal efficiency (%)	Adsorbent	Compound	Removal efficiency (%)
Powdered activated carbon	Diclofenac	96/ 98/ 99	Granulated activated carbon	Diclofenac	up to 98
	Sulfamethoxazole	2/ 33/ 62		Carbamazepine	23 -75
	Sulfametoxozole	2/ 33/62		Estrone	64
	Individual PAHs	7-31		17β-estradiol, 17α - ethinyestradiol	up to 43
	16 PAHs	23			
	Ibuprofen	16–30		Bisphenol A	66
	Sulfamethoxazole	36-56		Nonylophenol	84
	Diclofenac	38-46		Triclosan	95
	Naproxsen	52-58		Galaxolide	79
				Tonalide	67
Activated carbon/activated carbon fabric	Di(2-ethylohexylene) phthalate DEHP/	53-83	Activated carbon/activated carbon fabric	Diethyl phthalate DEP	90
				Di-n-butyl phthalate DBP	

n.m.- not mentioned

As in the case of coagulation, the scope of EC removal efficiency is broad and depends on the properties of the chemical compound and process parameters. Earlier co-author studies on the changes in PAH concentrations in water treatment processes showed that only 25% of PAHs were sorbed on activated carbon [50]. Pharmaceutical removal efficiency in this process is much higher. Values of up to 99% have been recorded after the use of powdered activated carbon. On coal deposits, on the other hand, the removal efficiency of these compounds is usually lower. Among the membrane processes in the removal of impurities classified as EC, the most important and most widely tested are pressure processes such as; reverse osmosis, nanofiltration, and ultrafiltration. Tables 3 and 4 present the values of retention coefficients of selected ECs in membrane processes as unitary or in integrated systems.

Table 3. Retention factors of selected micro-contaminants in membrane processes [31, 37, 42]

Process	Compound	Retention factor %	Process	Compound	Retention factor %
NF	Symazine	0-94	RO	DDT	99.9
	Atrazine	5-99		Diclofenac	95
	Bisphenol A	46-75		Ibuprofen	98-99
	Bisphenol F	75-78		Bisphenol A	up to 99
	4-Nonylofenol	44-70		Estradiol	up to 80
	Diclofenac	60		Benzafibrate	96
	Naproxen	60		Carbamazepine	up to 99.9
	17β- Ethinyestradiol			Naproxen	98
		90		Clofibric acid	up to 99
UF	PCDD	61-99			
	PCDF	92-99			
	Ibuprofen	7			
RO/NF/UF	Estron	100/63/37	RO/RO	Diclofenac	99.9/99.9
	Estriol	100/71/28		Ibuprofen	98/99
	17β- Ethinyestradiol	100/77/35		Naproxen	98/99
	Fluoranthene	40/46-90/66-89		Carbamazepine	99.9/99.9
	Benzo(A)Pyrene	63/96-99/66-89		Clofibric Acid	97/99
				Benzafibrate	96/99

RO- reversed osmosis, NF- nanofiltration, UF- ultrafiltration

Table 4. Retention factors of selected micro-contaminants in membrane processes integrated with the biological process (MBR, MBBR) [31, 37, 42, 55, 56]

Process	Compound	Retention factor %	Process	Compound	Retention factor %
MBR+RO	Salicylic acid	95.4	MBR	Naproxen	99-100
	Atenolol	99.5		Ketoprofen	92
	Triclosan	99.2		Diclofenac	17-87
	Pantachlorophenol	50.8		Carbamazepine	0-100
	Fenoprop	17.7		Sulfametaxozole	7-61
	Nonylophenol	100		Erythromycine	67
	Bisphenol A	90.5		Atenolol	66-99
	Estron	99.6		Metoproplol	59
	Estadriol	99.4		Bezabibrat	96
	17α-Ethinyestradiol	100		Clofibric acid	72
				Estrone/estriol	100
				Estradiol	up to 80
MBR+	Salicylic acid Triclosan	97.3		Bisphenol A	94-99
NF	Pantachlorophenol	98.7		Atrazine	68-97
	Fenoprop nonylophenol	59.1		Salicylic acid	98-100
	Bisphenol A	18.6		Caffeine	77
	Estron	96.6		Triclosan	99
	Estadriol	89.3		Octylophenol	70
	17α-Ethinyestradiol	99.3		Nonylophenole	98
		99.6		Pectachlorophenole	61
		94.0		Paracetamol	58
				Diazepam	67
MBR+UF	Salicylic acid Triclosan	92.6		17α-Ethinyestradiol	90-93
	Pantachlorophenol	99.2			
	Fenoprop nonylophenol	78.0			
	Bisphenol A	10.6	MBBR	Bisphenol A	27
	Estron	96.9		Atrazine	8
	Estadriol	98.6		Diclofenac	up to 80
	17α-Ethinyestradiol	99.4		Ibuprofen	100
		99.5		Naproxen	100
		95.5		Clofibric acid	up to 60

MBR- Membrane bioreactor; MBBR-Moving Bed Biofilm Reactor, RO- reversed osmosis, NF- nanofiltartion, UF- ultrafiltration

As the results of the research indicate, most membrane micro-pollutants can be removed with high efficiency in membrane processes. Comparative studies on estrogen removal from aqueous solutions in reverse osmosis, ultrafiltration and nanofiltration processes have shown that reverse osmosis was the most effective, with a removal rate of 99.9%. In the nanofiltration and ultrafiltration process, estrogen retention rates were lower (77 and 44%), respectively. Studies using different membranes showed that the retention rate of estrone and estradiol was in the range of 35- 99.9%. Higher values were found for ethinyl estradiol: 55 - 99.9% [57]. Also, Dudziak's research showed that the efficiency of estrogen separation in the nanofiltration process was affected by the presence of inorganic compounds. For example, the presence of NaCl at concentrations of 50 and 100mmol/L caused a decrease in the estrogen retention factor (bisphenols F and A, 4-tert-octylphenol and 4-nonylphenol) to 55%, and in the presence of $CaCl_2$ (1.0mmol/L) a decrease in the retention factor estrogen reached 17% [58]. Scientists indicate that the efficiency of hormone removal on membranes depends not only on the properties of individual compounds such as molar mass and hydrophobicity expressed by the octanol-water partition coefficient but also on the type and properties of membranes and the type of process. Natural hormones such as estrion, estriol, and estradiol with a partition coefficient value less than 4 were removed to a lesser extent than synthetic compounds (ethinyl estradione, mestranol) with a higher value of this indicator. The efficiency of natural estrogen separation did not depend on concentration, however, this relationship was directly proportional to synthetic hormones [32, 36]. In membrane processes coupled with biological efficiency, the removal of pharmaceuticals in single cases reached 100%. Much lower removal efficiency was reported for compounds classified as pesticides, nonylphenols, or disinfectants. Increasing the

efficiency of removing micro contaminants can be achieved in integrated processes in which, for example, separation on membranes is combined with coagulation or a biological process or chemical oxidation [36, 59-62]. As already mentioned, the degradation of micro-pollutants is ensured by in-depth oxidation processes. However, it is important to establish such process conditions to minimize the toxicity of post-process solutions. An example of the efficiency of removing selected micro-pollutants in these processes is included in Table 5.

Table 5. Effectiveness of removal of selected micro-contaminants in AOP processes [5, 21, 31, 37, 38, 46, 54, 63]

Treatment technology	Compounds	Removal efficiency (%)	Treatment technology	Compounds	Removal efficiency (%)
Hydrogen peroxide	16 PAHs	below 65	Electro-Fenton	Tetracycline	86
Fenton process		below 83		Sulfamethaxozole	100
				Atenolol	95
				Triclosan	100
				Tricarban	100
				Metoprolol	95
Photo-Fenton process		below 94%	Photo-catalysis/ Hydrogen peroxide	Aldrin	90
				Diazinon	99
Photolysis		below 78		Amoxiciclin	100
Ozone	Diclofenac	up to 90	Photo-electro-	Acetaminophen	97
(5mg/L)	Carbamazepine	up to 90	Fenton		
	Bezafibrate	0-50			
	DEET	50-80			
Ozone	Tonalide	79	Solar photo-Fenton	Atrazine	60
(15mg/L)	Galaxolide	up to 87		Triclosan	90
	Nonylophenol	up to 79		Carbamazepine	90
				Diclofenac	90
				Ibuprofen	90
				Naproxen	98
				Sulfametaxozole	95
				Caffeine	90
Photolysis	Ibuprofen	34	Solar photo-	Bisphenol A	85
UV254(10 min)	Diclofenac	100	catalysis	Diuron	85
	Sulfamethoxazole	51		Atenolol	85
	Carbamazepine	23		Ibuprofen	85
	Atrazine	69		Diclofenac	85
				Naproxen	85
				Caffeine	55
	16 PAHs	below 65			
Ozone (5mg/L) +	Ibuprofen	83	Gamma	Carbamazepine	100
hydrogen peroxide	Diclofenac	up to 99	radiation	Diclofenac	100
(3.5 mg/L)	Sulfamethoxazole	98		Ibuprofen	90
	Bisphenol A	up to 78		Ketoprofen	100
	Estrone/Estradiol	up to 98/83		Clofibric acid	100
	Atrazine	69		Amoxiciclin	95
	Triclosan	up to 99		Penicilin	81-92
				Sulfametoxozole	53
Photolysis	Ibuprofen	100/100	Anodic oxidation	Ketoprofen	100
UV254 (10/30 min)	Carbamazepine	75/100		Sulfametoxozole	100
+ hydrogen	Diclofenac	100/100			
peroxide (3.5	Sulfamethoxazole	98/ 100	Ultrasonic	Diclofenac	90
mg/L)	Atrazine	100/100	irradiation/TiO2		
Ozonolysis	Clarithomycin	94.3	UltrasoundUV/ Fe^{2+}	Bisphenol A	80
/ultrasound	Lindomycin	66.7			
	Ofloxacin	42.3			
	Sulfametazine	100			
	Enalapril	100			

DEET- N,N-Diethyl-3-methylbenzamide (insecticide)

As research results show, the degradation efficiency of most organic micro-pollutants in in-depth oxidation processes can reach 100%. The condition for achieving this effect is the optimization of process conditions such as: the choice of chemical reagents (oxidant, source of reactive radicals, catalyst) and determination of doses, exposure time to UV radiation and other parameters of the reaction environment (pH) [5, 21, 31, 37, 38, 46, 54, 63-67].

Discussions

Despite extensive literature on the transformation of organic micro-pollutants in the environment, researchers focus mainly on model solutions into which a specific amount of the test compound is introduced. Research using real wastewater (originating from municipal wastewater treatment plants, industrial plants) is conducted much less frequently and their results are difficult to compare due to the different characteristics of wastewater. In addition, research is carried out taking into account various active substances and different process conditions. Despite these discrepancies, the literature reports are consistent and confirm that in the processes applied in conventional wastewater treatment plants, compounds belonging to the EC or EDC group are removed, but the degree of removal of individual compounds varies and it is often insufficient for proper protection of receiving waters. Therefore, it is necessary to consider the use of additional processes for wastewater treatment. Experiments described in the literature confirm that the improvement of the quality of outflows from wastewater treatment plants can be obtained in the process of sorption (e.g. on activated carbon), coagulation or introduction of in-depth oxidation processes (ozonation, hydrogen peroxide, UV radiation, catalytic oxidation, ultrasound), using membrane processes (nanofiltration, reverse osmosis) or in integrated processes Table 6 presents a comparison of the described methods together with the advantages and disadvantages of individual solutions. In each of these cases, it is necessary to choose the proper technology adapted to the dominant micro-contaminants and their properties, and to determine the appropriate process conditions to ensure their effective removal and /or degradation. When choosing a method, it is also important to ensure that post-process solutions showing an acceptable level of toxicity are obtained.

Table 6. Comparison of the efficiency of micro-contaminants removal during various technological processes [5, 30, 31, 37, 42, 65, 66]

Process' parameters	EC	Efficiency L	Efficiency M	Efficiency H	Factors	Advantages	Problems
Conventional (activated sludge) -SRT -HRT -Organic loading -Redox conditions	Phs	+	+	+	-Hydrophobicity -Biodegradability	- not generating toxic active products -Low costs -Environmental friendly	- Micropollutants sorbed onto sewage sludge - Increase of environmental risk -Large amount of sewage sludge containing ECs -Disposal of sewage sludge
	PCP		+	+			
	Hs		+	+			
MBR -SRT -HRT -Organic loading -Redox conditions	Phs	+	+	+		-Small foot print -Effective for the removal of biorecalcitrant	-Inconsistent removal of polar and resistant pollutants -Membrane fouling -High energy consumption -sewage sludge
	PCP		+	+			
	Hs			+			
Coagulation -Dosage of chemicals -pH	Phs	+	+		-Hydrophobicity -Molecular size	-Reduced turbidity -Increased sedimentation rate	-introduction of salts -large amount of sludge -ineffective EC removal
	PCP		+	+			
	Hs	+					

Process' parameters	EC	Efficiency L	M	H	Factors	Advantages	Problems
Adsorption - Adsorbent properties -Dosage - Contact time -pH	Phs		+	+	-Hydrophobicity -Molecular size -Structure -Functional group		-Lower efficiency in the Presence of other compounds -Need for regeneration of adsorbents -Disposal of used adsorbents -High financial costs
	PCP		+	+			
	Hs			+			
Membrane processes (RO,UF,NF) -Transmembrane ne pressure -Membrane properties -pH -Feed quality	Phs		+	+	-Hydrophobicity -Molecular size	-Heavy metal removal -Desalination -Treating WWTP effluents	-Membrane fouling -Desorption of sorbed chemicals from membrane -Disposal of concentrate -High energy demand -High cost -Corrosive nature of treated water
	PCP			+			
	Hs		+	+			
Ozonation, AOP -Dosage -pH -Interfering ions -Other pollutants	Phs		+	+	Compound process	-Short degradation rate - High value of oxidation-reduction potencjal	- Formation of by-products -Interference of radical scavengers -High energy consumption -Residue oxidants
	PCP			+			
	Hs		+	+			
Photocatalysis -TiO_2 -Sunlight can be used by avoiding UV light	Phs				-Degrading persistent organic compounds	-High reaction rates upon using catalysts -Low price -Chemical stability of catalysts -Easy recovery of catalysts	-Difficult to treat large volume of wastewater -Separation and reuse of photocatalytic particles from slurry suspension
	PCP						
	Hs						

L-low, M-medium, H-high, Phs- pharmaceutics, PCP-personal Care Products, Hs-hormones

Conclusions

Taking into account the above literature data and the results of our research, it can be stated that:

- There are no emerging contaminants ECs and endocrine disruption EDC compounds in the legal regulations regarding the conditions for discharging wastewater into waters, which means that there is no obligation to control and monitor many of them in treated wastewater by conventional processes.
- The effectiveness of conventional wastewater treatment processes in the removal/degradation of organic micro-pollutants is insufficient for the proper protection of water resources and therefore, outflows from the treatment plant are a source of ECs / EDCs in surface waters. Protection of water environment against to micropollutatns is the important aspect of sustainable development.
- It is necessary to apply additional processes as part of the third stage of treatment, allowing for the highly effective removal of ECs /EDC from the wastewater treatment plant and at the same time minimizing toxicity.

Advanced wastewater technologies such as in-depth chemical oxidation and photo-oxidation, membrane processes as well as coagulation, adsorption, and their combinations are at the current stage of knowledge the proper direction in removing micro-pollutants from wastewater discharged to receivers.

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