21st International Conference Man and Working Environment
SEMSIE
Safety Engineering & Management - Science, Industry, Education

ORIGINAL SCIENTIFIC PAPER

DOI: 10.46793/SEMSIE25.013Z

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ENVIRONMENTAL RISK OF MICROPOLLUTANTS: THE IMPACT OF REVISED EU DIRECTIVE ON URBAN WASTEWATER

Abstract: *Contamination of the environment by micropollutants has potentially adverse consequences, raising severe concerns. They were detected and identified in surface, ground, and drinking waters as well as in soils worldwide. Wastewater treatment plant (WWTP) effluents are recognized as the main source of the global increase of emerging contaminants. On 26 October 2022, the European Commission published a proposal for the revision of the Council Directive of 21 May 1991 on the treatment of municipal wastewater entitled "Urban Wastewater Treatment Directive – UWWTD". With the ongoing amendment of EU legislation on urban wastewater treatment, stricter requirements for pollutant removal are expected, driving the need for innovative environmental technologies. Diverse pollutants in urban wastewater, including macronutrients and micropollutants, require advanced treatment technologies that integrate biological, physical, and chemical processes. Advanced oxidation processes (AOPs) offer several advantages for the removal of micropollutants from wastewater. They facilitate the degradation of pollutants rather than their concentration, as is the case in membrane or adsorption systems, resulting in more thorough removal from wastewater. These processes also do not generate solid residues, reducing the need for additional waste management measures. AOPs have a small footprint, making them suitable for implementation in a variety of wastewater treatment facilities.*

Keywords: advanced oxidation processes, revised EU directive, micropollutants, sewage sludge, wastewater

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INTRODUCTION

Contamination of the environment by micropollutants (MPs) has potentially adverse impacts, raising severe concerns. Micropollutants were detected and identified in surface, marine, ground, and drinking waters as well as in soils world-wide (Hermabessiere, 2017). Wastewater treatment plant (WWTP) effluents are recognized as the main source of emerging contaminants, causing their global environmental impact. The use of new chemicals and compounds is driven by development, population changes, and efforts to improve the well-being of the population (Dogruel et al., 2020). The use of pharmaceuticals in animal and meat production, aquaculture, disposal of expired medicines, and hospital activities can cause severe environmental pollution, usually detected too late when enabled by sophisticated analytical techniques (Kümmerer, 2009). As a result, bacterial resistance (Sambaza & Naicker, 2023) to antibiotics due to adaptation and adjustment to the presence of antibiotics can occur (Irfan et al., 2025). Therefore, such pollutants need to be removed before disposal of wastewater (WW) into the environment. The improvement of detection and monitoring of substances in surface, ground, and wastewaters is also accompanied by the implementation of up-to-date legislation (Derco et al., 2024).

MICROPOLLUTANTS

Growing environmental problems include the widespread occurrence and presence of micropollutants and new emerging substances, collectively called "emerging pollutants" (EPs) in the aquatic and terrestrial environments (Kravos et al., 2024). Micropollutants are characterized by their adverse environmental impact even at very low concentrations (μg L^{-1} to ng L^{-1}). These effects include acute and chronic toxicity, bioaccumulation and bioconcentration in food chains, genotoxicity, or endocrine effects (Derco et al., 2024). Micropollutants enter the water environment mainly through their concentration in wastewater treatment plants, as current treatment technologies are not designed to remove them efficiently. Their presence in urban WWs is a consequence of using personal care products, cleaning agents, washing, use of toilets, and disposal of unused or excreted pharmaceuticals (Gomes et al., 2017). Due to the serious negative effects on the environment, problems related to detection of low concentrations, and, in many cases, complex and variable chemical structure, the issue of MPs removal poses an urgent and current challenge to the development of treatment technologies for their removal, the investigation of their effects on the aquatic environment, and the potential of their possible penetration into groundwater (Lember et al., 2023; Derco et al, 2024).

NEW EU DIRECTIVE FOR URBAN WASTEWATER TREATMENT

On 26 October 2022, the European Commission published a proposal for the revision of the Council Directive of 21 May 1991 on the treatment of municipal wastewater "Urban Wastewater Treatment Directive – UWWTD" (European Commission, 2024). According to the revised directive, member states must collect and treat wastewater from all agglomerations above 1000 population equivalents (PE). All agglomerations between 1000 and 2000 PE need to be provided with collection systems and all sources of domestic wastewater need to be connected to these systems by 2035 (Derco et al., 2024). By 2039, the removal of nitrogen and phosphorus (tertiary treatment) will be mandatory for urban wastewater treatment plants larger than 150,000. For those urban wastewater treatment plants, by 2045, EU member states will have to apply additional treatment, known as quaternary treatment, to remove micropollutants (Table 1).

Table 1. *Groups of pollutants according to the EU directive proposal (EU, 2024).*

Group	Compound	Label	Function
I – Very easily decomposed	Amisulpride	AMI	Anti-psychotic
	Carbamazepine	CAR	Anti-epileptic drug
	Citalopram	CIT	Anti-depressant
	Clarithromycin	CLA	Antibiotic
	Diclofenac	DIC	Anti-rheumatic, analgesic
	Hydrochlorothiazide	HCH	Diuretic
	Metoprolol	MET	Beta blocker (heart)
	Venlafaxine	VEN	Anti-depressant
II – More easily removable	Benzotriazole	BZT	Anti-corrosive
	Candesartan	CAN	Anti-hypertension
	Irbesartan	IRB	Anti-hypertension
	4-methylbenzotriazole, 6-methylbenzotriazole 5-methylbenzotriazole	4MeBZT 6MeBZT 5MeBZT	Anti-corrosive

Producers of pharmaceuticals and cosmetics – the main source of micropollutants in urban wastewater – will need to contribute a minimum of 80% of the additional costs for the quaternary treatment, through an extended producer responsibility (EPR) scheme and in accordance with the 'polluter pays' principle (European Commission, 2024).

The new rules also introduce an energy neutrality target, meaning that by 2045, urban wastewater treatment plants treating a load of 10,000 PE and above will have to use energy from renewable sources generated by the respective plants (European Commission, 2024).

The proposed EU directive requires individual member states to define areas in which the concentration or accumulation of micropollutants poses a risk to human life and/or the environment. The removal of micropollutants must be achieved by applying quaternary treatment. By 2035, all WWTPs larger than 100,000 PE must be equipped with a quaternary treatment, while at least 50% of WWTPs larger than 10,000 PE also must have quaternary treatment. By 2040, all WWTPs larger than 10,000 PE in the areas where micropollutants pose a risk to human health or the environment should also be upgraded to the quaternary treatment stage. For quaternary treatment, 80% removal efficiency of at least 6 of the 12 micropollutants from Table 1 is mandatory (Kardos et al., 2025).

ADVANCED OXIDATION PROCESSES (AOPs)

With the ongoing amendment of EU legislation on urban wastewater treatment, stricter requirements for pollutant removal are expected, driving the need for innovative environmental technologies (Derco et al., 2024). Diverse pollutants in urban wastewater, including macronutrients and micropollutants, require advanced treatment technologies that integrate biological, physical, and chemical processes. Advanced oxidation processes (AOPs) offer several advantages for the removal of micropollutants from wastewater. First, they boast fast reaction rates for most organic pollutants, ensuring efficient degradation in a relatively short time frame (Boševski & Žgajnar Gotvajn, 2023).

Table 2. *Groups of AOPs according to sources of hydroxyl radicals (Žgajnar Gotvajn et al., 2023).*

General name of AOP	Source of hydroxyl radicals
Photolysis	UV
Ozone-based processes	O_3 O_3/UV O_3/H_2O_2 O_3/H_2O_2/UV
Hydrogen-based processes	H_2O_2/UV H_2O_2/Fe^{2+} (Fenton) H_2O_2/Fe^{3+} (Fenton-like) H_2O_2/Fe^{2+}/UV (Photo-Fenton)
Heterogenous catalysis	TiO_2/UV TiO_2/UV/H_2O_2
Sonochemical processes	Ultrasound 20 kHz–2 MHz
Electrochemical oxidation	Electric current 2–20A Electrolysis in aquatic medium
Cavitation	Ultrasound Laser Hydrodynamic Particle

They facilitate the degradation of pollutants rather than their concentration, as is the case in membrane or adsorption systems, resulting in more thorough removal from wastewater. These processes also do not generate solid residues, reducing the need for additional waste management measures (Satyam & Patra, 2025).

AOPs have a small footprint, making them suitable for implementation in a variety of wastewater treatment facilities. They could even completely mineralize most contaminants and ensure their transformation into harmless by-products. However, AOPs have some disadvantages (Cuerda-Correa et al., 2020). They may produce unknown products during the oxidation process, which may require further analysis to ensure the safety of the treated water. The water matrix can reduce their efficiency causing different interferences and the presence of residual oxidants, which can be a problem that requires careful monitoring and pretreatment measures in order to mitigate their effects on treatment efficiency.

The term Advanced Oxidation Processes (AOPs) describes those oxidation processes (Figure 2) that are based on the high oxidative capacity of the hydroxyl radical (·OH). Other reactive oxygen species and radicals of other ions also contribute to the efficiency of the processes (Ribeiro et al., 2015). They differ from each other depending on the method of radical formation and whether a catalyst is used. They mostly involve the *in situ* formation of hydroxyl radicals, which react rapidly with most organic substances, with the exception of chlorinated alkanes. AOPs can be roughly divided into two groups: homogeneous and heterogeneous processes, further classified into those that require an external energy source (radiation, ultrasound, electricity) and those that do not (Mahmoodi & Pishbin, 2025).

Hydroxyl radicals are very suitable for use on an industrial scale because they meet three key criteria (Brillas et al., 2009):

- they do not form solid waste;
- they are non-toxic and have a very short lifespan;
- they do not directly cause corrosion.

In addition to the above, the reactions take place at atmospheric pressure and room temperature, so the oxidation technology with hydroxyl radicals can also be described as environmentally friendly. They rank second in terms of oxidation potential, immediately behind fluorine. On the other hand, a significant disadvantage of AOPs could be high cost due to the use of reagents (e.g. hydrogen peroxide) and energy (ozone or UV light generation). Both are necessary to produce an adequate amount of hydroxyl radicals for a sufficient treatment effect. The most important parameter is the dose ratio between the mass of oxidant and the mass of pollution. Despite their wide applicability, hydroxyl radicals also have their limitations. However, AOPs are considered as a group of sustainable water remediation techniques (Satyam & Patra, 2025).

Ozone-based AOPs

In aqueous solutions of organic substances, COD (Chemical Oxygen Demand) first begins to decrease during ozonation. As the oxidation of the organic molecule progresses and CO_2 begins to form, the TOC (Total Organic Carbon) of the aqueous solution also begins to decrease. Complete oxidation of pollutants in aqueous solutions, down to CO_2, water, and inorganic components (nitrite, nitrate, sulphate, phosphate, etc.) is usually uneconomical, and in some cases not even possible, because, for example, acetic acid (due to its molecular structure) does not react with ozone (Ribeiro et al. 2015). The main goal of ozonation is therefore mainly the oxidation or decomposition of organic matter to the point where it becomes biodegradable or at least less harmful to aquatic and terrestrial (micro)organisms (Gottschalk et al., 2010). This could be particularly valuable for persistent micropollutants (Mahmoodi & Pishbin, 2025).

Ozone reacts with substances in two ways: by direct reaction of dissolved ozone with the organic molecule or by indirect reaction via hydroxyl radicals. The extent of both mechanisms and the degree of decomposition of pollutants in the direct or indirect mode depend on several factors, the most important of which are the nature of the pollutant, the ozone dose, and the pH of the medium in which ozonation is carried out. In acidic conditions ($pH < 4$), direct reaction with ozone usually dominates, while at $pH > 9$, the most important oxidation pathway is indirect, i.e., with hydroxyl radicals (Cuerda-Correa et al., 2020).

AOPs FOR REMOVAL OF SELECTED PHARMACEUTICALS – A CASE STUDY

Test compound

The purpose of this study was to measure the effect of ozone dose on the reduction of COD (Chemical Oxygen Demand), TOC (Total Organic Carbon), and increased biodegradability of model urban wastewater containing levofloxacin (LVX). It is a non-biodegradable antibiotic from the group of fluoroquinolones (Gong et al., 2016). The sites of ozone attack of the LVX molecule are shown in Figure 1 (El Najjar et al., 2013).

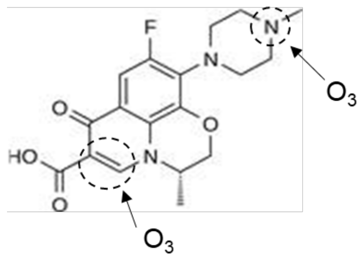

Figure 1. *Levofloxacin (LVX) with proposed sites for reaction with ozone (El Najjar et al., 2013).*

Levofloxacin is an antibacterial agent with a broad spectrum of activity against Gram-positive and Gram-negative bacteria and atypical respiratory pathogens. It is active against both penicillin-susceptible and penicillin-resistant bacteria.

MATERIALS AND METHODS

Ozone was led via a ceramic dispenser at the bottom of a bubble glass column with a volume of 3,500 mL (Žgajnar Gotvajn & Boševski, 2021). The water solution of LVX was pumped with a peristaltic laboratory pump through a column (1 mL s^{-1}) in a closed loop. Nominal ozone concentration in the gas phase was 140 g m^{-3} and the total capacity of ozone production was 7 g h^{-1}. Initial LVX concentration was 100 mg L^{-1}. At 15, 30, 45, 90, 120, 135, and 180 minutes, 30 mL of sample was taken to determine COD and TOC. For the purpose of the biodegradability test, samples were taken after 90 and 180 minutes of ozonation. Final samples were also used for determination of toxicity of activated sludge to microorganisms.

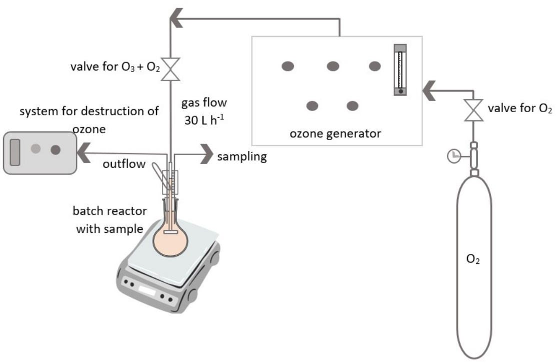

Figure 2. *Laboratory system for ozonation (Courtesy of N. Lekše, 2004).*

RESULTS AND DISCUSSION

LVX in concentration of 100 mg L^{-1} was not biodegradable (less than 10%). Samples after 90 and 180 minutes of ozonation were completely biodegradable. Both exhibited less than 2 days of lag phase; on day 7 more than 75% of biodegradability was determined. The ninety-minute ozonated sample completely biodegraded on day 22, while the 180-minute ozonated sample was completely degraded on day 17. No abiotic degradation was detected (less than 2%). Initial toxicity to microorganisms of activated sludge expressed as EC_{50} value was 1.115 ± 298 mg L^{-1} and it was reduced during ozonation (EC_{50} exceeded 5,000 mg L^{-1}). It can be concluded that ozonation efficiently degrades LVX to at least more biodegradable by-products without toxicity to microorganisms of activated sludge and thus enables further biological treatment of LVX-containing model wastewater. Treatment efficiency during ozonation of LVX according to COD and TOC is presented in Table 3.

Removal of COD was high, 74% (at an ozone dose of 0.40 mol_{ozone} mol $_{COD}^{-1}$), as was the reduction of TOC (47%). Longer ozonation or time-related higher ozone dose did not result in significant improvement in % of LVX removal. The difference in COD and TOC removal indicated the formation of by-products. LVX was oxidized, but not completely mineralized to carbon dioxide, water, and anions.

Table 3. *Treatment efficiency during ozonation of levofloxacin according to COD and TOC.*

Ozone dose (mol_{ozone} mol_{COD}^{-1})	Removal efficiency (%)	
	COD	TOC
0	0	0
0.1	65 ± 3	35 ± 3
0.2	65 ± 1	40 ± 2
0.3	67 ± 2	42 ± 1
0.4	74 ± 4	47 ± 1

However, pH decreased during oxidative treatment from 7.2±0.2 to 5.9±0.4 indicating the formation of simpler acidic products. This was also confirmed by the other toxicity and biodegradability studies (Urbanc, 2022). Reduction of pH could at the same time also shift the ozonation mechanism to direct ozonation rather than oxidation with hydroxyl radicals and thus reduce the oxidation potential of the system and decrease its non-selectivity. However, in the case of LVX it was proven that simple, non-catalytic ozonation is able to reduce its concentration in urban wastewaters.

CONCLUSION

New legislation mandating the monitoring of selected micropollutants in urban wastewaters and the implementation of quaternary treatment in wastewater treatment plants has forced future research and recommendations for effective removal of emerging contaminants. AOPs have a small footprint, making them suitable for implementation in a variety of wastewater treatment facilities. However, they have some disadvantages. They may produce unknown products during the oxidation process, which may require further analysis to ensure the safety of the treated water. The water matrix can reduce their efficiency, causing different interferences and the presence of residual oxidants can also be a problem. This requires careful monitoring and pretreatment measures to mitigate their effects on treatment efficiency. To fulfil the requirements of new legislation to prevent the impact on the environment and human health, numerous studies have yet to be conducted.

ACKNOWLEDGEMENTS

This study was financed by the Slovenian Research and Innovation Agency (ARIS), research program Chemical Engineering (P2-0191). The authors acknowledge the support of the Centre for Research Infrastructure at the University of Ljubljana, Faculty of Chemistry and Chemical Technology, which is part of the Network of Research and Infrastructural Centres UL (MRIC UL) and is financially supported by the Slovenian Research Agency ARIS (Infrastructure programme No. I0-0022).

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