Practical application of UVOX Redox® for pharmaceutical removal from liquid digestate in two biogas plants

Moradi, Nazanin; Lopez-Vazquez, Carlos; Hernandez, Hector Garcia; Proskynitopoulou, Vera; Vouros, Anastasios; Garagounis, Ioannis; Lorentzou, Souzana; Brdjanovic, Damir; van Loosdrecht, Mark C.M.; More Authors

DOI
10.1016/j.eti.2023.103473

Publication date
2024

Document Version
Final published version

Published in
Environmental Technology and Innovation

Citation (APA)
Moradi, N., Lopez-Vazquez, C., Hernandez, H. G., Proskynitopoulou, V., Vouros, A., Garagounis, I., Lorentzou, S., Brdjanovic, D., van Loosdrecht, M. C. M., & More Authors (2024). Practical application of UVOX Redox® for pharmaceutical removal from liquid digestate in two biogas plants. *Environmental Technology and Innovation*, *33*, Article 103473. https://doi.org/10.1016/j.eti.2023.103473

Environmental Technology & Innovation 33 (2024) 103473

Contents lists available at ScienceDirect

Environmental Technology & Innovation

journal homepage: www.elsevier.com/locate/eti

Practical application of UVOX Redox® for pharmaceutical removal from liquid digestate in two biogas plants

Nazanin Moradi [a,b,*], Carlos Lopez-Vazquez [a], Hector Garcia Hernandez [a], Vera Proskynitopoulou [c], Anastasios Vouros [c], Ioannis Garagounis [c], Souzana Lorentzou [c], Kyriakos D. Panopoulos [c], Damir Brdjanovic [a,b], Mark C.M. van Loosdrecht [b], Francisco J. Rubio-Rincón [a]

[a] *Water Supply, Sanitation and Environmental Engineering Department, IHE Delft Institute for Water Education, Westvest 7, 2611 AX Delft, the Netherlands*

[b] *Department of Biotechnology, Delft University of Technology, van der Maasweg 9, 2629 HZ Delft, the Netherlands*

[c] *ARTEMIS Laboratory, Chemical Process and Energy Resources Institute, Centre for Research and Technology Hellas, 57001 Thessaloniki, Greece*

ARTICLE INFO

Keywords:
Liquid digestate
Pharmaceuticals
UVOX Redox®
Surrogate method

ABSTRACT

In recent decades, there has been a growing focus on the management and valorization of digestate, primarily driven by its nutrient-rich composition, which positions it as a promising resource for biofertilizer production. However, several countries still restrict the direct application of digestate due to its potential environmental hazard, which includes the presence of contaminants of emerging concern (CECs) such as pharmaceuticals. This paper explores the efficacy of a novel UV/ozone-based technology, UVOX Redox®, in removing prevalent pharmaceuticals, including antibiotics and non-steroidal anti-inflammatory drugs (NSAIDs), from the digestate of two biogas plants. In both cases, UVOX showed to be a feasible solution for pharmaceutical removal from digestate. Addition of hydrogen peroxide further increased the process efficiency, achieving > 90% removal of all compounds within an hour. The energy per order (E_{EO}) value for all the studied pharmaceuticals was less than the reported median E_{EO} for O_3 and UV treatment, showcasing notable energy efficiency in UVOX technology. Moreover, the research highlights that the presence of ions augments the removal efficiency when applying the UVOX technology. In addition, the research results revealed a significant correlation between the effectiveness of the UVOX technology and UV transmittance, with R^2 exceeding 90% for pharmaceuticals and 75% for Dissolved Organic Carbon (DOC). This finding suggests that UV transmittance can serve as a viable surrogate method for implementing this advanced oxidation process in practical applications.

Abbreviations: AD, Anaerobic Digestion; AOPs, Advanced Oxidation Processes; CECs, Contaminants of Emerging Concern; DIC, Diclofenac; DOC, Dissolved Organic Carbon; DOX, Doxycycline; IBU, Ibuprofen; NOMAD, Novel Organic recovery using Mobil Advanced technology; NSAIDs, Nonsteroidal Anti-Inflammatory Drugs; OTC, Oxytetracycline; ROS, Reactive Oxidative Species; SED, Selective Electrodialysis; SMN, Sulfamethazine; SMX, Sulfamethoxazole; TCN, Tetracycline; UVA, UV Absorbance; UVT, UV Transmittance.

* Corresponding author at: Water Supply, Sanitation and Environmental Engineering Department, IHE Delft Institute for Water Education, Westvest 7, 2611 AX Delft, the Netherlands.

E-mail address: n.moradi@un-ihe.org (N. Moradi).

https://doi.org/10.1016/j.eti.2023.103473
Received 30 October 2023; Received in revised form 29 November 2023; Accepted 2 December 2023

1. Introduction

Organic waste constitutes a substantial proportion of global waste, averaging 46%, with varying rates across different countries (Worldbank.org). Anaerobic digestion (AD) plants present a sustainable solution by converting organic waste into renewable energy and valuable nutrients. The produced digestate is a nutrient-rich resource with potential applications in agriculture, serving as a fertilizer, irrigation fluid, and soil conditioner (Wang and Lee, 2021). However, the direct application of digestate to soil or its discharge can lead to undesirable consequences, including NH_3 and N_2O emissions (Crolla et al., 2013), acidification, eutrophication, and reducing worm populations through high ammonium-N loading rates (Moinard et al., 2021).

Furthermore, over the past few decades, the use of active pharmaceutical compounds such as antibiotics, non-steroidal anti-inflammatory drugs (NSAIDs), and hormones in farming for animal growth and disease control has been significantly increased (Kasumba et al., 2020; Nurk et al., 2019; Widyasari-Mehta et al., 2016). These compounds are typically non-biodegradable, with only 10–20% assimilated by animals. The concentration of these compounds in livestock manure varies between several to 15,200 μg/kg (Yang et al., 2022b). During anaerobic digestion process of livestock manure, pharmaceutical can be removed from liquid phase by biodegradation or sorption onto biological sludge (Liu et al., 2018; Yang et al., 2022b). However, sorption is a phase transfer mechanism and cannot exclude the risk of pharmaceutical discharge into the environment. Furthermore, biodegradation fails to remove non-biodegradable pharmaceutical such as chlortetracycline (Qiang et al., 2019). Therefore, anaerobic digestion is reported to have a moderate effect on pharmaceutical with an average of 47–72% for different antibiotics for instance (Yang et al., 2022b). Different approaches including additives (Zhang et al., 2018; Zhou et al., 2021), pretreatment such as thermal method (Yin et al., 2020), advanced anaerobic system and co-digestion methods (Huang et al., 2018) have been investigated to improve removal of antibiotics during anaerobic digestion process. Although these methods were successful in increasing antibiotic removal during anaerobic digestion process, a significant portion of these compounds still is reported to end up in digestate derived from manure and slurries, with concentrations ranging from 120 μg/L for tetracycline to 66,400 μg/L for chlortetracycline, for instance (Kasumba et al., 2020; Nurk et al., 2019). Therefore, the discharge of digestate can pose potential environmental hazards and contribute to development of antibiotic-resistant bacteria (Gurmessa et al., 2020; Reygaert, 2018).

Furthermore, due to a lack of an available and cost-effective technology, turning digestate into an environmentally-friendly biofertilizer is not an option in different countries. Consequently, the only available alternative for disposing of digestate is to send it to landfills, which may not be an ideal solution from an environmental perspective.

To address these issues, a Novel Organic recovery using Mobil Advanced technology (NOMAD) was developed to serve decentralized rural plants, small treatment plants and small-scale AD markets. NOMAD streamlines the handling of digestate by installing all necessary technologies into two trucks, making it mobile across various AD plants. The NOMAD process encompasses several key steps, including pasteurization, solid-liquid separation, filtration, nutrient recovery, pharmaceutical removal through UVOX Redox® technology (a novel UV/O_3 system), and additional treatment such as reverse osmosis (RO), if necessary.

This hybrid technology has been already tested in several AD plants across Europe. This research specifically focuses on evaluating the effectiveness of UVOX Redox® in removing pharmaceuticals from digestate in two distinct AD plants. The first study site, located in Kozani, Greece, is a pig manure biogas plant that receives animal waste, urine, manure, and corn silage as feedstock. The resulting digestate is presently utilized as a land amendment by local farmers. The second site, situated in Malta, is associated with a sewage treatment plant where the biogas plant receives sludge from the treatment of urban wastewater, farmyard waste, and urban waste from the sewer collection network. The generated digestate is currently disposed of through landfilling.

The UVOX Redox® system is an UV-based Advanced oxidation process (AOPs) that employs a combination of ozone and UV light to enhance the degradation of pharmaceutical compounds, thereby increasing their removal efficiency. Among all existing methods, AOPs are known as the most effective techniques to remove persistent contaminants of emerging concern, which are not removed in biological treatment (De la Cruz et al., 2012; Dong et al., 2022; Kulišťáková, 2023). AOPs are characterized by generation of reactive oxidative species (ROS) such as $OH^\bullet$ radicals. Ozone, an AOP-like process, has demonstrated effectiveness in removing pharmaceuticals from both drinking water and wastewater (Bui et al., 2016; de Oliveira et al., 2020; Hansen et al., 2016). However, there are some limitations associated with ozonation, for instance low mineralization (Miklos et al., 2018). Furthermore, O_3 is less effective in degradation of organic compounds without electron-rich functional group (Lee et al., 2013). To overcome these limitations, the integration and combination of O_3 with an activated method has been suggested (Saeid et al., 2018). For instance, integration of O_3 with UV (254 nm) increases the degradation efficiency of organic matter (Gassie and Englehardt, 2019; Lin et al., 2014). In the presence of UV light, O_3 decomposes to form $OH^\bullet$ radicals that have 10^6 to 10^{12} times higher oxidation capacity than O_3 (Miklos et al., 2018; Von Sonntag, 2008). This integration combines two degradation pathways including the reaction of molecular ozone with organic matter, and the reaction of generated $OH^\bullet$ radicals with organic matter (Coha et al., 2021; Liu et al., 2021). The combination of UV/O_3 has been successfully applied for TOC removal (Keen et al., 2016; Wols and Hofman-Caris, 2012), and pharmaceutical removal from wastewater (Khan et al., 2020). The main drawback of this application is that both the ozone generator and the UV source have a high electricity demand which results in higher cost (Miklos et al., 2018). The UVOX Redox®, however, is a novel UV/O_3 system that has been recently invented for further commercially application and development of AOPs. This innovative technology generates ozone from atmospheric oxygen through the use of a UV lamp, eliminating the need for oxygen supply tanks and ozone generators. Consequently, it significantly reduces both the electricity demand and the associated costs related to ozone generation (Ekowati et al., 2019). Promisingly, the UVOX Redox® system has undergone recent testing in swimming pool water, where it has been reported to effectively remove certain pharmaceutical compounds during treatment (Ekowati et al., 2019).

While promising, the UVOX Redox® technology has never been evaluated for the removal of pharmaceuticals from a high-strength water matrix. Digestate liquids are characterized by a substantial load of organic and inorganic materials, whereas the concentration of pharmaceuticals is significantly lower by several orders of magnitude. These organic and inorganic compounds can potentially impede the efficiency of UVOX Redox® through multiple mechanisms, including obstructing UV penetration and $OH^{\bullet}$ generation, influencing ozone solubility, as well as their competition effect to consume oxidative species. Therefore, the objective of this research was to (i) evaluate the effectiveness of UVOX Redox® for pharmaceutical removal from digestate in different AD plants and its role within the NOMAD technology, (ii) evaluate the contribution of $OH^{\bullet}$ radicals in the removal efficiency, (iii) optimize technology sequence in the NOMAD technology, and (iv) propose an easily-monitored surrogate method for removal efficiency.

In this study, the selection of pharmaceuticals included the most frequently utilized veterinary antibiotics in food processing animals, which encompassed doxycycline (DOX), tetracycline (TCN), oxytetracycline (OTC), sulfamethoxazole (SMX), sulfamethazine (SMN) (Yang et al., 2022a), as well as the widespread NSAIDs present in different types of sludge, including ibuprofen (IBU) and diclofenac (DIC) (Ajibola et al., 2021).

2. Materials and methods

2.1. Chemicals

All pharmaceuticals including doxycycline (DOX), tetracycline (TCN), oxytetracycline (OTC), sulfamethoxazole (SMX), sulfamethazine (SMN), ibuprofen (IBU), and diclofenac (DIC) were purchased from Sigma Aldrich, Chemie GmbH (Germany). Prior to the experiment, the digestate sample was spiked by these compounds to a final concentration of 100 µg/L each.

2.2. UVOX Redox® equipment within the NOMAD truck

The UVOX Redox® was purchased from WAPURE International GmbH (Germany) and installed on the truck as a part of the novel mobile technology for digestate treatment. This equipment consists of a UV chamber constructed from PE100 HDPE, four UV lamps with a total power consumption of 800 W housed within a quartz tube, an O_3-air Xyclon injector device, completed with a booster

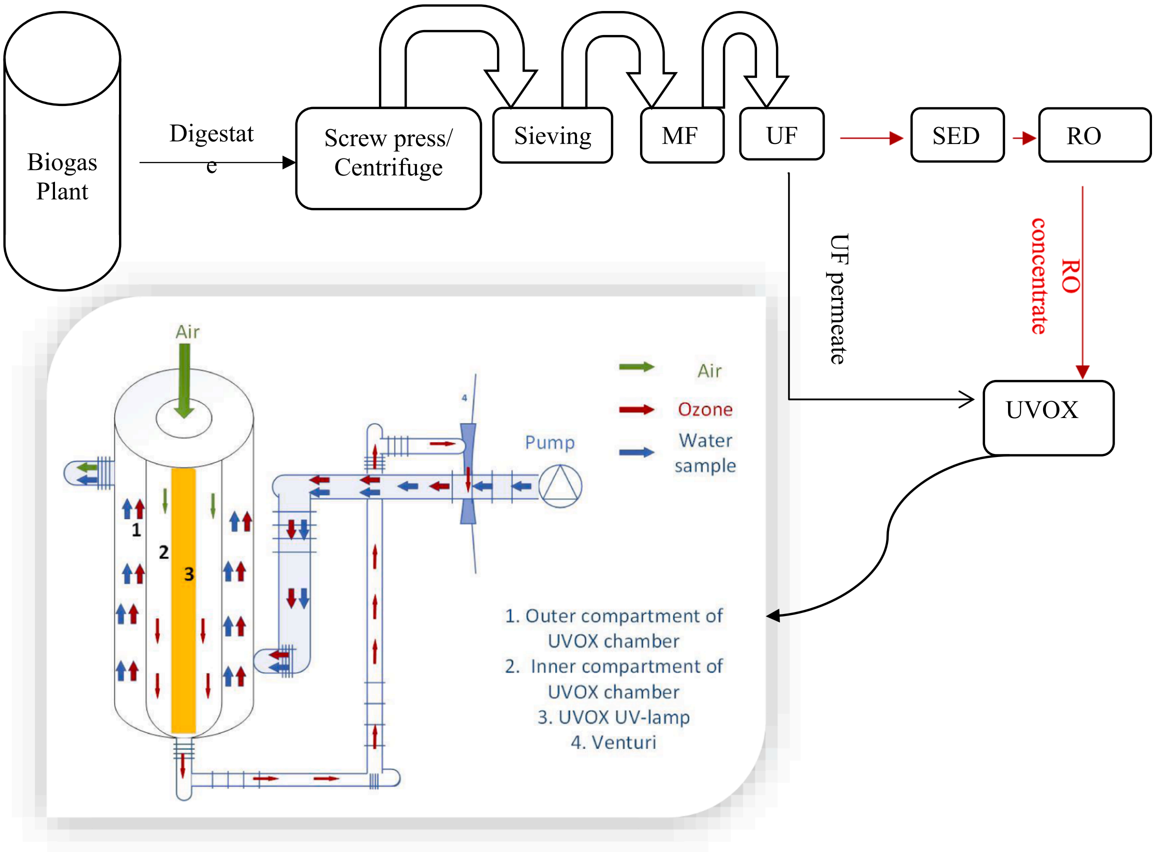


Fig. 1. Simplified process-flow diagram of the different technologies in the NOMAD truck and the compartments and ozone generation mechanism of the UVOX Redox® technology. MF: Microfiltration, UF: Ultrafiltration, SED: Selective electrodialysis (nutrient recovery module), RO: Reverse osmosis. (Adapted from (UVOX.com)). The sequence of technologies before UVOX is shown by red- arrow in the first case study, and by black arrow in the second case study.

pump, a power module and relevant connecting cables. The setup also incorporates a UV-compact measurement device designed to record the percentage of UV light (254 nm) transmitted through a 10 mm liquid sample, hereafter referred to as UVT at T10. The UVOX Redox® technology utilizes powerful UV lights to generate strong oxidative species. The process begins with the introduction of air into the inner compartment of the UVOX chamber, facilitated by a venturi (Xyclon injector) that creates a vacuum effect. Subsequently, atmospheric oxygen is converted into ozone as it is exposed to UV lamps emitting light at a wavelength of 185 nm. The resultant ozonated gas is then injected into the water via the Xyclon injector system. The water and gas mixture are subjected to further UV light exposure (254 nm) within the UVOX outer reaction chamber. Through this process, ozone in the water generates $OH^{\bullet}$ radicals, leading to a notable increase in the relative oxidation potential from 2.07 (for O_3) to 2.8 (for $OH^{\bullet}$). Before commencing the experiments, a baseline measurement was conducted using tap water, revealing a maximum UVT of 95% at T10 and a maximum dissolved ozone concentration of 2 mg/L over a 5-hour duration. A simplified process-flow diagram of the NOMAD truck and the different compartments of the UVOX Redox® is shown in Fig. 1.

2.3. *Design of experiments per study sites*

The experiments were conducted at two distinct study sites, each with its unique design, aimed at assessing the effectiveness of the UVOX system in pharmaceutical removal. To determine its feasibility and establish the optimal treatment sequence within the mobile unit, the application of UVOX was executed on the digestate liquid after nutrient recovery and ion removal in the first case study (Greece), and before nutrient recovery in the second case study (Malta). In both study sites, the UVOX experiment was carried out in a recirculating mode, processing a minimum of 450 litters of the sample with flow rate of 13.5 m^3h^{-1} within a 22-hour timeframe. The experimental design for each study site is outlined as follows:

Case study 1: Pig manure biogas plant, Kozani, Greece.

In the first biogas plant in Greece, the experiment was designed to assess the efficiency of UVOX system to remove pharmaceuticals, and the potential effect of hydrogen peroxide. This set of experiment was conducted after nutrient recovery module. Therefore, following the anaerobic digestion process, the digestate was pumped out of the fermenter and directed into a compressor separator device equipped with 0.5 mm slits situated on-site. The resulting liquid digestate was then collected and transferred to truck containers for further separation. This separation process involved a series of sieves, followed by microfiltration (MF) down to 1 μm and ultrafiltration (UF). Subsequently, the liquid fraction underwent treatment in a selective electrodialysis (SED) module. This specialized module was constructed by combining standard ion exchange membranes and monovalent selective ion exchange membranes to fractionate and concentrate nutrient ions from the digestate, particularly for struvite recovery.

The effluent from the SED process then underwent reverse osmosis (RO), and the resulting RO concentrate was utilized in the UVOX experiment. Notably, the RO concentrate was characterized by a substantial load of organic material and exhibited coloration, resulting in an initial UV transmittance reading of zero in the UVOX system. Consequently, the RO concentrate was diluted until the UV intensity reached a minimum threshold, as detected by the UV-compact sensor. The working solution, comprising the diluted RO concentrate, featured a DOC concentration of 200 mg/L, with no detectable ammonia and a pH level of 8. Before initiating the experiments, this solution was spiked with a pharmaceutical cocktail, each compound present at a concentration of 100 μg/L. Along with the baseline measurement (mentioned in Section 2.2.), two more experiments were conducted in Greece, with and without hydrogen peroxide (Table 1).

Case study 2: Sewage Treatment Plant, Malta.

In the second biogas plant in Malta, the experiments were primarily aimed at assessing the potential impact of matrix components, particularly ions, on the removal of pharmaceutical compounds. Therefore, the selective electrodialysis (SED) module was omitted prior to the use of the UVOX system. Following the anaerobic digestion process, the resulting digestate was directed to centrifuges situated at the treatment plant. The liquid digestate supernatant, subsequently, was collected and transferred to the truck containers integrated into the ultrafiltration system. Thereafter, the liquid fraction was subjected to the UVOX experiment, following appropriate dilution until a minimum UV transmittance reading was recorded by the UV-compact sensor. The diluted digestate supernatant was characterized by a DOC of 365 mg/L, ammonia of 354 mg NH_4-N/L, and a pH level of 8. This working solution was spiked with the pharmaceuticals (100 μg/L each) prior to the experiments, and the experiments were conducted as shown in Table 1.

Experiment M4 was designed based on the quenching method (Guo et al., 2022) to assess the potential generation of $OH^{\bullet}$ radicals in the UVOX system. Tert-butanol (TBA) was added in a molar ratio of TBA/O_3 of 7 (based on the maximum dissolved ozone measured in

Table 1
Experimental design for pharmaceutical removal in both case studies.

Case study	Exp.	Treatment	Sampling time	H_2O_2 /DOC ratio:	Objective
Greece	G1	UVOX	2 min, 20 min, 1 h, 2 h, 5 h, 22 h in both the experiments	0	Pharmaceutical removal
	G2	UVOX+H_2O_2		6.6	Effect of H_2O_2 in removal
Malta	M1	UVOX	2 min, 20 min, 1 h, 2 h, 5 h, 22 h in all the experiments	0	Pharmaceutical removal
	M2	UVOX+H_2O_2		1.6	Effect of H_2O_2 dosage in removal
	M3	UVOX+H_2O_2		6.6	
	M4	UVOX+TBA		0	To assess the potential contribution of $OH^{\bullet}$ radicals

exp M1).

2.4. On-site measurement

pH was measured using a portable pH-meter (WTW-3310), temperature was recorded with an in-line temperature sensor, UV transmittance (%) at T10 was recorded using an in-line UV-compact sensor, and dissolved ozone was measured manually by using

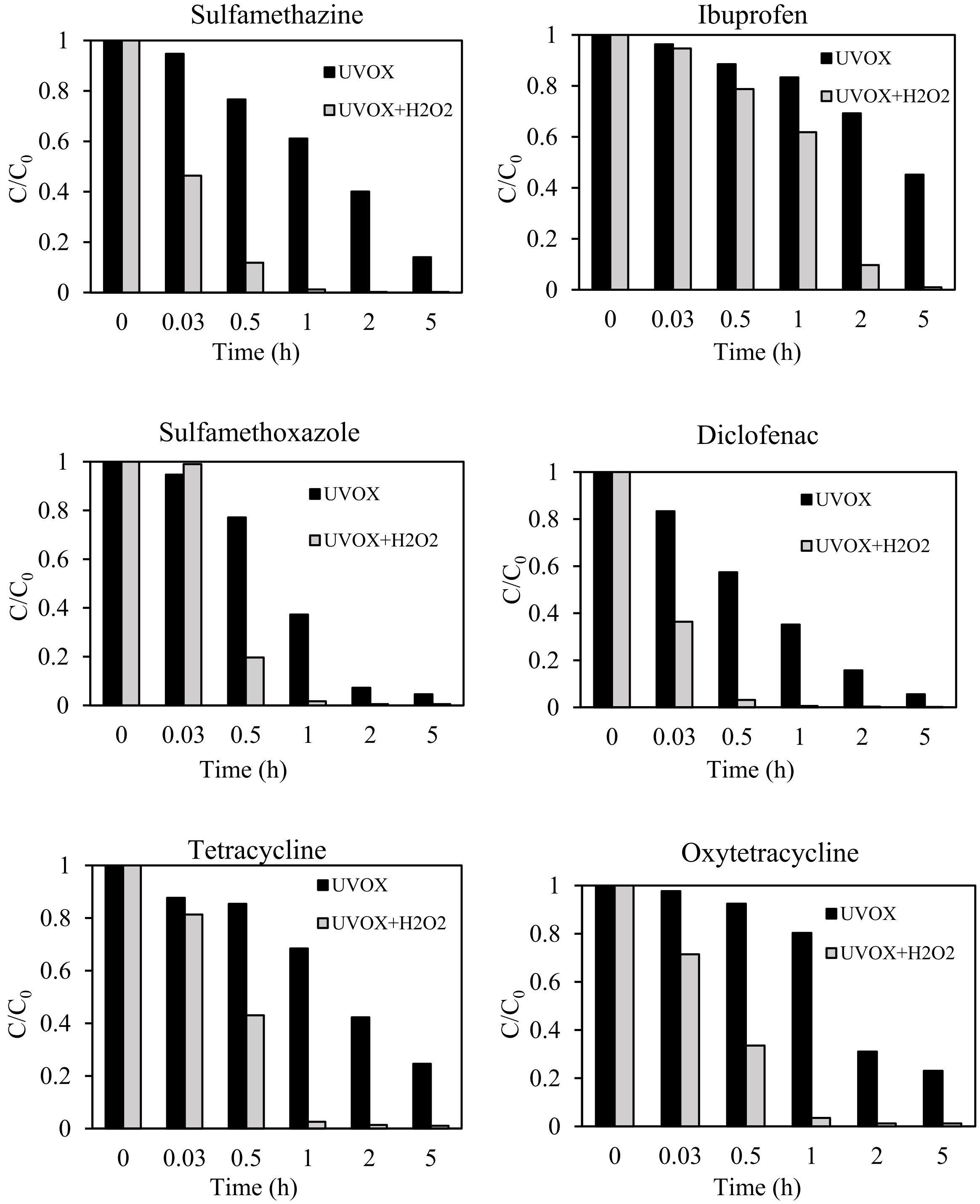


Fig. 2. Removal as function of time for six pharmaceuticals from liquid digestate after ion removal in nutrient recovery module by using UVOX and UVOX+H_2O_2 in first case study: biogas plant, Greece (Exp. G1 and G2).

Hach Ozone AccuVac® (MR) ampules and a portable spectrometer DR-1900.

2.5. Analytical determinations

Dissolved organic carbon (DOC) were determined using a TOC analyser from Shimadzu (the Netherlands). The collected samples for pharmaceutical analysis were spiked with sodium thiosulfate to a final concentration of 80 mg/L to remove the residue of the oxidant, and kept in the freezer (−18 °C) in glass stoppered bottle wrapped in aluminum foil prior to the analysis. The analyses were

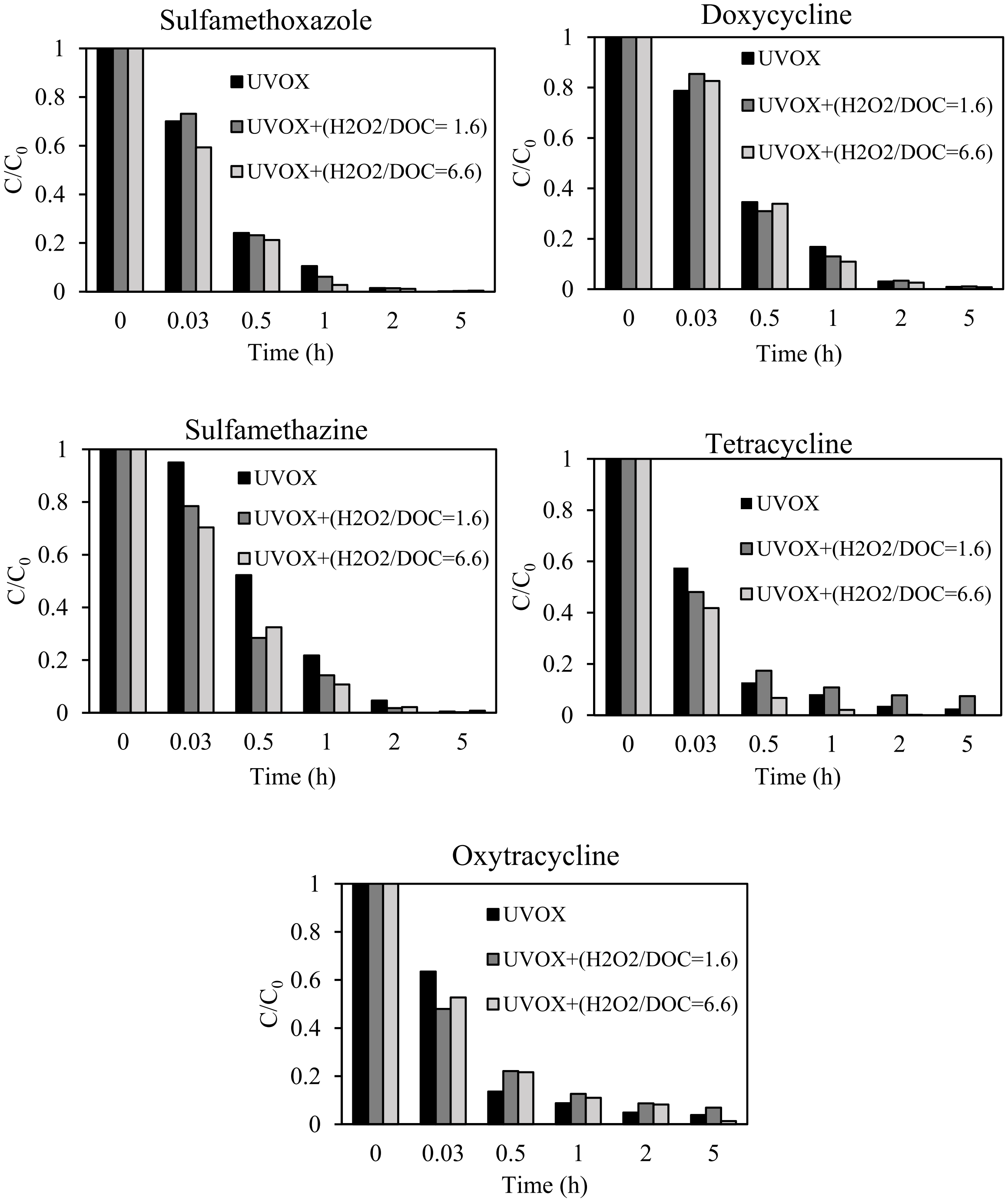


Fig. 3. Removal as function of time for five pharmaceuticals from liquid digestate using UVOX and UVOX+H_2O_2 in second case study: treatment plant, Malta.

performed by Laboratorios Tecnológicos de Levante (Valencia, Spain) (Certificate no. 121/LE1782) where the following methods were applied: For antibiotics, the sample was stirred and filtered by filter of 13 mm PTFE Hydrophilic, 0.45 µm Teknokroma (Ref TR-F1–0021). The filtrate was collected in vial and analysed by direct injection into high-performance liquid chromatography (Agilent HPLC Agilent 1260), equipped with triple quadrupole-mass spectrometer (Agilent QQQ Agilent 6460). The applied column was Eclipse plus C18 (2.1 × 100 mm, 1.8 µm) with mobile Phase A: Water 0.1% formic acid, and mobile Phase B: acetonitrile 0.1% formic acid with the flow of 0.3 mL/min. The linear range was between 0.5 and 500 ppb with detection limit of 0.5 µg/L.

For NSAIDs, the sample was stirred and filtered by filter of 13 mm PTFE Hydrophilic, 0.45 µm Teknokroma (Ref TR-F1–0021), and the filtrate was collected in vial and analysed by direct injection into the same HPLC-QQQ but equipped with Poroshell 120 Phenyl-Hexyl column (3.0 × 100 mm, 2.7 mm) with mobile phase A: Water 0.1 mM ammonium fluoride, mobile phase B: methanol 0.1 mM ammonium fluoride with the flow of 0.4 mL/min. The linear range was between 0.1 and 100 ppb with detection limit of 0.1 µg/L.

2.6. Energy consumption in UVOX Redox® technology

With AOPs being energy-intensive processes (Miklos et al., 2018), assessment of operational energy consumption is crucial for economic purposes. The energy consumption in UVOX system was calculated by using electrical energy per order (E_{EO}) proposed by International Union of Pure and Applied Chemistry (IUPAC) and described by Bolton et al. (2001). Since in UVOX system ozone is generated by the means of UV irradiation, it is considered as an UV-based AOP system. Therefore, for each pharmaceutical, the energy consumption of UV lamp ($E_{EO,\ UV}$), was determined by Eq. (1).

$$E_{EO,UV} = \frac{1000 \times W \times t}{V \times \log\left(\frac{C_0}{C_t}\right)} \tag{1}$$

Where, $E_{EO,UV}$ is electrical energy per order (kW h m^{-3}) for UV irradiation, W is the total power of the UV lamp (kW), V is the total volume of recirculated water (L) within the treatment time t (h), C_0 and C_t are the concentration (mg/L) of the target contaminant at time 0 and time t, respectively.

The equivalent energy per order in case of using H_2O_2 ($E_{EO,H2O2}$) can be calculated as per Eq. (2) (Katsoyiannis et al., 2011; Rosenfeldt et al., 2006)

$$E_{EO,H2O2} = E_{EQ,H2O2} \times C_{H2O2} \tag{2}$$

Where, $E_{EQ,H2O2}$ is the equivalent electrical energy consumption per mole of utilized H_2O_2, and it is equal to 0.241 kWh M^{-1} based on what was reported by Guo et al. (2018) and Sgroi et al. (2021). C_{H2O2} is the concentration (M) of H_2O_2. The energy per order was then determined as per Eq. (3).

$$E_{EO} = E_{EO,UV} + E_{EO,H2O2} \tag{3}$$

3. Results and discussion

3.1. Pharmaceutical removal in both case studies (Exp. G1 and G2) and (Exp. M1-M3)

During the experiment with UVOX treatment (Exp. G1), no target compound was found after 22 h treatment in the water collected from the UVOX process. By adding extra H_2O_2 to the system (Exp. G2), the removal efficiency for all the studied compounds increased and a faster removal was observed during the treatment. A complete removal of all compounds was achieved in 1 h, except for ibuprofen which required 5 h for complete removal (Fig. 2). Fig. 2 shows the removal profile in both treatment in the first 5 h.

In the second study site (Malta), pharmaceutical removal was notably faster compared to the first study site. Regardless of the H_2O_2 dosage, all the target compounds were effectively removed within 2 h. As depicted in Fig. 3, increasing the H_2O_2/DOC ratio from 0 to 1.6 and 6.6 resulted in only a slight improvement in the removal efficiency of the target compounds. For instance, the removal of sulfamethazine increased from 79% to 88% and 90%, and the removal of sulfamethoxazole increased from 90% to 94% and 98%.

Both figures illustrate distinct removal profiles for various compounds. The enhancement in the removal efficiency in the presence of H_2O_2 in first case study aligns with the finding of Liu et al. (2016) who reported an increase in antibiotic removal by adding H_2O_2 to UV-based AOPs, and with the findings of Martini et al. (2018), who reported an enhancement in antibiotic removal in the presence of H_2O_2 in O_3-based AOPs. Furthermore, the second case study exhibited a faster removal rate compared to the first. As elaborated and discussed further below, the removal of pharmaceuticals can be influenced by factors such as the removal mechanism within the UVOX chamber, the molecular structure of pharmaceuticals compound, as well as the effect of the psychochemical characteristics of the digestate matrix influenced by the previous technologies prior to the UVOX treatment.

3.1.1. Effect of O_3/ $OH^{\bullet}$ generation mechanism, and added H_2O_2 on removal process

Oxidation of pharmaceutical compounds and organic matter involves two mechanisms: (i) a direct mechanism, in which molecular ozone selectively targets and degrades specific compounds that contain electron-rich functional groups (Asghar et al., 2022; Feng et al., 2016); and (ii) an indirect mechanism in which ozone decomposes and via a chain of reactions produces $OH^{\bullet}$ radicals which oxidizes the organic matter non-selectively (Khan et al., 2020). Within the UVOX chamber, $OH^{\bullet}$ radicals are generated through the irradiation of O_3 in water with UV light at 254 nm. Therefore, The effectiveness of the indirect mechanism via $OH^{\bullet}$ radicals is significantly dependant on the penetration of UV light into the water sample.

During the UVOX treatment, the low UVT at the initial stage of digestate treatment, gradually increased over time in both case studies. As Fig. 4 shows, the UVT in the first case study (Exp. G1), rose from 0.3% to 38%, and in the second case study (Exp. M1), it increased from 0.33% to 41% after 22 h.

The initial low UVT can be attributed to the presence of organic matter, including aromatic compounds responsible for the brownish-gray color in digestate (Marcilhac et al., 2014). These aromatic compounds absorb UV light, hindering its penetration into the water sample, and adversely impacts $OH^{\bullet}$ radical formation and the indirect removal mechanism. This phenomenon is consistent with the findings of Yang et al. (2021) who reported changes in specific UV absorbance along with the degradation of aromatic compounds. Therefore, at the early stage of UVOX treatment, due to low UV penetration, pharmaceutical oxidation primarily depends on the direct mechanism of molecular ozone.

The indirect removal mechanism, however, can accelerate in the UVOX treatment by adding H_2O_2, which increases a chain of reaction leading to $OH^{\bullet}$ radical formation (Merényi et al., 2010; Rekhate and Srivastava, 2020). The substantial increase in DOC removal with H_2O_2 compared to without H_2O_2 (Fig. 4), indicates the efficiency of the indirect mechanism. Furthermore, the removal of pharmaceuticals was increased with H_2O_2; for instants, the removal of the most persistent pharmaceutical, ibuprofen, increased from 65% to $>$ 98% with H_2O_2 (Fig. 2). This aligns with previous reports on the enhanced performance of ozone-based and UV-based advanced oxidation processes with the addition of H_2O_2 (Adil et al., 2020; Martini et al., 2018).

The rapid increase in UVT in the first 2 h with H_2O_2, coinciding with the removal of all target pharmaceuticals and the disappearance of digestate coloration, was followed by a slower rate of increase (Fig. 4), potentially indicating a gradual oxidation of organic matter. This might be attributed to the initial addition of H_2O_2 as a single shot at the beginning of the experiment. Considering the decomposition of H_2O_2 over time, gradual addition might optimize the process further. This aligns with previous research by St. Laurent et al. (2007) and Woodard and Curran (2006) who noted that while H_2O_2 in contact with UV light or O_3 produces $OH^{\bullet}$ radicals, the compound tends to decompose over time into O_2 and H_2O.

The final experiment (Exp. M4) aimed to assess the respective contributions of O_3 and $OH^{\bullet}$ to the removal process by introducing tert-butanol (TBA) as a quencher. The results (Fig. 5) demonstrated a positive effect of combination of O_3 and $OH^{\bullet}$ radicals on DOC removal, emphasizing the substantial contribution of $OH^{\bullet}$ to the UVOX treatment's efficiency. A statistical comparison of the results

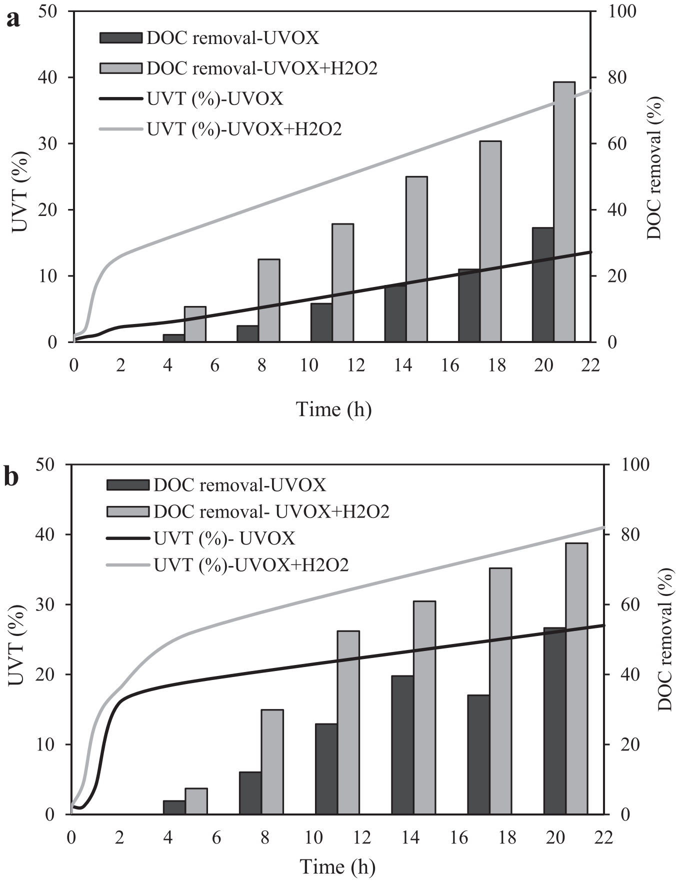


Fig. 4. UV transmittance (UVT) pattern during UVOX treatment with and without H_2O_2 in (a) first case study (Greece), and (b) second case study (Malta).

revealed that DOC removal in the presence of the quencher was significantly lower than its absence (p-value= 0.009 <0.05). Specifically, DOC removal in the 22-hour treatment with the quencher was 27% lower than that observed in the UVOX treatment without the quencher. This aligns with the findings of Guo et al. (2022) who reported that in a quencher/O_3 molar ratio between 5 and 10, TBA effectively quenches all $OH^\bullet$ radicals due to its high concentration and fast reaction with $OH^\bullet$.

In contrast, the observed pattern during the initial 1-hour treatment indicated that quenching $OH^\bullet$ radicals did not significantly affect DOC removal. It confirms that the primary removal mechanism in this phase involved the reaction between molecular ozone and organic compounds.

3.1.2. *Effect of molecular structure on removal of pharmaceuticals*

Within the UVOX experiments, various compounds exhibited distinct removal patterns, indicating the influence of their molecular structures. For instance, in Exp. G1, sulfamethoxazole was effectively removed within 2 h, while ibuprofen's removal did not exceed 65%, even after 5 h. As illustrated in Table 2, compounds containing electron-rich functional group, such as the aniline group in sulfamethazine and sulfamethoxazole, the amine and phenyl groups in tetracycline and oxytetracycline, and the aromatic amine in diclofenac, readily undergo electrophilic ozone reactions (Antoniou et al., 2013; Huber et al., 2005). Nevertheless, compounds lacking electron-rich functional groups, like ibuprofen, exhibit slower removal with ozone. As indicated in Table 2, ibuprofen has a carboxyl group on its aromatic ring, which acts as a withdrawal functional group, reducing the negative charge density of the aromatic ring (Antoniou et al., 2013; Moradi et al., 2023). Therefore, the electrophilic reaction of ozone is less effective in removing ibuprofen, and its removal primarily depends on $OH^\bullet$ radicals, a stronger oxidant that non-selectively targets all organic compounds (Khan et al., 2020). Consequently, the addition of H_2O_2 substantially enhanced ibuprofen removal, reaching 90% within 2 h (Fig. 2).

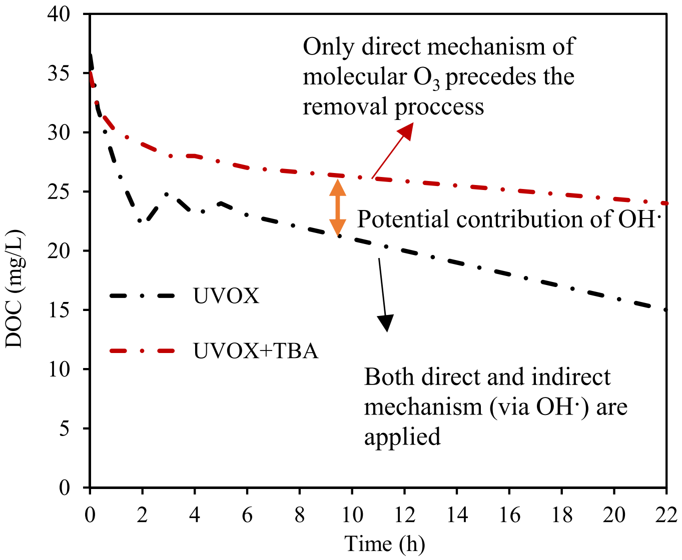
Diclofenac, on the other hand, contains withdrawal groups in both aromatic rings, namely the carboxyl group in one ring and the chloride group in another (Table 2). Nevertheless, the electron-rich aromatic amine situated between the two rings readily undergoes the electrophilic reaction with ozone (Antoniou et al., 2013). Therefore, diclofenac was effectively removed even in the absence of H_2O_2, with an 85% removal within 2 h, underscoring the selectivity of ozone reactions.

The comparatively slow removal of ibuprofen during UVOX treatment has also been reported by Ekowati et al. (2019) during application of UVOX to remove micropollutant from swimming pool, where there was minimal inhibition by organic matter, unlike in this study. In their study, no significant ibuprofen removal was reported during UVOX treatment, but the combination of UVOX and chlorination resulted in complete ibuprofen removal within 25 h (Ekowati et al., 2019). This discrepancy could be attributed to the involvement of other highly reactive oxidative species with a higher redox potential than O_3, such as $Cl^\cdot$ with a redox potential of 2.4 V (Guo et al., 2020).

3.1.3. *Sequence order of technologies in NOMAD truck and its effect on removal*

The second case study in Malta demonstrated faster and more effective removal compared to the first case study in Greece. For instance, sulfamethazine achieved complete removal within 2 h in Malta, even without the use of H_2O_2, whereas in Greece, the removal efficiency for the same compound reached only 58% within 2 h and 78% within 5 h (Fig. 2 and Fig. 3). Furthermore, the removal of DOC in the first case study over 22 h reached up to 34%, while in the second case study, without the use of H_2O_2, a removal of 58% was observed (Fig. 4).

Despite maintaining similar operational conditions in both case studies, the accelerated removal observed in Malta prompts an exploration into the potential influence of specific compounds on the underlying mechanisms governing pharmaceutical removal. In



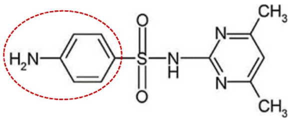
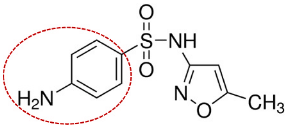
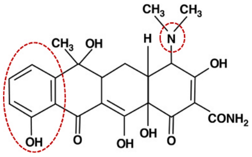
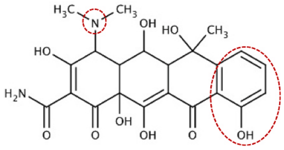
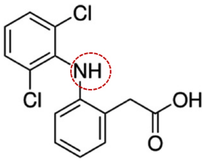
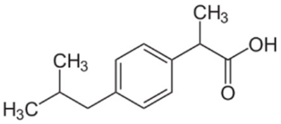
Only direct mechanism of molecular O_3 precedes the removal proccess

Potential contribution of $OH^\cdot$

Both direct and indirect mechanism (via $OH^\cdot$) are applied

Fig. 5. Effect of the TBA quencher on DOC removal (TBA/max dissolved O_3: 7).

Table 2
Molecular structure of investigated pharmaceuticals and their electron-rich functional groups highlighted by red circles for potential electrophilic ozone reactions.

Compound	Molecular structure
Sulfamethazine	
Sulfamethoxazole	
Tetracycline	
Oxytetracycline	
Diclofenac	
Ibuprofen	

the first case study (Exp. G1 and G2 in Greece), the procedural sequence involved nutrient recovery through Selective electrodialysis (SED) preceding the UVOX treatment. Conversely, in the second case study (Exp. M1 to M4 in Malta), the digestate supernatant underwent direct UVOX treatment. As a result, the liquid in Malta (Exp. M1 to M4) inherently exhibited a higher concentration of ions compared to the liquid in Greece (Exp. G1 and G2).

The presence of specific ions can enhance the solubility and decomposition of ozone due to their catalytic effect, thus promoting the generation of reactive oxidative species (ROS), such as $OH^{\bullet}$ radicals. For instance, Psaltou et al. (2019) reported an increase in ozone decomposition, $OH^{\bullet}$ formation, and pCBA degradation in the presence of Fe^{2+} and Co^{2+}. This is attributed to the catalytic impact of these metals on the ozonation process, with direct reactions of Fe^{2+} with ozone (Eq. (4)), and Co^{2+} with O_3 (Eq. (5)), resulting in $OH^{\bullet}$ production (Aihara et al., 2021; Kasprzyk-Hordern et al., 2003).

$$Fe^{2+} + H_2O + O_3 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} + O_2 \tag{4}$$

$$Co^{2+} + H_2O + O_3 \rightarrow Co(OH)^{2+} + OH^{\cdot} + O_2 \tag{5}$$

In our study, the water sample treated in Greece underwent the nutrient recovery step, during which monovalent and divalent ions were removed before UVOX treatment. For instance, the concentration of Fe^{2+} in the digestate supernatant was 12.5 mg/L, whereas after the SED process, it was below the detection limit. Lyngsie et al. (2018) also observed a positive effect of Fe^{2+} in removing dimethoxyhydroquinone in the O_3/H_2O_2 process, which supports the result of this study.

Based on these findings, it is recommended that further studies explore the feasibility of incorporating cobalt or iron, rather than H_2O_2, to enhance pharmaceutical removal performance in the UVOX unit. This suggestion is particularly relevant as these ions can maintain stability for more extended periods, and both serve as micronutrients essential for plant growth (Gomes et al., 2021).

3.2. Energy consumption in UVOX Redox® technology

To evaluate the efficiency of AOPs, electric cost is considered as the main operational cost (Cardoso et al., 2016; Mehrjouei et al., 2014). Bolton et al. (2001) introduced the concept of energy per order (E_{EO}) as a metric for comparing the effectiveness of various treatments within AOPs. In current research, the second case study demonstrated enhanced results in pharmaceutical removal, attributed to the sequence of applied technologies. Therefore, an energy efficiency analysis was conducted for the experiments in this case study, and the resulting E_{EO} values are presented in Table 3. In UVOX treatment, the determined E_{EO} for all the studied compounds was < 0.087 kW h m^{-3}, showcasing notable energy efficiency of UVOX technology in compare with other O_3-based and UV-based AOPs. Within AOPs, a comprehensive review by Miklos et al. (2018) ranks ozonation as the most energy-efficient AOP-like treatment, with a median E_{EO} of 0.15 kW h m^{-3} followed by UV/O_3 treatment with a median E_{EO} of 0.7 kW h m^{-3} and UV/H_2O_2 with a median E_{EO} of 0.75 kW h m^{-3}.

It worth noting that O_3 used in UVOX treatment is generated by a UV irradiation without employing an ozone generator, resulting in lower energy consumption than conventional O_3 and UV/O_3 treatments. For instance, in a pilot-scale treatment to remove different micropollutant from municipal wastewater, the reported E_{EO} for sulfamethoxazole in UV/O_3 treatment was 0.068 kW h m^{-3} and in O_3 treatment was 0.245 kW h m^{-3} (Sgroi et al., 2021). While in our study the E_{EO} value for the same compound was 0.059 kW h m^{-3}.

The addition of H_2O_2 increased the E_{EO} for all studied compound, reflecting its equivalent energy per order (as per Eq. (2)), consistent with the result reported by Sgroi et al. (2021). However, in all cases, the E_{EO} remained below the median E_{EO} reported for conventional UV/O_3 and UV/H_2O_2 treatments (Miklos et al., 2018), underscoring the efficiency of UVOX treatment.

The E_{EO} values in Table 3 were determined based on the total volume of diluted digestate (450 L) recirculating during the treatment time. It is important to note that in full-scale practice the required water for dilution, will be recirculated from the effluent of the UVOX unit. This recirculation process ensures that the extra water for dilution does not contribute to additional water usage but rather is part of a closed-loop system. In this context, to maintain the same dilution factor applied in this study (60 litters of digestate in a final volume of 450 L), the input digestate should get a flow rate of 1.8 m^3 h^{-1}, and the recirculated treated water a flow rate of 11.7 m^3 h^{-1}, resulting in a total working sample flow of 13.5 m^3 h^{-1}. This recirculation approach reflects a practical strategy for managing water usage in full-scale applications. To provide insights into the potential energy consumption in this scenario, the E_{EO} calculation was repeated for the volume of digestate recirculating within the treatment time without dilution (60 litters of digestate with a flow of 1.8 m^3 h^{-1}). In this context, the recalculated E_{EO} values for the same compounds ranged between 0.44 kW h m^{-3} to 0.65 kW h m^{-3} in UVOX treatment and between 0.31 kW h m^{-3} to 0.8 kW h m^{-3} for UVOX/H_2O_2 treatment. Importantly, these values still fall within the range of energy-efficient treatments, aligning with previous comprehensive review by Miklos et al. (2018) that shows AOPs with an E_{EO} value < 1 kWh m^{-3} represent a practical and feasible range for full-scale applications.

3.3. Surrogate-based monitoring

In this study, a significant correlation was observed between the rising trend of UV transmittance (UVT) and the removal of DOC (Fig. 4). Given that the UVOX Redox® is equipped with a compact UV monitor, developing an UV-based surrogate method for UVOX efficiency was explored. The correlation between UVT and DOC, as well as between UVT and sulfamethoxazole (SMX), a representative pharmaceutical compound found in digestate, was evaluated in Exp. G1 and G2. As depicted in Fig. 6, the logarithmic decrease of DOC and SMX correlates with the logarithmic increase in UVT. The data showed the best fit with an exponential formula, as shown in Eq. (6) for DOC in the absence of H_2O_2 (Exp. G1), Eq. (7) for DOC in the presence of H_2O_2 (Exp. G2), Eq. (8) for SMX in the absence of H_2O_2 (Exp. G1), and Eq. (9) for SMX in the presence of H_2O_2 (Exp. G2). These results are in line with the findings of Yang et al. (2021) who proposed an exponential correlation between UV absorbance and the degradation of organic matter.

Table 3
Electrical energy per order (E_{EO} (kW h m^{-3})) for the removal of the studied pharmaceutical.

	E_{EO} (kW h m^{-3})	
	UVOX	UVOX/H_2O_2
Sulfamethoxazole	0.059	0.086
Sulfamethazine	0.087	0.107
Tetracycline	0.054	0.083
Oxytetracycline	0.056	0.11
Doxycycline	0.058	0.149

$$\ln\frac{DOC_0}{DOC} = 1.03e^{0.112\ln(UVT/UVT_0)} \tag{6}$$

$$\ln\frac{DOC_0}{DOC} = 1.28e^{0.23\ln(UVT/UVT_0)} \tag{7}$$

$$\ln\frac{SMX_0}{SMX} = 1.9e^{1.62\ln(UVT/UVT_0)} \tag{8}$$

$$\ln\frac{SMX_0}{SMX} = 2.44e^{1.27\ln(UVT/UVT_0)} \tag{9}$$

The correlation observed in this study stems from the influence of organic matter reactivity and affinity towards oxidants. The reactivity of organic matter is predominantly determined by active aromatic sites and their strong affinity for oxidants (Chon et al., 2015). Initially, when UVT is low, the generation of $OH^{\bullet}$ radical is restricted, and the dominant removal mechanism involves direct oxidation through molecular ozone. As discussed earlier, the aromatic ring provides an electron-rich site for the reaction with molecular ozone, resulting in the oxidation of aromatic rings. Therefore, the UV absorbance associated with the aromatic compounds decreases. The decrease in UV absorbance corresponds to an increase in UVT. Chon et al. (2015) noted that the oxidation of aromatic compounds leads to a decrease in UV absorbance in the water matrix, supporting the finding of this study. The elevated UVT facilitates an increased generation of $OH^{\bullet}$ radicals, thereby contributing to the removal process.

Various studies support the outcomes of this investigation. Chys et al. (2017) established a correlation between UV absorbance at 254 nm and the removal of trace organic matter during the ozonation of municipal wastewater. Similarly, Park et al. (2017) identified a correlation between the oxidation of trace organic compounds and UV absorbance at 254 nm, and total fluorescence (TF). Furthermore, recent work by Yang et al. (2021) demonstrated a correlation between the removal of micropollutants and UV absorbance at 254 nm. All these findings supports the results of the present study, underscoring the efficacy of UV-based surrogate methods in monitoring the removal of target compounds and organic matter during treatment processes.

The surrogate method was applied in the second case study for Exp. M1 and M3 to predict DOC and SMX removal using the obtained equations. The level of agreement between the actual measured data and the predicted values was assessed using the normalized root mean squared deviation (NRMSD) as expressed in Eq. (10) (Oehmen et al., 2010).

$$NRMSD = \frac{\sqrt{\frac{\sum_{i=1}^{n}\left(x_{meas,i}-x_{pred,i}\right)^2}{n}}}{x_{meas,\max} - x_{meas,\min}} \tag{10}$$

Where, x_{meas} and x_{pred} are measured and predicated data, $x_{meas,\max}$ and $x_{meas,\min}$ are the maximum and minimum measured concentration, and n is the number of data points. Validation of the surrogate method in the second case study (Exp. M1 and M3) showed high predictive accuracy for DOC removal, with NRMSD values of 0.12 in UVOX treatment and 0.14 in UVOX/H_2O_2 treatment, corresponding to approximately 87% and 86% predictive capability. However, for SMX removal, the agreement was lower at 77%. It is worth noting that these surrogate-based equations can potentially be improved by considering shorter sampling time intervals.

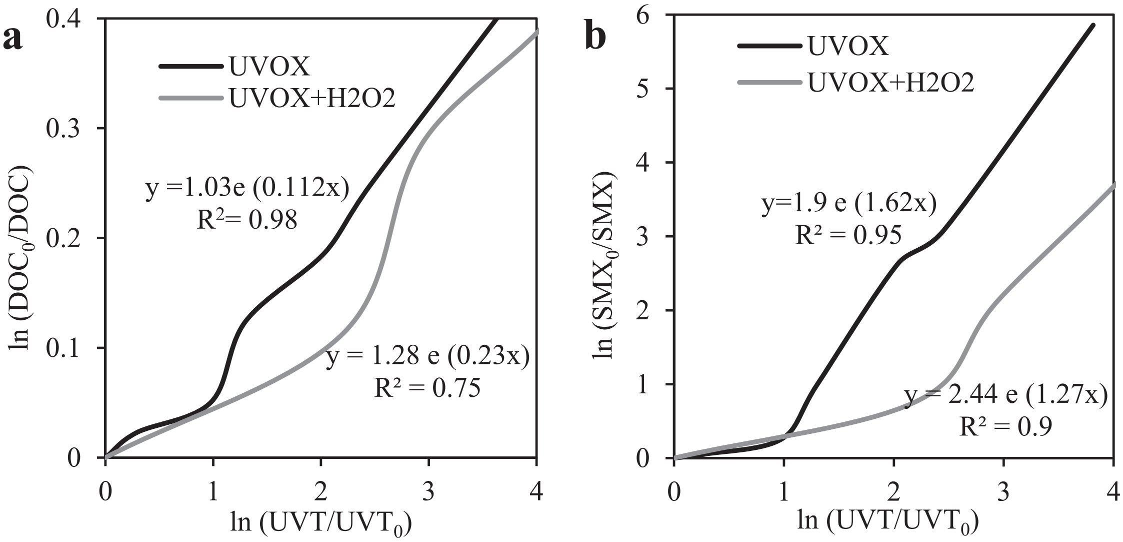


Fig. 6. Oxidation of (a) DOC and (b) SMX as a function of the UVT when treating the digestate in the UVOX (black line) and in the UVOX with the addition of H_2O_2 (gray line).

4. Conclusions

This study delivers crucial insights into the application and effectiveness of the UVOX Redox® technology within the NOMAD mobile unit, which is specifically designed for nutrient recovery and pharmaceutical removal. The sequencing of technologies within this innovative mobile system has a profound impact on removal efficiency. Notably, the direct treatment of liquid digestate following solid/liquid separation and preceding the nutrient recovery module resulted in a faster removal of over 90% of pharmaceuticals within a maximum of 2 h, even without the addition of H_2O_2. However, when the UVOX treatment was applied after the nutrient recovery modules, the efficiency of UVOX decreased, and achieving 90% removal of pharmaceuticals required a longer period (e.g., 90% removal of sulfamethazine took 5 h). Furthermore, this research introduced an easily-monitored surrogate method, UVT, which exhibits a strong correlation with DOC and pharmaceutical removal. The outcomes of this study hold the potential to enhance the practical implementation of this innovative technology, aligning with the broader objectives of establishing sustainable solutions for digestate recycling and promoting the advancement of circular economy strategies and goals.

Funding

This article has been developed under the NOMAD project. The project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 863000.

CRediT authorship contribution statement

Souzana Lorentzou: Project administration. **Damir Brdjanovic:** Supervision. **Kyriakos D. Panopoulos:** Project administration, Supervision. **Vera Proskynitopoulou:** Methodology. **Hector Garcia Hernandez:** Conceptualization, Methodology, Supervision. **Ioannis Garagounis:** Methodology. **Anastasios Vouros:** Methodology. **Francisco J. Rubio-Rincón:** Conceptualization, Funding acquisition, Methodology, Project administration, Supervision. **Mark C.M. van Loosdrecht:** Supervision. **Carlos Lopez-Vazquez:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Nazanin Moradi:** Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

Authors would like to appreciate all the help provided by Panagiotis Dimopoulos Toursidis in operating the UVOX Redox® machine.

References

Adil, S., Maryam, B., Kim, E.-J., Dulova, N., 2020. Individual and simultaneous degradation of sulfamethoxazole and trimethoprim by ozone, ozone/hydrogen peroxide and ozone/persulfate processes: a comparative study. Environ. Res. 189, 109889 https://doi.org/10.1016/j.envres.2020.109889.

Aihara, H., Watanabe, S., Shibata, A., Mahardiani, L., Otomo, R., Kamiya, Y., 2021. Oxidative decomposition of ammonium ion with ozone in the presence of cobalt and chloride ions for the treatment of radioactive liquid waste. Prog. Nucl. Energy 139, 103872. https://doi.org/10.1016/j.pnucene.2021.103872.

Ajibola, A.S., Fawole, S.T., Ajibola, F.O., Adewuyi, G.O., 2021. Diclofenac and ibuprofen determination in sewage sludge using a QuEChERS approach: occurrence and Ecological risk assessment in three Nigerian wastewater treatment plants. Bull. Environ. Contam. Toxicol. 106 (4), 690–699. https://doi.org/10.1007/s00128-021-03139-1.

Antoniou, M.G., Hey, G., Rodríguez Vega, S., Spiliotopoulou, A., Fick, J., Tysklind, M., la Cour Jansen, J., Andersen, H.R., 2013. Required ozone doses for removing pharmaceuticals from wastewater effluents. Sci. Total Environ. 456–457, 42–49. https://doi.org/10.1016/j.scitotenv.2013.03.072.

Asghar, A., Lutze, H.V., Tuerk, J., Schmidt, T.C., 2022. Influence of water matrix on the degradation of organic micropollutants by ozone based processes: a review on oxidant scavenging mechanism. J. Hazard. Mater. 429, 128189 https://doi.org/10.1016/j.jhazmat.2021.128189.

Bolton, J.R., Bircher, K.G., Tumas, W., Tolman, C.A., 2001. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems (IUPAC technical report). Pure Appl. Chem. 73 (4), 627–637. https://doi.org/10.1351/pac200173040627.

Bui, X.T., Vo, T.P.T., Ngo, H.H., Guo, W.S., Nguyen, T.T., 2016. Multicriteria assessment of advanced treatment technologies for micropollutants removal at large-scale applications. Sci. Total Environ. 563–564, 1050–1067. https://doi.org/10.1016/j.scitotenv.2016.04.191.

Cardoso, J.C., Bessegato, G.G., Boldrin Zanoni, M.V., 2016. Efficiency comparison of ozonation, photolysis, photocatalysis and photoelectrocatalysis methods in real textile wastewater decolorization. Water Res. 98, 39–46. https://doi.org/10.1016/j.watres.2016.04.004.

Chon, K., Salhi, E., von Gunten, U., 2015. Combination of UV absorbance and electron donating capacity to assess degradation of micropollutants and formation of bromate during ozonation of wastewater effluents. Water Res. 81, 388–397. https://doi.org/10.1016/j.watres.2015.05.039.

Chys, M., Audenaert, W.T.M., Deniere, E., Mortier, S.T.F.C., Van Langenhove, H., Nopens, I., Demeestere, K., Van Hulle, S.W.H., 2017. Surrogate-based correlation models in view of real-time control of ozonation of secondary treated municipal wastewater—model development and dynamic validation. Environ. Sci. Technol. 51 (24), 14233–14243. https://doi.org/10.1021/acs.est.7b04905.

Coha, M., Farinelli, G., Tiraferri, A., Minella, M., Vione, D., 2021. Advanced oxidation processes in the removal of organic substances from produced water: potential, configurations, and research needs. Chem. Eng. J. 414 https://doi.org/10.1016/j.cej.2021.128668.

Crolla, A., Kinsley, C., Pattey, E., 2013. In: Wellinger, A., Murphy, J., Baxter, D. (Eds.), The Biogas Handbook. Woodhead Publishing, pp. 302–325. https://doi.org/10.1533/9780857097415.2.302.

De la Cruz, N., Giménez, J., Esplugas, S., Grandjean, D., De Alencastro, L.F., Pulgarín, C., 2012. Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. Water Res. 46 (6), 1947–1957. https://doi.org/10.1016/j.watres.2012.01.014.

Dong, G., Chen, B., Liu, B., Cao, Y., de Jourdan, B., Stoyanov, S.R., Ling, J., Ye, X., Lee, K., Zhang, B., 2022. Comparison of O_3, UV/O_3, and UV/O_3/PS processes for marine oily wastewater treatment: degradation performance, toxicity evaluation, and flocs analysis. Water Res. 226, 119234 https://doi.org/10.1016/j.watres.2022.119234.

Ekowati, Y., Ferrero, G., Farré, M.J., Kennedy, M.D., Buttiglieri, G., 2019. Application of UVOX Redox® for swimming pool water treatment: microbial inactivation, disinfection byproduct formation and micropollutant removal. Chemosphere 220, 176–184. https://doi.org/10.1016/j.chemosphere.2018.12.126.

Feng, M., Yan, L., Zhang, X., Sun, P., Yang, S., Wang, L., Wang, Z., 2016. Fast removal of the antibiotic flumequine from aqueous solution by ozonation: Influencing factors, reaction pathways, and toxicity evaluation. Sci. Total Environ. 541, 167–175. https://doi.org/10.1016/j.scitotenv.2015.09.048.

Gassie, L.W., Englehardt, J.D., 2019. Mineralization of greywater organics by the ozone-UV advanced oxidation process: Kinetic modeling and efficiency. Environ. Sci. Water Res. Technol. 5 (11), 1956–1970. https://doi.org/10.1039/c9ew00653b.

Gomes, D.G., Pieretti, J.C., Rolim, W.R., Seabra, A.B., Oliveira, H.C., 2021. In: Jogaiah, S., Singh, H.B., Fraceto, L.F., Lima, Rd (Eds.), Advances in Nano-fertilizers and Nano-pesticides in Agriculture. Woodhead Publishing, pp. 111–143. https://doi.org/10.1016/B978-0-12-820092-6.00005-7.

Guo, K., Wu, Z., Yan, S., Yao, B., Song, W., Hua, Z., Zhang, X., Kong, X., Li, X., Fang, J., 2018. Comparison of the UV/chlorine and UV/H_2O_2 processes in the degradation of PPCPs in simulated drinking water and wastewater: kinetics, radical mechanism and energy requirements. Water Res. 147, 184–194. https://doi.org/10.1016/j.watres.2018.08.048.

Guo, K., Wu, Z., Fang, J., 2020. In: Hernández-Maldonado, A.J., Blaney, L. (Eds.), Contaminants of Emerging Concern in Water and Wastewater. Butterworth-Heinemann, pp. 367–408. https://doi.org/10.1016/B978-0-12-813561-7.00010-9.

Guo, Y., Long, J., Huang, J., Yu, G., Wang, Y., 2022. Can the commonly used quenching method really evaluate the role of reactive oxygen species in pollutant abatement during catalytic ozonation? Water Res. 215, 118275 https://doi.org/10.1016/j.watres.2022.118275.

Gurmessa, B., Pedretti, E.F., Cocco, S., Cardelli, V., Corti, G., 2020. Manure anaerobic digestion effects and the role of pre- and post-treatments on veterinary antibiotics and antibiotic resistance genes removal efficiency. Sci. Total Environ. 721, 137532 https://doi.org/10.1016/j.scitotenv.2020.137532.

Hansen, K.M.S., Spiliotopoulou, A., Chhetri, R.K., Escolà Casas, M., Bester, K., Andersen, H.R., 2016. Ozonation for source treatment of pharmaceuticals in hospital wastewater – ozone lifetime and required ozone dose. Chem. Eng. J. 290, 507–514. https://doi.org/10.1016/j.cej.2016.01.027.

Huang, B., Wang, H.-C., Cui, D., Zhang, B., Chen, Z.-B., Wang, A.-J., 2018. Treatment of pharmaceutical wastewater containing β-lactams antibiotics by a pilot-scale anaerobic membrane bioreactor (AnMBR). Chem. Eng. J. 341, 238–247. https://doi.org/10.1016/j.cej.2018.01.149.

Huber, M.M., GÖbel, A., Joss, A., Hermann, N., LÖffler, D., McArdell, C.S., Ried, A., Siegrist, H., Ternes, T.A., von Gunten, U., 2005. Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. Environ. Sci. Technol. 39 (11), 4290–4299. https://doi.org/10.1021/es048396s.

Kasprzyk-Hordern, B., Ziółek, M., Nawrocki, J., 2003. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. Appl. Catal. B Environ. 46 (4), 639–669. https://doi.org/10.1016/S0926-3373(03)00326-6.

Kasumba, J., Appala, K., Agga, G.E., Loughrin, J.H., Conte, E.D., 2020. Anaerobic digestion of livestock and poultry manures spiked with tetracycline antibiotics. J. Environ. Sci. Health Part B Pestic. Food Contam. Agric. Wastes 55 (2), 135–147. https://doi.org/10.1080/03601234.2019.1667190.

Katsoyiannis, I.A., Canonica, S., von Gunten, U., 2011. Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O_3/H_2O_2 and UV/H_2O_2. Water Res. 45 (13), 3811–3822. https://doi.org/10.1016/j.watres.2011.04.038.

Keen, O.S., Love, N.G., Aga, D.S., Linden, K.G., 2016. Biodegradability of iopromide products after UV/H2O2 advanced oxidation. Chemosphere 144, 989–994. https://doi.org/10.1016/j.chemosphere.2015.09.072.

Khan, A.H., Khan, N.A., Ahmed, S., Dhingra, A., Singh, C.P., Khan, S.U., Mohammadi, A.A., Changani, F., Yousefi, M., Alam, S., Vambol, S., Vambol, V., Khursheed, A., Ali, I., 2020. Application of advanced oxidation processes followed by different treatment technologies for hospital wastewater treatment. J. Clean. Prod. 269, 122411 https://doi.org/10.1016/j.jclepro.2020.122411.

Kulišťáková, A., 2023. Removal of pharmaceutical micropollutants from real wastewater matrices by means of photochemical advanced oxidation processes – a review. J. Water Process Eng. 53, 103727 https://doi.org/10.1016/j.jwpe.2023.103727.

Lee, Y., Gerrity, D., Lee, M., Bogeat, A.E., Salhi, E., Gamage, S., Trenholm, R.A., Wert, E.C., Snyder, S.A., Von Gunten, U., 2013. Prediction of micropollutant elimination during ozonation of municipal wastewater effluents: use of kinetic and water specific information. Environ. Sci. Technol. 47 (11), 5872–5881. https://doi.org/10.1021/es400781r.

Lin, C., Zhang, W., Yuan, M., Feng, C., Ren, Y., Wei, C., 2014. Degradation of polycyclic aromatic hydrocarbons in a coking wastewater treatment plant residual by an O_3/ultraviolet fluidized bed reactor. Environ. Sci. Pollut. Res. 21 (17), 10329–10338. https://doi.org/10.1007/s11356-014-3034-1.

Liu, B., Chen, B., Zhang, B., Song, X., Zeng, G., Lee, K., 2021. Photocatalytic ozonation of offshore produced water by TiO_2 nanotube arrays coupled with UV-LED irradiation. J. Hazard. Mater. 402 https://doi.org/10.1016/j.jhazmat.2020.123456.

Liu, H., Pu, C., Yu, X., Sun, Y., Chen, J., 2018. Removal of tetracyclines, sulfonamides, and quinolones by industrial-scale composting and anaerobic digestion processes. Environ. Sci. Pollut. Res. 25 (36), 35835–35844. https://doi.org/10.1007/s11356-018-1487-3.

Liu, Y., He, X., Fu, Y., Dionysiou, D.D., 2016. Degradation kinetics and mechanism of oxytetracycline by hydroxyl radical-based advanced oxidation processes. Chem. Eng. J. 284, 1317–1327. https://doi.org/10.1016/j.cej.2015.09.034.

Lyngsie, G., Krumina, L., Tunlid, A., Persson, P., 2018. Generation of hydroxyl radicals from reactions between a dimethoxyhydroquinone and iron oxide nanoparticles. Sci. Rep. 8 (1), 10834 https://doi.org/10.1038/s41598-018-29075-5.

Marcilhac, C., Sialve, B., Pourcher, A.-M., Ziebal, C., Bernet, N., Béline, F., 2014. Digestate color and light intensity affect nutrient removal and competition phenomena in a microalgal-bacterial ecosystem. Water Res. 64, 278–287. https://doi.org/10.1016/j.watres.2014.07.012.

Martini, J., Orge, C.A., Faria, J.L., Pereira, M.F.R., Soares, O.S.G.P., 2018. Sulfamethoxazole degradation by combination of advanced oxidation processes. J. Environ. Chem. Eng. 6 (4), 4054–4060. https://doi.org/10.1016/j.jece.2018.05.047.

Mehrjouei, M., Müller, S., Möller, D., 2014. Catalytic and photocatalytic ozonation of tert-butyl alcohol in water by means of falling film reactor: kinetic and cost-effectiveness study. Chem. Eng. J. 248, 184–190. https://doi.org/10.1016/j.cej.2014.03.047.

Merényi, G., Lind, J., Naumov, S., Sonntag, Cv, 2010. Reaction of Ozone with hydrogen peroxide (peroxone process): a revision of current mechanistic concepts based on thermokinetic and quantum-chemical considerations. Environ. Sci. Technol. 44 (9), 3505–3507. https://doi.org/10.1021/es100277d.

Miklos, D.B., Remy, C., Jekel, M., Linden, K.G., Drewes, J.E., Hübner, U., 2018. Evaluation of advanced oxidation processes for water and wastewater treatment – a critical review. Water Res. 139, 118–131. https://doi.org/10.1016/j.watres.2018.03.042.

Moinard, V., Redondi, C., Etiévant, V., Savoie, A., Duchene, D., Pelosi, C., Houot, S., Capowiez, Y., 2021. Short- and long-term impacts of anaerobic digestate spreading on earthworms in cropped soils. Appl. Soil Ecol. 168, 104149 https://doi.org/10.1016/j.apsoil.2021.104149.

Moradi, N., Vazquez, C.L., Hernandez, H.G., Brdjanovic, D., van Loosdrecht, M.C.M., Rincón, F.R., 2023. Removal of contaminants of emerging concern from the supernatant of anaerobically digested sludge by O_3 and O_3/H_2O_2: ozone requirements, effects of the matrix, and toxicity. Environ. Res. 235, 116597 https://doi.org/10.1016/j.envres.2023.116597.

Nurk, L., Knörzer, S., Jacobi, H.F., Spielmeyer, A., 2019. Elimination of sulfonamides and tetracyclines during anaerobic fermentation - a "Cheshire Cat" phenomenon. Sustain. Chem. Pharm. 13 https://doi.org/10.1016/j.scp.2019.100157.

Oehmen, A., Lopez-Vazquez, C.M., Carvalho, G., Reis, M.A.M., van Loosdrecht, M.C.M., 2010. Modelling the population dynamics and metabolic diversity of organisms relevant in anaerobic/anoxic/aerobic enhanced biological phosphorus removal processes. Water Res. 44 (15), 4473–4486. https://doi.org/10.1016/j.watres.2010.06.017.

de Oliveira, M., Frihling, B.E.F., Velasques, J., Filho, F.J.C.M., Cavalheri, P.S., Migliolo, L., 2020. Pharmaceuticals residues and xenobiotics contaminants: occurrence, analytical techniques and sustainable alternatives for wastewater treatment. Sci. Total Environ. 705, 135568 https://doi.org/10.1016/j.scitotenv.2019.135568.

Park, M., Anumol, T., Daniels, K.D., Wu, S., Ziska, A.D., Snyder, S.A., 2017. Predicting trace organic compound attenuation by ozone oxidation: development of indicator and surrogate models. Water Res. 119, 21–32. https://doi.org/10.1016/j.watres.2017.04.024.

Psaltou, S., Karapatis, A., Mitrakas, M., Zouboulis, A., 2019. The role of metal ions on p-CBA degradation by catalytic ozonation. J. Environ. Chem. Eng. 7 (5), 103324 https://doi.org/10.1016/j.jece.2019.103324.

Qiang, H., Yang, Y., Li, N., Song, Y., Li, Y., 2019. Effect of chlortetracycline concentration on mesophilic anaerobic digestion characteristics and antibiotic degradation of chicken manure. Trans. CSAE 35, 181–190.

Rekhate, C.V., Srivastava, J.K., 2020. Recent advances in ozone-based advanced oxidation processes for treatment of wastewater-a review. Chem. Eng. J. Adv., 100031 https://doi.org/10.1016/j.ceja.2020.100031.

Reygaert, W.C., 2018. An overview of the antimicrobial resistance mechanisms of bacteria. AIMS Microbiol. 4 (3), 482–501. https://doi.org/10.3934/microbiol.2018.3.482.

Rosenfeldt, E.J., Linden, K.G., Canonica, S., von Gunten, U., 2006. Comparison of the efficiency of.OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2. Water Res. 40 (20), 3695–3704. https://doi.org/10.1016/j.watres.2006.09.008.

Saeid, S., Tolvanen, P., Kumar, N., Eränen, K., Peltonen, J., Peurla, M., Mikkola, J.-P., Franz, A., Salmi, T., 2018. Advanced oxidation process for the removal of ibuprofen from aqueous solution: a non-catalytic and catalytic ozonation study in a semi-batch reactor. Appl. Catal. B Environ. 230, 77–90. https://doi.org/10.1016/j.apcatb.2018.02.021.

Sgroi, M., Snyder, S.A., Roccaro, P., 2021. Comparison of AOPs at pilot scale: energy costs for micro-pollutants oxidation, disinfection by-products formation and pathogens inactivation. Chemosphere 273, 128527. https://doi.org/10.1016/j.chemosphere.2020.128527.

St. Laurent, J.B., de Buzzaccarini, F., De Clerck, K., Demeyere, H., Labeque, R., Lodewick, R., van Langenhove, L., 2007. In: Johansson, I., Somasundaran, P. (Eds.), Handbook for Cleaning/Decontamination of Surfaces. Elsevier Science B.V., Amsterdam, pp. 57–102. https://doi.org/10.1016/B978-044451664-0/50003-6.

UVOX.com. The UVOX REDOX® Process. https://www.uvox.com/how/.

Von Sonntag, C., 2008. Advanced Oxidation Processes: Mechanistic aspects, pp. 1015–1021. 10.2166/wst.2008.467.

Wang, W., Lee, D.-J., 2021. Valorization of anaerobic digestion digestate: a prospect review. Bioresour. Technol. 323, 124626 https://doi.org/10.1016/j.biortech.2020.124626.

Widyasari-Mehta, A., Hartung, S., Kreuzig, R., 2016. From the application of antibiotics to antibiotic residues in liquid manures and digestates: a screening study in one European center of conventional pig husbandry. J. Environ. Manag. 177, 129–137. https://doi.org/10.1016/j.jenvman.2016.04.012.

Wols, B.A., Hofman-Caris, C.H.M., 2012. Review of photochemical reaction constants of organic micropollutants required for UV advanced oxidation processes in water. Water Res. 46 (9), 2815–2827. https://doi.org/10.1016/j.watres.2012.03.036.

Woodard, Curran, I., 2006. In: Woodard, Curran, I. (Eds.), Industrial Waste Treatment Handbook, second edition. Butterworth-Heinemann, Burlington, pp. 149–334. https://doi.org/10.1016/B978-075067963-3/50009-6.

Worldbank.org. Trends in Solid Waste Management.

Yang, G., Xie, S., Yang, M., Tang, S., Zhou, L., Jiang, W., Zhou, B., Li, Y., Si, B., 2022a. A critical review on retaining antibiotics in liquid digestate: potential risk and removal technologies. Sci. Total Environ. 853, 158550 https://doi.org/10.1016/j.scitotenv.2022.158550.

Yang, L., Si, B., Tan, X., Xu, J., Xu, W., Zhou, L., Chen, J., Zhang, Y., Zhou, X., 2022b. Valorization of livestock manure for bioenergy production: a perspective on the fates and conversion of antibiotics. Resour. Conserv. Recycl. 183, 106352 https://doi.org/10.1016/j.resconrec.2022.106352.

Yang, Y., Liu, Z., Demeestere, K., Van Hulle, S., 2021. Ozonation in view of micropollutant removal from biologically treated landfill leachate: removal efficiency, OH exposure, and surrogate-based monitoring. Chem. Eng. J. 410, 128413 https://doi.org/10.1016/j.cej.2021.128413.

Yin, F., Dong, H., Zhang, W., Zhu, Z., Shang, B., 2020. Additional function of pasteurisation pretreatment in combination with anaerobic digestion on antibiotic removal. Bioresour. Technol. 297, 122414 https://doi.org/10.1016/j.biortech.2019.122414.

Zhang, Z., Gao, P., Cheng, J., Liu, G., Zhang, X., Feng, Y., 2018. Enhancing anaerobic digestion and methane production of tetracycline wastewater in EGSB reactor with GAC/NZVI mediator. Water Res. 136, 54–63. https://doi.org/10.1016/j.watres.2018.02.025.

Zhou, H., Cao, Z., Zhang, M., Ying, Z., Ma, L., 2021. Zero-valent iron enhanced in-situ advanced anaerobic digestion for the removal of antibiotics and antibiotic resistance genes in sewage sludge. Sci. Total Environ. 754 https://doi.org/10.1016/j.scitotenv.2020.142077.