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COMPARISON OF THE QUATERNARY TREATMENT TECHNOLOGIES IN MUNICIPAL WASTEWATER PURIFICATION

A NEGYEDIK TISZTÍTÁSI FOKOZAT TECHNOLÓGIÁINAK ÖSSZEHASONLÍTÁSA A KOMMUNÁLIS SZENNYVÍZTISZTÍTÁSBAN

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Abstract

The removal of micropollutants during wastewater treatment is an essential element of pollution control due to the last amendment of the Directive 91/271/EEC. Reducing and control at the source is usually the most cost-effective measure for a given substance or group of substances, but wastewater treatment plants with load above 150.000 PE (and between 10.000 and 150.000 PE based on the recieving watercourse or environmental risk assessment) have to reduce and remove the micropollutant in the future. The treatment plants have to install technologies which are optimal to eliminate the micropollutant (fourth stage or quaternary treatment technologies). The main quaternary treatment technologies are the different form of activated carbon filtration, membrane technologies (e.g. nanofiltration or reverse osmosis) and Advanced Oxidation Processes, AOP (e.g. ozone treatment). Among the options available for the removal of micropollutants, the most cost-effective solutions are activated carbon processes, ozone treatment, and their combination in different process configurations. At present, the combination of ozone treatment and activated carbon filtration is an effective technology to degrade the micropollutants, also the antibiotic resistant genes, and also remove the harmful by-products from the AOP treatment. For each wastewater treatment plant, it is necessary to individually examine which technology will be the most optimal to accomplish the new requirements.

Keywords: *Directive 91/271/EEC, micropollutants, activated carbon filtration, membrane technology, incineration*
JEL code: *Q53, Q55*

Összefoglalás

A mikroszennyező anyagok eltávolítása a szennyvíztisztítás során a 91/271/EGK irányelv legutóbbi módosítása miatt a szennyezés-szabályozás egyik lényeges eleme lett. Általában a legköltséghatékonyabb intézkedés egy adott anyag vagy anyagcsoport esetében a forrásnál történő csökkentés. A 150.000 LE feletti terhelésű szennyvíztisztító telepeken (ezen felül a befogadó vízfolyás vagy környezeti kockázatértékelés alapján a 10.000 és 150.000 LE közötti terhelésű telepeken is) a jövőben kötelező lesz a mikroszennyezők eltávolítása. A *tisztítótelepeknek olyan technológiákkal kell kiegészíteniük a meglévő tisztítósort, amelyek optimálisak a mikroszennyező anyagok eltávolítására (negyedik fokozatú technológiák). A fő negyedik fokozatú technológiák a különböző aktívszenes szűrési konstrukciók, a membrántechnológiák (pl. nanoszűrés vagy fordított ozmózis) és a nagyhatékonyságú oxidációs eljárások (pl. ózonos kezelés). A mikroszennyező anyagok eltávolítására rendelkezésre álló lehetőségek közül a legköltséghatékonyabb megoldás az aktívszénszűréses eljárások, az ózonos kezelés, illetve ezek kombinációja különböző folyamatkonfigurációkban. Jelenleg az ózonos kezelés és az aktívszénszűrés kombinációja egy hatékony technológia a mikroszennyező anyagok, valamint az antibiotikum rezisztencia gének bontására és a folyamat során keletkező káros melléktermékek eltávolítására. Minden szennyvíztisztító telepnél egyedileg szükséges megvizsgálni, hogy melyik technológia a legoptimálisabb az új követelmények teljesítésére.*

Kulcsszavak: *91/271/EGK irányelv, mikroszennyezők, aktívszénszűrés, membrántechnológia, szennyvíziszap égetés*

Introduction

Wastewater treatment systems are designed to reduce or minimise the environmental impact of wastewater, while meeting the discharge parameters set by the authorities. One consequence of population and economic activity growth is an exponential increase in the generation of anthropogenic waste, which includes wastewater and sewage sludge from wastewater treatment. Most of the various micropollutants (e.g. pharmaceuticals, microplastics) in wastewater and sewage sludge are non-biodegradable, persistent compounds, and even at low concentrations (µg/L, ng/L, or µg/kg dry solid, ng/kg dry solid) can have adverse effects on human health and the ecosystem. While local and EU legislation in the field of agricultural use of sewage sludge does not yet contain requirements for micropollutants, the latest amendment of Directive 91/271/EEC already pays particular attention to the issue of micropollutants in the field of wastewater treatment (e.g. obligations for the installation of quaternary treatment of wastewater treatment, which is determined depending on the load and risk analysis at each treatment plant). The modified Directive also deals with the monitoring of micropollutants in wastewater treatment and sewage sludge treatment technologies, but little is known about the migration and enrichment properties of these compounds in the wastewater-sludge-soil system, and the local legislation on the use of wastewater and sewage sludge for agricultural purposes currently limits the concentrations of certain harmful elements and compounds only to those described in Annex 5 of Government Decree 50/2001 (III.4.) in Hungary. The conventional wastewater treatment plants do not currently have a treatment process specifically designed to remove micropollutants, but the technology in treatment plants with a load of over 150.000 population equivalent (PE) should be upgraded to a fourth treatment stage within a specified timeframe according to the amendment of Directive 91/271/EEC.

Requirements for treated effluent wastewater in Hungary

Table 1. Requirements for the quality of wastewater at the point before introduction into surface water

Implemented load capacity (PE)	Limit values of pollutants (mg/L) or minimum removal efficiency (%)									
	Chemical oxigen demand (COD)		Biochemical oxigen demand (BOD_5)		Total suspended solids (TSS)		Total phosphorus (TP)		Total nitrogen (TN)	
									V.1.-XI.15	XI.16.-IV.30
	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	mg/L
< 600	300	70	80	75	100	-	-	-	-	-
601 - 2000	200	75	50	80	75	-	-	-	-	-
2 001 - 10 000	125	75	25	70-90	35	90	-	-	-	-
10 001 - 100 000	125	75	25	70-90	35	90	2	80	15	25
> 100 000	125	75	25	70-90	35	90	1	80	10	20

Source: DECREE 28/2004 (XII. 25.)

Municipal wastewater treatment technology, the treatment of incoming raw wastewater, goes through a multi-stage treatment system. The treated wastewater leaving the wastewater treatment technology is cleaned at the plants in such a way that it does not pose a risk to the status of the receiving waterbody and its biota. The quality of treated wastewater must comply with various parameters, which are set out in Decree 28/2004 (XII. 25.) of the Ministry of Environment and Water (on limit values for discharges of water pollutants and certain rules for their application) (Table 1) in our country. If the receiving waterbody is sensitive from an environmental point of view, more stringent emission limit values may apply to a given treatment plant and will be laid down in the water operating permit for the treatment plant.

With regard to the quality of treated wastewater, so far there were no obligations in the legal regulatory environment regarding the concentration or the removal efficiency of micropollutants. The latest amendment of the Urban Wastewater Treatment Directive includes requirements for the implementation of the quaternary treatment and for the qualitative and quantitative monitoring of micropollutants. One of the main cause for the amendment of the Directive could be the increased spread of antibiotic resistance, which poses a serious risk to human health. In addition to the problem associated with the high consumption of antibiotics, the presence of microplastics, other pharmaceutical substances, pesticides, etc. in wastewater on a micro- or nanogram/L (in some cases even mg/L) concentration can cause adverse effects in the environment and in living organisms. Their removal from wastewater is therefore an important task for the future activities of the wastewater treatment industry. The stage of wastewater treatment aiming at the removal of these micropollutants is called quaternary treatment (or fourth treatment stage).

Stages and equipment of conventional wastewater treatment technology

A conventional municipal wastewater treatment technology consists of three stages of treatment: mechanical (primary), biological (secondary) and tertial stage (tertiary treatment), the latter is the removal of residual nitrogen and phosphorus content of wastewater using chemical or biological technology.

In wastewater treatment plants, the first (mechanical) stage includes all the technologies and equipment used to remove the larger particulate, floating, fibrous or suspended solids in the wastewater. Mechanical pre-treatment often begins with a stone trap to remove heavy, particulate contaminants, followed by screens (coarse and/or fine screen), usually with a 5-12 mm bar distance, to separate larger floating, fibrous contaminants. The screens are followed by a sand trap, usually combined with a grease trap basin, and then pre-sedimentation comes to separate the suspended solid fraction of organic matter content (raw or primary sludge) by primary clarifiers.

The second (biological) stage, following the mechanical stage, usually comprises an activated sludge reactor (possibly supplemented by a fixed film system) and subsequent secondary clarifiers. In the biological treatment stage, soluble organic matter content, sometimes excess nitrogen or phosphorus content is removed from the wastewater by bacterial metabolism. The bacteria attached to each other to form flocs, and these mass of flocs forms the activated sludge. During the post-sedimentation, the activated sludge is separated from the treated wastewater. The major proportion of activated sludge is recirculated to the activated sludge reactors to maintain the adequate sludge concentration.

In order to prevent eutrophication, which threatens the oxygen supply in waterbodies, the efficient removal of nutrients (N and P forms) is an important task for wastewater treatment plants. Therefore, if nitrogen and/or phosphorus removal cannot be achieved with sufficient efficiency in the second stage, it is necessary to integrate it into the third treatment stage to complete the removal of nutrients from wastewater. In the case where the treated effluent needs to be disinfected before discharge into the receiving waterbody, this technological step is also included in the third stage of treatment.

The introduction and operation of the fourth stage (quaternary) treatment, which aims to remove micropollutants, has so far been implemented in some countries. In the absence of an obligation to install a quaternary treatment, a statutory concentration limit value or a required removal efficiency, only a few countries (e.g. Switzerland, Japan, Canada, Sweden) currently have a quaternary treatment. The latest amendment of 91/271/EEC directive requires all treatment plants with a load above 150.000 PE to install and operate a fourth treatment stage by 2045, furthermore plants between 10.000 and 150.000 PE may also be required to integrate a quaternary treatment technology after a preliminary investigation and risk assessment.

There are several technologies available for the removal of micropollutants, each with different advantages. The choice of the quaternary treatment technology should be based on a preliminary assessment of the influent raw sewage and the specificities of the treatment plant, and may even include a combination of technologies to achieve the appropriate removal efficiency.

Technologies for the removal of micropollutants (quaternary treatment)

Activated carbon filtration

Activated carbon is carbon produced by pyrolysis of carbon-containing materials (e.g. wood, lignite, walnut shells) at high temperatures, activated by steam and chemicals, and is used as an auxiliary material in many environmental and remediation technologies. It has a very high specific surface area of hundreds to thousands of m^2/g. Activated carbon technologies act as a quaternary treatment by adsorbing micropollutants. The contaminants remain bound to the activated carbon in their original form, so if activated carbon containing micropollutants is incorporated into the sewage sludge, the agricultural use of the sludge may become limited (GARAI, 2024).

Activated carbon is produced and used in powdered activated carbon (PAC) and granular activated carbon (GAC) forms. The powdered activated carbon can be fed directly into the reactor (e.g. activated sludge reactor) or into a separate reactor after biological treatment and post-settling, followed by phase separation. After phase separation, the activated carbon must be regenerated, e.g. with microwave (GARAI, 2024).

Granular activated carbon is used in separated reactors placed at the end of the wastewater treatmnet process. The carrier bed can be a fixed carrier bed with a large particle size or a fluid carrier bed (floating) with a smaller particle size. The effluent to be treated should contain as little suspended solids as possible. The average retention time in an activated carbon-filled reactor is 6 to 10 minutes per void volume and 20 to 30 minutes per reactor volume. The efficiency of the carrier bed, the efficiency of the microcontaminant removal, decreases during use of activated carbon. The spent carrier bed can be regenerated at high temperatures of 1200 °C with losses (GARAI, 2024).

Advantages of activated carbon technologies:

- Compared to other quaternary treatment technologies, activated carbon processes have lower investment and operating costs
- Activated carbon is readily available
- This technology can be combinated well with other technologies for the removal of micropollutants: activated carbon processes help to adsorb harmful oxidation by-products (OBP) from the treated wastewater.

Disadvantages of activated carbon technologies (BEZSENYI et al., 2024):

- Significant regeneration costs, spent activated carbon waste management costs
- Increasing amount of biological sludge
- Limited agricultural use of activated carbon sludge, significant costs of sludge disposal
- The binding of micropollutants depends on the physico-chemical properties of the compounds
- The process is limited in the removal of antibiotic resistance genes

Membrane technology

The different types of filtration differ basically only in the pore size of the filter system. This can be seen in Figure 1, which classifies the membrane technologies and the retained materials during the process. The pore size refers to the ability of the filter to filter out particles of a certain size. For example, a 0.20 micron (µm) membrane will filter out particles > 0.2 µm from the treated stream.

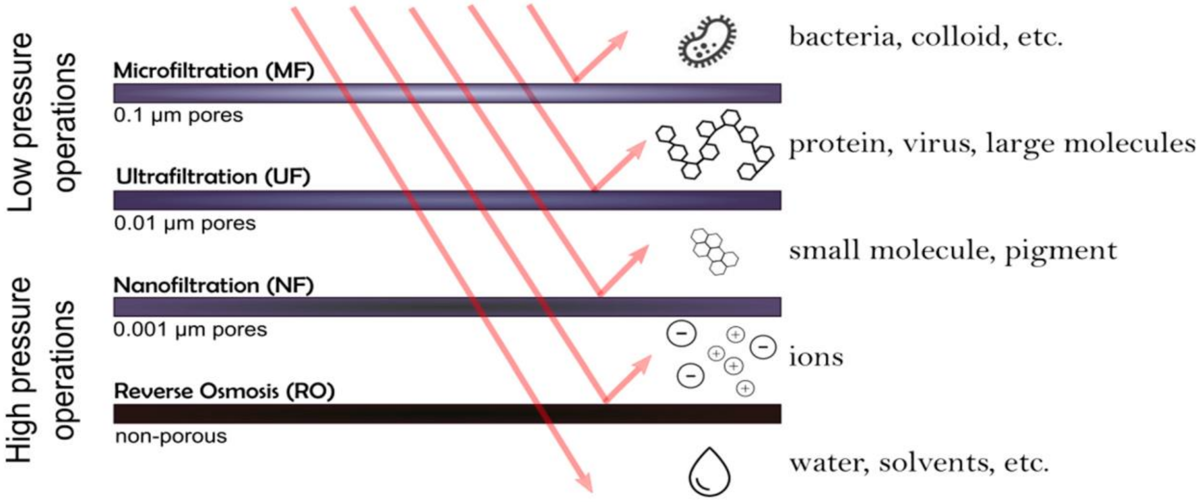

Figure 1. Types of filtration and retained molecules and microorganisms

Source: GARCÍA ET AL., 2021

Because of the typical molecule size range of micropollutants, microfiltration (MF) and ultrafiltration (UF) are not effective processes as quaternary treatment, but are systems that only reduce suspended solids and turbidity. The pore size of the applied membrane filters is well above the molecular size of the micropollutants (MF: ~0.1 µm, UF: ~0.01 µm) and are therefore not effective in separating them from the water phase. Even nanofiltration (NF) and reverse osmosis (RO) membranes are permeable to several micropollutants (e.g. aspirin, metformin, paracetamol).

Membrane filters are categorised according to their nominal molecular weight limit (NMWL) or molecular weight cutoff (MWCO), which can be determined by the molecular weight (MW) of the filtered compounds. In case of ultrafiltration, a 30.000 UF membrane will retain a protein molecule with a molecular weight of 30.000 Da (Dalton or g/mol). NF membrane filters have a MWCO of 100-2000 Da and a pore size in the range 0.5-2.0 nm. For RO membrane filters the MWCO is usually <200 Da (most commonly 100 Da). In general, micropollutants, e.g. pharmaceutically active compounds (PhACs) include compounds with low molecular weight, therefore even an RO membrane filter cannot permeate this micropollutants: e.g. aspirin with a molecular weight of 180 Da, metformin (MW = 129 Da), paracetamol (MW = 151 Da), amphetamine (MW = 135 Da), or metformin (MW = 129 Da) (BEZSENYI et al., 2024).

It is important to note that membrane technologies are not necessarily the best solutions for the treatment of wastewaters with high concentration of micropollutants, especially the Membrane Bioreactor (MBR). The microorganisms in the wastewater or in the activated sludge produce extracellular polymeric substances (EPS), which are natural polymers secreted by microorganisms. The presence of xenobiotics can induce the EPS productions of the bacteria (HENRIQUES – LOVE, 2007). Wastewaters from hospitals or pharmaceutical factories could contain micropollutants (PhACs) in high amount, therefore microorganisms in MBR systems could clog the membrane filters with the produced EPS. As a result, membrane technologies may not be the best option to treat wastewaters from hospitals or pharmaceutical factories.

Due to the many disadvantages of membrane filtration, it is expected to play a minor role in the development of wastewater treatment technology for micropollutant removal. Their disadvantages are:

- High investment and operating costs
- Only able to filter a certain molecular size range of micropollutants
- Does not break down micropollutants, only concentrates them. In some respects this is also true for MBR systems, where micropollutants that are resistant to biodegradation are retained together with the activated sludge. In the filtered sludge or concentrate, the micropollutants are present in their unchanged forms. The concentrate has to be subjected to further treatment or disposal (e.g. with incineration or Advanced Oxidation Process), which can increase the costs (AROLA et al., 2017).

Advanced Oxidation Processes

A common feature of Advanced Oxidation Processes (AOP) is that aggressive radicals, mainly hydroxyl radicals ($^{\bullet}OH$), initiate the transformation and degradation processes. The most common forms of AOP are shown in Figure 2.

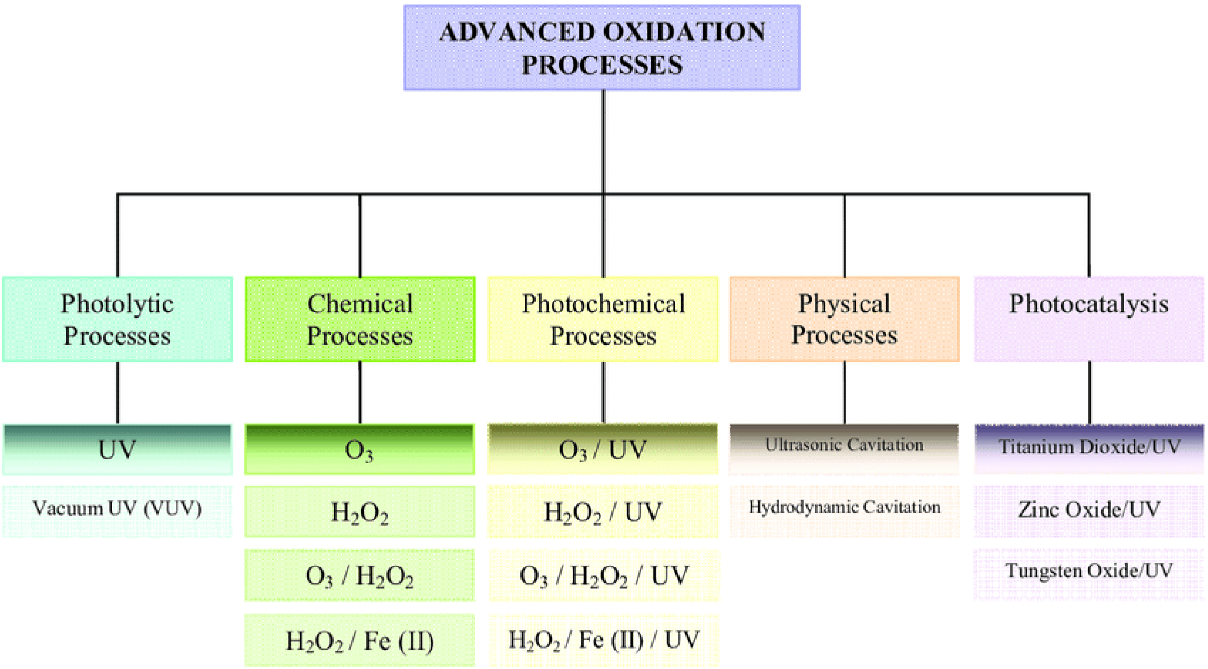

Figure 2. Advanced Oxidation Processes (AOP)
Source: CHIRWA – BAMUZA-PEMU, 2010

Often, radicals are oxygen-, nitrogen-, sulphur- or carbon-centred molecules, that react very rapidly with other compounds to acquire electrons. They are able to degrade the structure of organic molecules that are not or not easily biodegradable, thus they indirectly have cell-destructive and teratogenic effects (DOMBI – ILISZ, 1999, ILISZ et al., 2006, OTURAN – AARON, 2014).

Some examples of reactive radicals are: superoxide anion radical ($O_2^{\bullet -}$), peroxyl radicals ($RO_2^{\bullet -}$), hydroxyl radical ($^{\bullet}OH$), peroxide ion ($O_2^{\bullet -}$), singlet oxygen ($^1O_2$), hydroxide ion (OH^-), sulphate radical ($SO_4^{\bullet -}$), carbonate radical ($CO_3^{\bullet -}$) (KUMARI – KUMAR, 2023). The black dot „•” marks the unpaired electron on the valence shell. These radicals are non-selective and have a high oxidation-reduction potential (GARCIA-SEGURA – BRILLAS, 2017). Among them, the hydroxyl radical has the highest oxidation-reduction potential (E° = 2.7-2.8 V), making it the most efficient oxidant among those listed (SHANMUGAVEL et al., 2023). The reduction potential of reactive oxidants relevant for wastewater treatment is collected in Table 2.

Table 2. Reduction potential of reactive oxidants relevant for wastewater treatment

OXIDATIVE MOLECULE/COMPOUND	OXIDATION-REDUCTION POTENTIAL (E°, V)
Fluorine (F_2)	3.03
Hydroxyl radical ($^{\bullet}OH$)	2.7-2.8 (acidic environment); 1.9
Sulfate radical ($SO_4^{\bullet -}$)	2.5 – 3.1
Singlet oxygen ($^1O_2$)	2.42
Chlorine radical anion ($Cl_2^{\bullet -}$)	2.09
Ozone (O_3)	2.07; 1.01 (pH =11-12)
Persulfate ($S_2O_8^{2-}$)	2.1

Hydrogen peroxide (H_2O_2)	1.78; 0.46 – 0.87 (pH = 7)
Oxide radical anion ($O^{\bullet-}$)	1.78
Permanganate (MnO_4^-)	1.7
Chlorine dioxide (ClO_2)	1.5
Superoxide radical ($O_2^{\bullet-}$)	1.0
Perhydroxyl radical ($HO_2^{\bullet}$)	0.79; 1.5
Chlorine (Cl_2)	0.42 – 0.60
Hypochlorous acid (HClO)	0.04 – 0.46

Source: SPOTHEIM-MAURIZOT et al., 2008, GUERRA-RODRÍGUEZ et al., 2018, KUMARI – KUMAR, 2023, SHANMUGAVEL et al., 2023

Oxidative radicals can modify the complex molecular structure of molecules through oxidation, hydroxylation, bond cleavage, desulfonation and deamination. During the oxidation of micropollutants, the parent compounds are broken down into low molecular weight organic acids. These biodegradable compounds are further oxidised to fully mineralise: H_2O, CO_2 and various inorganic compounds are formed as end products (including reduced reactive oxidants). These inorganic compounds can be treated or removed from the wastewater by conventional treatment methods, leaving only H_2O, CO_2, which represents the complete mineralisation of the contaminated phase (WOJNÁROVITS et al., 2022). Gamma irradiation and accelerated electrons are often used to model the AOP technologies. Achieving complete mineralisation is very difficult and not necessarily the goal of the process: transformation of micropollutant to biodegradable products (e.g. acetic acid) can be a significant step to enhance the micropollutant removal from wastewaters.

During the application of AOP, hydrogen peroxide (H_2O_2) is formed in a dose-dependent amount, which is toxic to living organisms above a certain concentration. A highly decomposable molecule, when it decomposes, water and oxygen are produced during the development of heat:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

When H_2O_2 reacts with organic molecules, it can induce significant chemical/structural changes in them, leading to the formation of more bioavailable molecules with simpler structures. This positive effect of H_2O_2 could be significant, as it forms in high concentrations during AOP treatments (SÁGI et al., 2016, BEZSENYI et al., 2021).

Organic and inorganic by-products produced during the oxidative degradation of various micropollutants, varies depending on the structure of the base compound: aldehydes, alcohols, carboxylic acids, inorganic compounds. These by-products could be advantageous and also harmful compounds. Some compounds, e.g. acetic acid, formic acid can be rapidly biodegradable substrates for bacteria of previous treatment stages. Other compounds, e.g. aldehydes or bromate (BrO_3^-) could have toxic, carcinogenic effects for the living organisms.

With the chemical degradation of micropollutants, AOP technologies could be a good choice. An important aspect is also that AOP can degrade the antibiotic resistance genes too, thereby could help to reduce the escalation of antibiotic resistance.

Advantages of AOP technologies:

- They do not transfer pollutants from one phase to another, as is the case when e.g. particularly hazardous, highly contaminated pharmaceutical wastewater is destroyed by incineration.
- They do not produce hazardous sludge during the treatment of pollutants, as membrane technologies do, where filtered, highly toxic pollutants need to be treated.
- In some cases, AOP can even ensure the complete mineralisation, i.e. mineralisation of the pollutants.
- AOP can also treat wastewaters that contain high levels of organic matter and cannot be treated by biological methods due to their low pH (SARAVANAN et al., 2022). Unlike membrane technologies and activated carbon filtration, AOP do not concentrate pollutants.
- It can be used in combination with other processes and in some cases its energy consumption is favourable. They have a strong oxidising capacity and a fast reaction rate, and they can also be used to treat compounds that are resistant to biodegradation and may be flammable (ATALAY – ERSÖZ, 2016). In contrast, activated carbon filtration, which also functions as biological filtration, only enhances biodegradation processes that are already taking place. Molecules that are resistant to biodegradation either bind to the activated carbon and accumulate, or are removed with the treated effluent.
- AOP can also inactivate pathogens not removed during secondary treatment (LUO et al., 2014, ATALAY – ERSÖZ, 2016, SARAVANAN et al., 2022).

Disadvantages of AOP technologies:

- Toxic by-products are very often produced when AOP are used. For example, chemical compounds containing nitro groups (nitroproducts). The oxidative degradation of nitrogen-containing pollutants releases nitrate, nitrite and ammonium ions. The formation of nitroproducts is associated with reactive nitrogen forms such as nitrate radicals ($NO_3^{\bullet}$), nitrite radicals ($NO_2^{\bullet}$), nitric oxide radicals ($NO^{\bullet}$) and peroxynirite ($ONOO^{-}$). In some cases, secondary reactions of mineralised nitrogen species (nitrate, nitrite) with the parent or intermediate compound result in multiple nitroproducts (RAYAROTH et al., 2022).
- Not all processes are scalable to industrial needs (e.g. photocatalysis, ultrasonic cavitation).
- They are generally characterised by higher investment and operating costs than conventional methods.
- In some cases, oxidant concentration control and pH correction control are unavoidable, and process limitations may also be related to pH variations (particle aggregation, modification of surface properties of heterogeneous catalysts) (ATALAY – ERSÖZ, 2016).

Treatment with ozone

Ozone oxidation is the best known AOP process for the removal of micropollutants and the most widely used in practice. Ozone acts to transform micropollutants either directly or through the formation of hydroxyl radicals (GARAI, 2024):

$$O_3 + H_2O \rightarrow HO_3^+ + OH^-$$
$$HO_3^+ + OH^- \rightarrow 2HO_2$$
$$O_3 + HO_2 \rightarrow HO^\bullet + 2O_2$$
$$HO^\bullet + HO_2 \rightarrow H_2O + O_2$$

It is produced by high-voltage electrostatic discharge from air or pure oxygen in ozone generators. The energy demand for production is significant, with the use of ozone purification increasing the energy demand of a conventional wastewater treatment plant by 20-30% (GARAI, 2024).

The degradation efficiency of micropollutants with oxidation by ozone varies from compound to compound. For many micropollutants, a degradation efficiency of 80% can be achieved at a dosage of 0.5 - 1.0 g O_3 /g DOC. The required ozone dose is increased by the dissolved organic carbon, nitrogen dioxide and suspended solids content of the water to be treated. The retention time can be in the range of 10-14 minutes at peak time. The gas leaving the ozone reactor must be ozone-depleted. This can be done by chemical dosing (e.g. hydrogen peroxide, sodium bisulfite, calcium thiosulfate), UV irradiation or activated carbon (GARAI, 2024).

The formation of aldehydes (formaldehyde, acetaldehyde and glyoxal) depends on the ozone/total organic carbon (TOC) ratio, with maximum aldehyde formation measured at a ratio of 1 - 1.1. NAWROCKI et al. identified two groups of aldehydes with different effects. The concentration of the compounds in the first group (e.g. formaldehyde, acetaldehyde) is strongly dependent on the ozone dosage, whereas the concentration of the second group of aldehydes (e.g. glyoxal, methylglyoxal) appears to be relatively independent of the ozone dosage (NAWROCKI et al., 2003).

An increase in toxicity after ozone exposure has been observed in several studies, leading to mortality and developmental retardation of juvenile rainbow trout (*Oncorhynchus mykiss*) (STALTER et al. 2010a) and inhibition of reproduction of the small annelid worms of the genus Lumbriculus (STALTER et al. 2010b). Induced mortality in zebra mussels (*Dreissena polymorpha*) (STALTER et al. 2010b) and growth inhibition in frogfishes (*Lemna sp.*) (MAGDEBURG et al., 2012) have also been observed. An increase in genotoxic and mutagenic potential after ozonation has also been reported (PETALA et al., 2008, STALTER et al., 2010a). These effects were attributed to the formation of toxic oxidation by-products (OBP) during ozonation, such as aldehydes, which could be removed e.g. with sand filtration after ozonation process. Contradictory results have also been reported, showing a reduction in toxicity during ozonation (TAKANASHI et al., 2002, REUNGOAT et al., 2010, MISÍK et al., 2011). Careful planning is key in the ozonation process, longer reaction times promote the degradation of labile intermediates (PETALA et al., 2006, MARGOT et al., 2013).

An important consequence of the use of ozonation technologies can be the formation of bromate (BrO_3^-) in bromide (Br^-) containing waters, a potential carcinogen (JAHAN et al., 2021, MORRISON et al., 2023). Therefore, it is recommended to avoid ozonation if the bromide concentration in wastewater is higher than 0.4 mg/L. Bromide in wastewater can be attributed to both natural and anthropogenic sources (e.g. incinerators, landfills) (FALÅS et al., 2022).

Ozonation for the removal of organic micropollutants from municipal wastewater has been extensively studied over the last decade and has been developed into a well-established technology in Switzerland and Germany. It is generally accepted that after ozone treatment, biological post-treatment should be applied to degrade potentially toxic and/or carcinogenic OBP generated during the oxidation process. However, there is still debate on the appropriate design and operation of such a post-treatment step. Several systems for post-treatment have been studied. For example, fixed-bed bioreactors, moving-bed bioreactors, constructed wetlands, integrated solutions with ozonation as an intermediate step in the sludge treatment process or deep-bed filters have been tested. The latter is the most commonly used technology, with sand or granular activated carbon (GAC) loading.

Integrating the quaternary treatment into the existing wastewater treatment technology – Treatment plants in Budapest

The North-Pest Wastewater Treatment Plant and the Budapest Central Wastewater Treatment Plant discharge the treated wastewater into the main branch of the Danube, while the South-Pest Wastewater Treatment Plant discharges into the Ráckeve (Soroksári)-Danube, which is a sensitive waterbody. Therefore, only in the case of the South-Pest Wastewater Treatment Plant, a disinfection procedure is necessary. This is currently done with 254 nm wavelength UV-C irradiation. In the case of such plants, it is advisable to choose a quaternary treatment technology that replaces the high energy consumption of the UV equipment and has a disinfection effect. Ozonation supplemented with biologically active post-filtration can be a suitable technology. At the same time, it must be checked whether the number of indicator organisms (Coliform group) after the activated carbon filtration is sufficiently low to ensure the limit values for the effluent treated wastewater. An alternative solution can be the combination of UV irradiation with hydrogen peroxide dosage, but its effectiveness can only be ensured by providing adequate exposure time and UV irradiation of adequate intensity. The residence time is insufficient with the current design of the technology. Adding activated carbon to the activated sludge basin is not feasible at the South-Pest Wastewater Treatment Plant due to the construction of the special Living Machines Technology (Organica®).

The efficiency of the MBBR and MBR system alone is not sufficient to achieve a stable micropollutant removal efficiency above 80% (according to the Directive 91/271/EEC). In the case of the membrane technology, only RO could ensure the fulfillment of the requirements, not nanofiltration. In the case of using membrane filtration, it is generally true that the pollution will be only concentrated, and the treatment and placement of the resulting concentrate requires additional solutions, which impairs cost-effectiveness. Membrane technologies are also expensive to maintain. In addition, their micropollutant removal efficiency is not 100%, because the membranes used can be permeable in the case of low molecular weight, uncharged molecules (see above).

In the case of the North-Pest Wastewater Treatment Plant and the Budapest Central Wastewater Treatment Plant, independent activated carbon dosing may also be a suitable option on the biological stage, but the ozone + GAC/BAC solution is expected to be a more efficient construction. The ozone+GAC combination can be a cost-effective solution when considering the 80% removal requirement.

Summary

In the case of micropollutants, the discharge from wastewater treatment plants is one of the most important entry points into the environment, despite the fact that wastewater is not actually the source but the carrier of these pollutants. The removal of micropollutants during wastewater treatment is an essential element of pollution control. This does not reduce the importance of other measures, such as measures taken at the source of rainwater overflows or the limitation of these outflows (whose relative contribution to pollution increases if the removal of micropollutants at the wastewater treatment plant is effective). Control at the source is usually the most cost-effective measure for a given substance or group of substances (eg perfluorinated compounds). The main quaternary treatment technologies to remove micropollutants are activated carbon filtration (BAC, PAC or GAC construction), membrane technologies (e.g. nanofiltration or reverse osmosis) and Advanced Oxidation Processes, AOP (e.g. ozone treatment). Among the options available for the removal of micropollutants, the most cost-effective solutions are activated carbon processes, ozone treatment, and their combination in different process configurations. At present, the combination of ozone treatment and activated carbon filtration is an effective technology to degrade the micropollutants, also the antibiotic resistant genes, and also remove the harmful by-products from the AOP treatment. For each wastewater treatment plant, it is necessary to individually examine which technology will be the most optimal. In some cases, membrane filtration processes can prove to be a cost-effective alternative, especially when the limits of the treated wastewater are extremely strict (for example, in the case of waterbodies are used for the production of drinking water).

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