

Article

Evaluation of Heterogeneous Catalytic Ozonation for Micropollutants Removal from Wastewater: Application of a Pre-Industrial-Scale Unit

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Abstract: The present study evaluates the application of heterogeneous catalytic ozonation for the removal of micropollutants from wastewater effluent in a pre-industrial-scale unit, consisting of a post-filtration, an ozone dilution, a catalytic ozonation, and a final biological stabilization step. The important step of ozone dilution is optimized by the use of a hollow fiber membrane that minimizes the loss of ozone gas due to the transfer of ozone to the liquid phase mainly by diffusion. It is observed that the efficiency of this sub-system is maximized for the dead-end operation of the membrane and the introduction of ozone gas to the shell side and liquid phase to the lumen side of the membrane module. Under these conditions, the concentration of dissolved ozone is directly dependent on the ratio of ozone gas feed to the wastewater flow subjected to post-treatment. Regarding the removal of MPs, part of their degradation already takes place at this stage (i.e., during ozone dilution), while after the post-treatment of wastewater effluent in the catalytic ozonation bed, the MP degradation yield ranges from 35% up to complete removal, depending on the type and properties of the specific MP. The addition of a final biological filtration bed to the overall treatment unit significantly increased its performance, regarding the removal of MPs, enhancing it by an additional removal rate that can reach up to 30%.

Keywords: micropollutants; emerging contaminants; wastewater; WWTP; hollow fiber membranes; heterogeneous catalytic ozonation; pilot-scale unit



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1. Introduction

Micropollutants (MPs), also referred to as emerging contaminants, typically consist of synthetic or natural compounds discharged from various sources, ultimately entering water bodies primarily at trace levels, ranging from a few nanograms per liter (ng/L) to several micrograms per liter (µg/L) [1–3]. They encompass primarily pharmaceuticals, personal care products, pesticides, stimulants, persistent organic pollutants, and micro- and nano-plastics, posing potential adverse effects on living organisms and environmental processes [4,5]. Researchers have predominantly identified wastewater treatment plants (WWTPs) as the primary origin of MPs in aquatic environments [5,6]. While WWTPs utilize microorganisms to eliminate common organic compounds and nutrients from wastewater, their efficacy in MP removal is typically constrained and variable, ranging from 12.5% to 100% for certain frequently encountered compounds [7]. The diminished removal efficiency

could stem from low concentrations, the inherently stable chemical structures of MPs, or inadequate conditions in WWTP facilities [7,8].

Given the challenge of conventional WWTPs in removing MPs, alternative or additional treatment methods such as chemical oxidation, adsorption, or membrane filtration have been explored [9–11]. One promising approach for eliminating a broad spectrum of emerging and high-risk MPs involves chemical oxidation using ozone, either directly or indirectly [11–14]. Ozone treatment has demonstrated high effectiveness due to direct ozone reactions with some organic compounds and ozone decomposition into hydroxyl radicals (HO•), potent non-selective reactive oxygen species (ROS) [6,13,15]. However, ozone decomposition in water involves parallel reactions, potentially impeding less reactive ROS from degrading MPs. To enhance the ozone degradation efficiency for MPs, ozone can be combined with certain catalysts to promote ozone decomposition into HO• [16–18]. However, they often exhibit significant limitations such as low solubility [19] and high energy consumption [20], resulting in slow or incomplete oxidation reactions or high operational costs [21]. These drawbacks are mainly attributed to reduced mass transfer, stemming from ozone gas dispersion in the liquid phase through bubbles. These challenges can be mitigated by diffusing ozone into water/wastewater through appropriate membrane modules [22].

Utilizing membranes presents an efficient alternative for ozone–water/–wastewater contact, with the membrane serving as an interface between the gas and liquid phases. This method offers several advantages over conventional ozone mass transport methods, including minimal ozone gas loss, as the latter is mainly transferred through diffusion, leading to greater ozone dissolution in the aqueous phase and consequently lower energy requirements. Hollow fiber membranes are usually employed in this case due to their high surface-to-volume ratio [21,23]. However, existing studies on ozone mass transfer through membranes primarily focus on “flow-through” ozone diffusion processes, where ozone gas exits the membrane.

While this operation facilitates ozone mass transfer calculations, significant ozone gas loss occurs in the outflow stream, potentially leading to lower performance than calculated. To fully exploit ozone, the gas phase must be entirely transported to the liquid phase, suggesting that hollow fiber membranes should be operated in a dead-end mode without a gas outlet. In this context, the authors conducted a series of experiments in a continuous-flow pilot unit to examine ozone mass transfer under various operating conditions and the impact of hollow fiber membrane dead-end function on ozone transport to the liquid phase [24]. The study results suggested that optimizing the ozonation process involves selecting appropriate membranes (in terms of construction material and geometrical characteristics) and adjusting the ozone-gas-to-water flow ratio, leading to significant treatment cost reductions during process scaling-up. These findings guided the membrane selection for ozone gas diffusion in the liquid phase in the pre-industrial-scale unit used in the present study to study MP removal through heterogeneous catalytic ozonation. The ozone efficiency of the selected membrane under real conditions was evaluated through an extensive experimental campaign under different conditions (water quality, open-/dead-end membrane function, introduction of ozone gas into membrane shell/lumen) and operating parameters (liquid flow velocity, ozone gas mass flow rate) [24].

Nevertheless, the primary aim of the present research remained to assess the potential of certain materials to serve as efficient catalysts for MP ozonation, studying low-concentration MP removal in a pre-industrial-scale unit, and simulating real process conditions. To achieve this objective, the authors conducted this study based on earlier research. Previous pertinent studies indicated that introducing suitable solid materials into an ozonation system could contribute to MP degradation, influenced by factors such as the physicochemical characteristics of the catalyst, its affinity with the contaminant, and the solution matrix. In particular, it was concluded that the PZC value of solid materials and their wettability are crucial to the affinity and interaction between ozone and their surface. Neutrally charged hydrophilic surfaces were found to accelerate ozone decomposition into

HO• [25,26]. The optimal conditions for micropollutant removal through heterogeneous catalytic ozonation include a pH near 8 and a temperature around 25 °C [27,28]. Catalysts with neutral charge, moderate/high wettability, and moderate adsorption capacity, in combination with typical WWTP pH values (around 7.5), enhance ozone contact with the catalyst surface and its subsequent decomposition into HO•. Zeolite and PET emerged as the most efficient materials for catalyzing MP ozonation in both batch mode [25,26] and continuous-flow experiments [27,28]. This study examines the catalytic action of these materials during MP ozonation in a specifically constructed pre-industrial-scale unit, comprising post-filtration, ozone dilution, catalytic ozonation, and biological stabilization steps for treating common WWTP effluents.

2. Results and Discussion

2.1. Ozone Transfer to the Liquid Phase

2.1.1. Effect of Main Process Parameters

The dissolved ozone concentrations produced in the pre-industrial-scale unit using the PTFE hollow fiber membrane are depicted in Figure 1. The results are presented versus the ozone gas mass flow rate for different liquid velocities. The diagrams in Figure 1a correspond to the open-end operation of the membrane (i.e., with a gas outlet), introducing the ozone gas into the lumen (membrane fibers), and using water as the liquid phase, while Figure 1b shows the respective diagrams resulting from the same operating conditions of the membrane but using the secondary treated effluent wastewater as the liquid phase. As can be observed from the comparison of these diagrams, in order to achieve the same values of dissolved ozone concentrations at the membrane outlet, different ozone gas mass flow rates were required, namely almost 3 times higher for the treated wastewater (Figure 1b) when compared to water (Figure 1a). This fact was due to the higher concentrations of organic matter, of MPs, as well as other compounds in the case of wastewater, which reacted with (and consumed) the ozone and, consequently, increased the demand for ozone gas mass supply at the membrane inlet.

Figure 1c,d present the ozone dilution achieved in the pre-industrial-scale unit for the post-treatment of secondary effluent, applying a dead-end operation of the membrane and the introduction of ozone gas to the lumen and the membrane shell, respectively. A comparison between Figure 1b,c indicates that the dead-end operation of the membrane, i.e., without a separate gas outlet, significantly increased its efficiency in terms of ozone transfer to the liquid phase, as was also observed in a relevant study examining the application of dead-end hollow fiber membranes for the optimization of ozonation process [24]. Specifically, for the production of dissolved ozone at a concentration of 1 mg/L, the demand for ozone gas mass flow rate decreased twice from the open-end to the dead-end operation, while it became even smaller as the desired value of dissolved ozone concentration increased, reaching up to 3 times less for 4 mg/L. A significant increase in membrane efficiency, regarding ozone dilution, was also achieved by introducing the ozone gas to the shell side and the liquid phase to the lumen side of the hollow fiber membrane (Figure 1d), as has also been observed by other researchers [29]. This increase, in the case of the pre-industrial-scale unit and for the operating conditions examined, could reach up to 4 mg/L of additional dissolved ozone in the liquid phase (for a constant ozone gas mass flow rate). Finally, as observed in all these diagrams, an increase in the ozone gas mass flow rate led to higher dissolved ozone concentrations, while the application of greater liquid flow velocities adversely affected the dissolution of ozone in the liquid phase. Namely, the dissolved ozone concentration was directly dependent on the ratio of the ozone gas feed to the liquid flow.

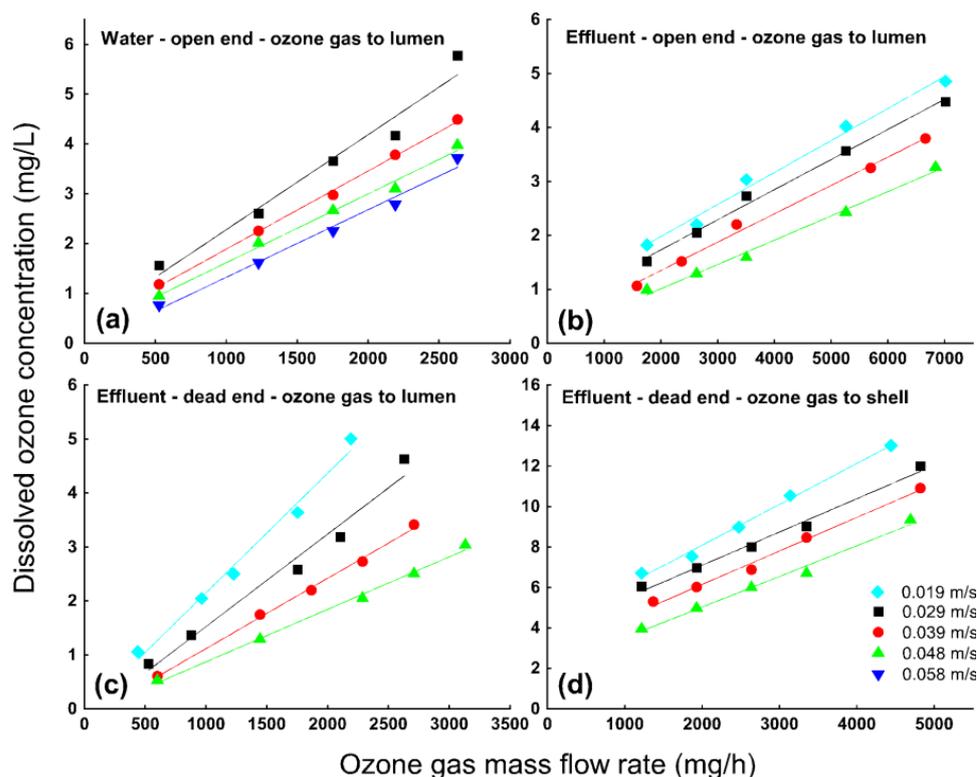


Figure 1. Dissolved ozone concentrations versus ozone gas mass flow rate for different liquid flow velocities. (a) Liquid phase: water; membrane operation: open-end; ozone gas introduction: into the membrane lumen. (b) Liquid phase: wastewater effluent; membrane operation: open-end; ozone gas introduction: into the membrane lumen. (c) Liquid phase: wastewater effluent; membrane operation: dead-end; ozone gas introduction: into the membrane lumen. (d) Liquid phase: wastewater effluent; membrane operation: dead-end; ozone gas introduction: into the membrane shell.

2.1.2. Membrane Performance

To quantify the membrane performance, regarding the transfer of ozone to the liquid phase, the ratio of the ozone mass flow rate in the liquid phase (dissolved) to the ozone gas mass flow rate (feed) was calculated (Figure 2). Corresponding to the diagrams in Figure 1, it was observed that the efficiency of the post-treatment system was greater when treating water (Figure 2a) than when treating (treated) wastewater (Figure 2b), while it was maximized for the dead-end operation (Figure 2c) for the introduction of ozone gas to the shell side and of the liquid phase to the lumen side of the hollow fiber membrane (Figure 2d). In this case, the system performance appeared to vary significantly with the ozone gas mass flow rate demand. In other words, as the desired value of dissolved ozone at the membrane outlet increased, and consequently the requirement for ozone gas supply increased, the treatment system's performance decreased. This fact was probably due to the increase in ozone gas losses when greater mass flow rates were applied.

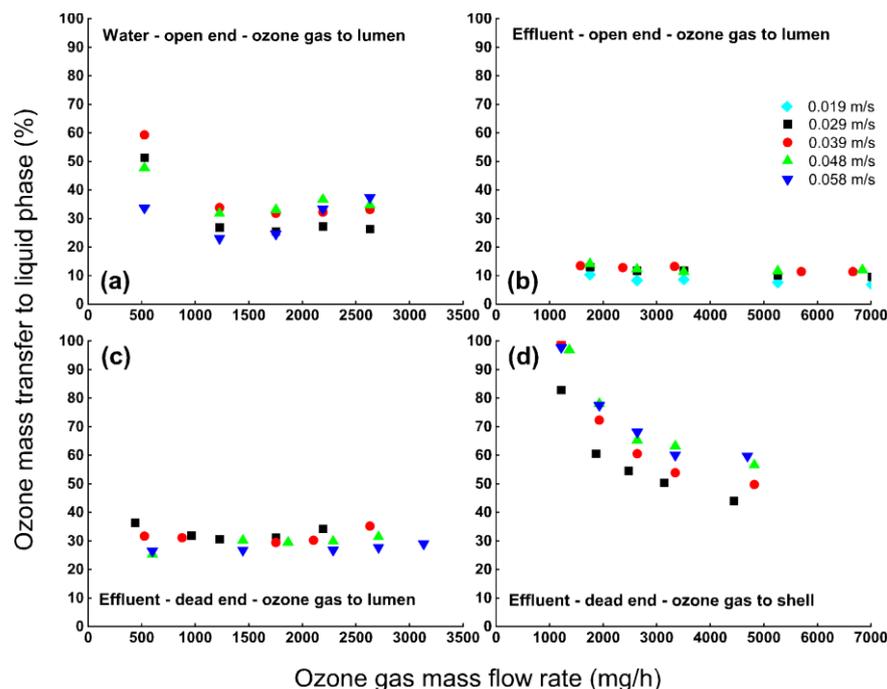


Figure 2. Ozone mass transfer to liquid phase (%) versus the ozone gas mass flow rate for different liquid flow velocities. (a) Liquid phase: water; membrane operation: open-end; ozone gas introduction: into the membrane lumen. (b) Liquid phase: wastewater effluent; membrane operation: open-end; ozone gas introduction: into the membrane lumen. (c) Liquid phase: wastewater effluent; membrane operation: dead-end; ozone gas introduction: into the membrane lumen. (d) Liquid phase: wastewater effluent; membrane operation: dead-end; ozone gas introduction: into the membrane shell.

2.2. Heterogeneous Catalytic Ozonation

The efficiency of heterogeneous catalytic ozonation in the degradation of MPs was evaluated by means of evaluating the pre-industrial-scale unit's performance regarding the removal of selected (added) MPs. As aforementioned, the addition of selected MPs to the WWTP-treated effluent was carried out after the post-filtration step (first fixed bed), and their initial concentration was 2 μM . Figure 3 depicts the results of the operation of the unit under real ("field") conditions for the treatment of WWTP effluent with heterogeneous catalytic ozonation, using zeolite as a catalyst, with regard to the removal of selected MPs. As can be observed in Figure 3 ("p-CBA"), the performance of this treatment unit, considering P-chlorobenzoic acid (p-CBA) removal, increased with each successive treatment step. For an ozone gas supply equal to that at the existing ozonation unit of the "AINEIA" WWTP (16 L/h), almost one quarter of the added p-CBA was degraded during the dilution of ozone in the liquid phase (i.e., in the membrane), and an additional 10% was removed in the catalytic ozonation bed, while the biological stabilization bed contributed with an extra 30% to MP degradation, indicating the significance of this final post-treatment stage. It is considered that the ozonation of MPs in the presence of the catalyst (second fixed bed) led to their decomposition into different, biologically active, transformation products, which were then further degraded in the third fixed bed during the final biological stabilization–filtration of the treated effluent. This advantage of ozonation to transform organic substances into more polar compounds, thus resulting in an increased efficiency of biological treatment, is also supported by other researchers [11,30].

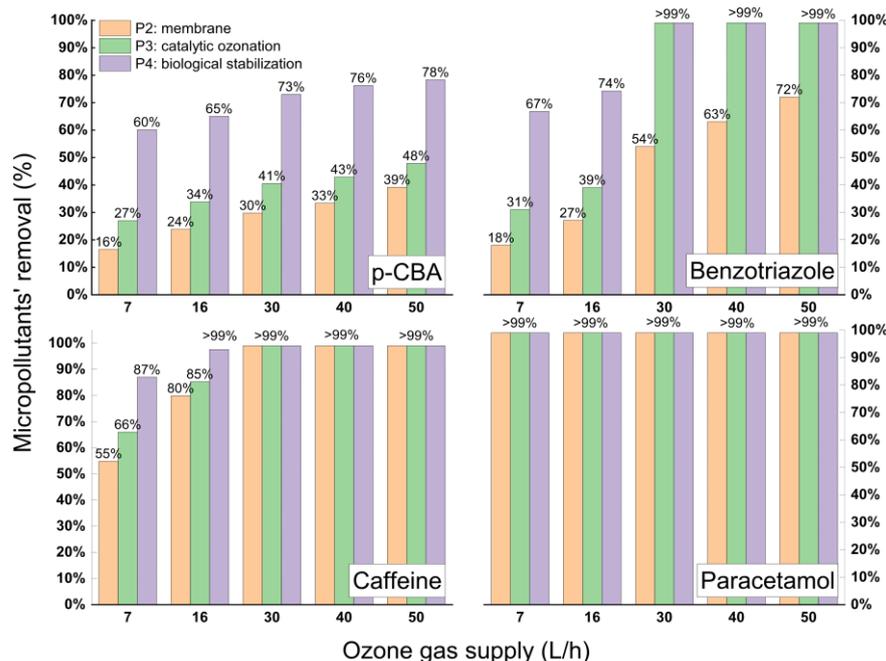


Figure 3. Achieved MP removal (%) after each treatment step in the pre-industrial-scale unit. MPs: p-CBA, benzotriazole, caffeine, paracetamol; catalyst: zeolite; treatment steps: P2: after the membrane, P3: after the catalytic ozonation (second fixed bed), P4: after the biological stabilization (third fixed bed).

An increase in the efficiency of the unit, regarding p-CBA removal, was also noted with the increase in the ozone gas supply to the system (Figure 3 “p-CBA”). When applying a supply of 7 L/h, corresponding to a dissolved ozone production equal to that estimated to be developed in the existing ozonation unit of the “AINEIA” WWTP, the removal rate of p-CBA was 60%, while this percentage could reach almost 80% for a higher ozone gas supply (50 L/h). Given that p-CBA reacts mainly with hydroxyl radicals and not with ozone molecules, this removal is indicative of the ozone decomposition in the membrane and in the catalytic bed towards the production of hydroxyl radicals, which are much stronger oxidants than ozone. In the case of benzotriazole (Figure 3 “Benzotriazole”), which, unlike p-CBA, can be degraded by ozone molecules, the removal appeared to be significantly greater, especially for an ozone gas supply of 30 L/h and above, where its degradation through the application of catalytic ozonation was complete. Caffeine (Figure 3 “Caffeine”), with a constant reaction rate with ozone of $k_{O_3} = 650 \text{ M}^{-1}\text{s}^{-1}$ (i.e., 32.5 times greater than that of benzotriazole) was removed by 87% with an ozone gas supply to the membrane of 7 L/h, while an increase in this value resulted in a more than 99% MP degradation. Finally, paracetamol (Figure 3 “Paracetamol”), presenting a very high reaction rate constant with ozone, was already completely removed after the second treatment step of the unit (i.e., ozone dilution in the membrane), even with the application of the lowest ozone gas supply.

The application of PET as a catalyst in the pre-industrial-scale unit resulted in similar degradation rates for all the examined MPs (Figure 4) as compared to those observed when using zeolite (Figure 3). Specifically, in the case of p-CBA (Figure 4 “p-CBA”) and for an ozone gas supply of 16 L/h, 25% of the added MP was degraded in the membrane module, and 33% was degraded after the catalytic ozonation step, while the final treatment step (i.e., biological stabilization bed) led to a further degradation rate of 63%. Increasing the ozone gas supply to the unit could result in significantly greater p-CBA removal rates, up to almost 75% for the highest ozone gas supply examined (50 L/h). The degradation rates for benzotriazole ranged from 55%, for an ozone gas supply of 7 L/h, to complete removal for a supply of 30 L/h and above. The complete degradation of caffeine was achieved by

using an ozone gas supply of 16 L/h, while for paracetamol, even the lowest ozone gas supply was sufficient to meet removal rates of more than 99% (Figure 4).

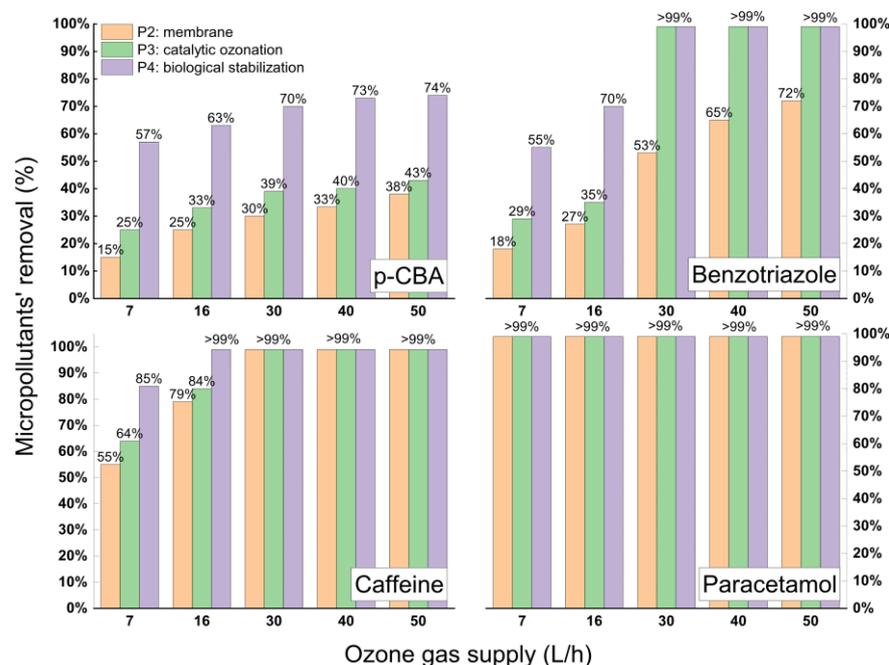


Figure 4. Achieved MP removal (%) after each treatment step in the pre-industrial-scale unit. MPs: p-CBA, benzotriazole, caffeine, paracetamol; catalyst: PET; treatment steps: P2: after the membrane, P3: after the catalytic ozonation (second fixed bed), P4: after the biological stabilization (third fixed bed).

3. Materials and Methods

3.1. Description of the “AINEIA” WWTP

The “AINEIA” WWTP (Figure S1) is situated at Aggelochori in central Macedonia, Greece, approximately 35 km distant from the urban center of Thessaloniki. The facility operates as a conventional treatment plant processing the wastewaters from the former touristic areas of Thessaloniki that currently correspond to around 8500 m³ of influent per day. The plant, initially designed to serve a population equivalent of 87,000 inhabitants, has functioned since 1997; however, sludge treatment units of thickening and anaerobic digestion were integrated into the operation in October 2014. The plant incorporates a combination of mechanical pre-treatment processes, secondary biological treatment, and final ozone disinfection. The primary treatment involves coarse screening and grit, grease, and sand removal. It features two primary and two secondary sedimentation tanks, with one primary tank dedicated to domestic septic wastewater equilibration/homogenization. Subsequent to the primary treatment, the effluent undergoes aerobic biological processes in a “carousel”-type tank with surface aeration followed by ozonation for disinfection before being discharged into the sea. Both primary and secondary sludges are thickened using gravity thickeners. Subsequently, all the sludge undergoes treatment in anaerobic digesters for stabilization, volume reduction, and biogas production. Final dewatering is achieved via belt filters, with the resulting product being potentially utilized as a soil amendment. Detailed data on the variation in BOD₅, COD, SS, T-N, NH₄-N, NO₃-N, and T-P levels in the influent and treated effluent over the study years are available in the Supplementary Materials (Figures S2 and S3).

3.2. Description of the Pre-Industrial-Scale Unit

In order to assess the performance of heterogeneous catalytic ozonation in removing MPs from wastewater, a pre-industrial-scale unit was conceptualized, constructed, and operated within the premises of the “AINEIA” WWTP. This unit comprises four distinct

operational sections, (a) post-filtration, (b) ozone dilution, (c) catalytic ozonation, and (d) biological stabilization, as depicted in Figure 5. The influent to the pre-industrial-scale unit is the secondary effluent of the “AINEIA” WWTP (after biological treatment and before disinfection), which is introduced into the unit at a flow rate of 200 L/h. Detailed descriptions of these sub-units are outlined below.

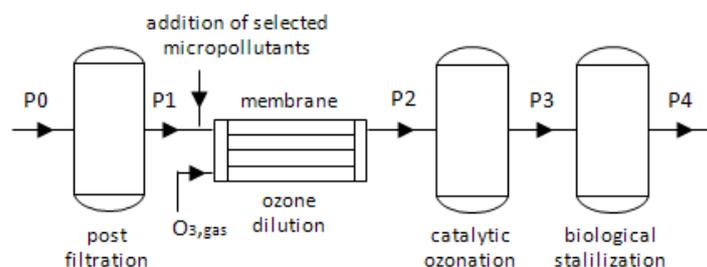


Figure 5. Schematic flowchart of the pre-industrial-scale unit.

(a) *Post-filtration*

The initial treatment stage features a fixed-bed column (with dimensions of $D = 480$ mm and $H = 3000$ mm) containing layers of sand and activated carbon. This included 10 cm of sand with 1.0–1.6 mm, 80 cm of sand with 0.4–0.8 mm, and 40 cm of activated carbon, facilitating the post-filtration of the WWTP’s secondary effluent. This process efficiently eliminates suspended solids and enhances the quality characteristics of the treated wastewater, preparatory to the subsequent treatment steps.

(b) *Ozone dilution*

Subsequent to the initial treatment stage, the treated wastewater enters a custom-made hollow fiber porous PTFE membrane module, provided by Markel Corporation, PA, USA. This module enables the contact and dissolution of ozone gas into the liquid phase. The specifications of the membrane are detailed in Table S1. Ozone gas, sourced from the existing generator within the WWTP (conventionally used for the disinfection of treated wastewater), is introduced into the module at a capacity of $190 \text{ g O}_3/\text{Nm}^3$. The flow rate of ozone gas is regulated by a solenoid valve and monitored using a 65 mm rotameter (PMR1-012111, AALBORG). A dissolved ozone meter (Q46, ATI) equipped with a corresponding sensor is installed post-membrane to ascertain the dissolved ozone concentration and validated using the standard indigo method [31].

(c) *Catalytic ozonation*

Catalytic ozonation takes place in a fixed-bed column (with dimensions of $D = 200$ mm and $H = 3000$ mm) containing layers of sand and solid material serving as a potential catalyst for the ozonation of MPs. This includes 10 cm of sand with 1.0–1.6 mm and 100 cm of catalyst material. Zeolite and PET were selected as the catalysts based on their demonstrated efficiency in catalyzing the ozonation of MPs and promoting the production of active radicals, as evidenced in prior laboratory-scale experiments [27]. The stability of the catalysts towards the ozonation process provides an additional advantage of reuse, since the continuous oxidation of MPs and their ozonation by-products constitutes, actually, a process that regenerates the catalyst [25]. A summary of the main physicochemical characteristics of these materials is provided in Tables S2 and S3.

(d) *Biological stabilization*

The final treatment stage involves a sand/activated carbon column (with dimensions of $D = 200$ mm and $H = 3000$ mm) for the biological stabilization of the treated wastewater. This comprises layers of 10 cm of sand with 1.0–1.6 mm, 70 cm of sand with 0.4–0.8 mm, and 40 cm of activated carbon. The objective is to further enhance the quality of the treated wastewater by removing transformation by-products resulting from the oxidation of MPs.

A detailed flowchart and photographic documentation of the pre-industrial-scale unit are available in the Supplementary Materials (Figures S4 and S5).

3.3. Micropollutant Removal

The application of heterogeneous catalytic ozonation for the removal of MPs from the treated wastewater was studied in the pre-industrial-scale unit by adding selected MPs to the effluent of the "AINEIA" WWTP and determining their concentrations after each treatment step and for each catalyst used; the sampling points of the pre-industrial-scale unit are listed in Table S4 of the Supplementary Materials. The addition of the selected MPs to the WWTP effluent was carried out after the post-filtration step (i.e., after the first fixed bed column) in the pre-industrial-scale unit, and their initial concentration was 2 μM . Table S5 (Supplementary Materials) lists the selected ("priority") MPs and presents their main physicochemical characteristics, as well as their respective reaction rate constants with ozone (k_{O_3} , $\text{M}^{-1}\text{s}^{-1}$) and hydroxyl radicals ($\text{HO}\bullet$, $\text{M}^{-1}\text{s}^{-1}$), while Figure S6 illustrates their structures.

P-CBA, benzotriazole, paracetamol, and caffeine (obtained from Sigma-Aldrich, Burlington, MA, USA) were used as typical/model organic compounds. P-chlorobenzoic acid (p-CBA), although rarely found in municipal wastewater treatment plant effluents, was employed as a model compound because it cannot be efficiently removed by the application of direct ozonation, while it presents a high reactivity with the secondarily produced hydroxyl radicals. Therefore, it was considered as an indirect scavenger of hydroxyl radicals in the heterogenous catalytic ozonation system. On the other hand, paracetamol and caffeine are compounds that are often found in these water sources, both in Greece and in European Union countries, in high concentrations compared to other MPs [32]. Finally, benzotriazole is a moderately ozone-reactive compound, which can be rather easily degraded by applying either single or catalytic ozonation, although the application of catalytic ozonation can decrease the required oxidation treatment time.

Micropollutants' Determination

MPs concentrations were measured at a High-Performance Liquid Chromatography system (HPLC Thermo Fisher Scientific Inc., model of UV Spectrum UV2000, Waltham, MA, USA) fitted with a 4.6–250 mm reversed phase column (AGILENT, model Eclipse Plus C18, Santa Clara, CA, USA).

4. Conclusions

The objective of this study was to apply all the knowledge acquired from recent past research on the efficient removal of MPs by the application of heterogeneous catalytic ozonation into the design and construction of a pre-industrial-scale unit operating as tertiary wastewater treatment step for MP degradation. The first part of the study was focused on the ozonation process and particularly on the assessment of the application of a hollow fiber membrane for the effective diffusion of ozone into the liquid phase. In general, increasing the ozone gas mass flow rate resulted in higher dissolved ozone concentrations, while the application of greater liquid flow velocities adversely affected the dissolution of ozone in the liquid phase. The experimental results confirmed that the dead-end operation of the membrane, i.e., without a separate gas outlet, significantly increased its efficiency in the transfer of ozone to the liquid phase. A significant increase in the membrane performance in ozone dilution was also achieved by introducing the ozone gas to the shell side and the liquid phase to the lumen side of the hollow fiber membrane.

The evaluation of heterogenous catalytic ozonation was performed by using zeolite and PET as catalysts (materials that were found to present optimum performance in previous research) and p-CBA, benzotriazole, paracetamol, and caffeine as typical MPs. Both materials displayed a notable catalytic action that significantly contributed to the removal of MPs. In the case of p-CBA and for an ozone gas supply of 16 L/h, 25% of the added MP was degraded in the membrane module, during ozone dilution, and an

additional 10% was degraded via catalytic ozonation, while a final treatment step of biological stabilization led to a more than 60% total degradation rate. The increase in the ozone gas supply to the unit resulted in significantly greater p-CBA removal rates, up to an average of 75% for the highest ozone gas supply examined (50 L/h). The degradation rates for benzotriazole ranged from 67% for zeolite application and 55% for PET, for an ozone gas supply of 7 L/h, to complete removal for 30 L/h and above. The complete degradation of caffeine was achieved with an ozone gas supply of 16 L/h, while for the case of paracetamol, even the lowest applied ozone gas supply was found to be sufficient to meet removal rates higher than 99%.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14040227/s1>, Table S1: Specifications of the membrane module used; Table S2: Main physicochemical characteristics of materials tested as catalysts; Table S3: Chemical composition of zeolite; Table S4: Sampling points; Table S5: Physicochemical characteristics of selected micropollutants at 20 °C; Figure S1: Diagram (a) and view (b) of wastewater treatment plant “AINEIA”; Figure S2: Variation in BOD₅, COD, SS, T-N, NH₄-N, NO₃-N, and T-P levels in the influent of WWTP for 2018–2021; Figure S3: Variation in BOD₅, COD, SS, T-N, NH₄-N, NO₃-N, and T-P levels in the treated effluent of WWTP for 2018–2021; Figure S4: Detailed flowchart of the pre-industrial-level unit; Figure S5: Photograph of the pre-industrial-level unit; Figure S6: Chemical structures of selected micropollutants. Refs. [33–37] are cited in the Supplementary Materials.

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Conflicts of Interest: Author Maria Salapasidou, Stefanos Kalandaridis, Panagiota-Aikaterini Palasantza, Georgios Germanidis and Panagiotis Diamantopoulos were employed by the company AKTOR S.A. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Chavoshani, A.; Hashemi, M.; Mehdi Amin, M.; Ameta, S.C. Introduction. In *Micropollutants and Challenges: Emerging in the Aquatic Environments and Treatment Processes*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 1–33.
2. Khan, F.S.A.; Mubarak, N.M.; Khalid, M.; Tan, Y.H.; Abdullah, E.C.; Rahman, M.E.; Karri, R.R. A Comprehensive Review on Micropollutants Removal Using Carbon Nanotubes-Based Adsorbents and Membranes. *J. Environ. Chem. Eng.* **2021**, *9*, 106647. [[CrossRef](#)]
3. Khan, A.; Ali, J.; Jamil, S.U.U.; Zahra, N.; Tayaba, T.B.; Iqbal, M.J.; Waseem, H. Chapter 22—Removal of Micropollutants. In *Environmental Micropollutants*; Hashmi, M.Z., Wang, S., Ahmed, Z., Eds.; Elsevier: Amsterdam, The Netherlands, 2022; pp. 443–461. ISBN 978-0-323-90555-8.
4. Karpińska, J.; Kotowska, U. New Aspects of Occurrence and Removal of Emerging Pollutants. *Water* **2021**, *13*, 2418. [[CrossRef](#)]
5. Abbasi, N.A.; Shahid, S.U.; Majid, M.; Tahir, A. Chapter 17—Ecotoxicological Risk Assessment of Environmental Micropollutants. In *Environmental Micropollutants*; Hashmi, M.Z., Wang, S., Ahmed, Z., Eds.; Elsevier: Amsterdam, The Netherlands, 2022; pp. 331–337. ISBN 978-0-323-90555-8.
6. Chávez, A.M.; Ribeiro, A.R.; Moreira, N.F.F.; Silva, A.M.T.; Rey, A.; Álvarez, P.M.; Beltrán, F.J. Removal of Organic Micropollutants from a Municipal Wastewater Secondary Effluent by UVA-LED Photocatalytic Ozonation. *Catalysts* **2019**, *9*, 472. [[CrossRef](#)]
7. Luo, Y.; Guo, W.; Ngo, H.H.; Nghiem, L.D.; Hai, F.I.; Zhang, J.; Liang, S.; Wang, X.C. A Review on the Occurrence of Micropollutants in the Aquatic Environment and Their Fate and Removal during Wastewater Treatment. *Sci. Total Environ.* **2014**, *473–474*, 619–641. [[CrossRef](#)]

8. Rios-Miguel, A.B.; van Bergen, T.J.H.M.; Zillien, C.; Ragas, A.M.J.; van Zelm, R.; Jetten, M.S.M.; Hendriks, A.J.; Welte, C.U. Predicting and Improving the Microbial Removal of Organic Micropollutants during Wastewater Treatment: A Review. *Chemosphere* **2023**, *333*, 138908. [[CrossRef](#)]
9. Gogate, P.R.; Pandit, A.B. A Review of Imperative Technologies for Wastewater Treatment II: Hybrid Methods. *Adv. Environ. Res.* **2004**, *8*, 553–597. [[CrossRef](#)]
10. Liu, Z.; Kanjo, Y.; Mizutani, S. Removal Mechanisms for Endocrine Disrupting Compounds (EDCs) in Wastewater Treatment—Physical Means, Biodegradation, and Chemical Advanced Oxidation: A Review. *Sci. Total Environ.* **2009**, *407*, 731–748. [[CrossRef](#)]
11. Dercó, J.; Gotvajn, A.Ž.; Čižmarová, O.; Dudáš, J.; Sumegová, L.; Šimovičová, K. Removal of Micropollutants by Ozone-Based Processes. *Processes* **2021**, *9*, 1013. [[CrossRef](#)]
12. Huber, M.M.; Göbel, A.; Joss, A.; Hermann, N.; Löffler, D.; McArdeell, C.S.; Ried, A.; Siegrist, H.; Ternes, T.A.; von Gunten, U. Oxidation of Pharmaceuticals during Ozonation of Municipal Wastewater Effluents: A Pilot Study. *Environ. Sci. Technol.* **2005**, *39*, 4290–4299. [[CrossRef](#)]
13. Lee, Y.; Kovalova, L.; McArdeell, C.S.; von Gunten, U. Prediction of Micropollutant Elimination during Ozonation of a Hospital Wastewater Effluent. *Water Res.* **2014**, *64*, 134–148. [[CrossRef](#)]
14. Alsager, O.A.; Alnajrani, M.N.; Abuelizz, H.A.; Aldaghmani, I.A. Removal of Antibiotics from Water and Waste Milk by Ozonation: Kinetics, Byproducts, and Antimicrobial Activity. *Ecotoxicol. Environ. Saf.* **2018**, *158*, 114–122. [[CrossRef](#)]
15. von Gunten, U. Ozonation of Drinking Water: Part I. Oxidation Kinetics and Product Formation. *Water Res.* **2003**, *37*, 1443–1467. [[CrossRef](#)]
16. Wang, J.; Chen, H. Catalytic Ozonation for Water and Wastewater Treatment: Recent Advances and Perspective. *Sci. Total Environ.* **2020**, *704*, 135249. [[CrossRef](#)]
17. Rathi, B.S.; Kumar, P.S.; Show, P.-L. A Review on Effective Removal of Emerging Contaminants from Aquatic Systems: Current Trends and Scope for Further Research. *J. Hazard. Mater.* **2021**, *409*, 124413. [[CrossRef](#)]
18. Nawrocki, J. Catalytic ozonation in water: Controversies and questions. Discussion Paper. *Appl. Catal. B* **2013**, *142–143*, 465–471. [[CrossRef](#)]
19. Bamperng, S.; Suwannachart, T.; Atchariyawut, S.; Jiratananon, R. Ozonation of Dye Wastewater by Membrane Contactor Using PVDF and PTFE Membranes. *Sep. Purif. Technol.* **2010**, *72*, 186–193. [[CrossRef](#)]
20. Hollender, J.; Zimmermann, S.G.; Koepke, S.; Krauss, M.; McArdeell, C.S.; Ort, C.; Singer, H.; von Gunten, U.; Siegrist, H. Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration. *Environ. Sci. Technol.* **2009**, *43*, 7862–7869. [[CrossRef](#)]
21. Wang, B.; Xiong, X.; Shui, Y.; Huang, Z.; Tian, K. A Systematic Study of Enhanced Ozone Mass Transfer for Ultrasonic-Assisted PTFE Hollow Fiber Membrane Aeration Process. *Chem. Eng. J.* **2019**, *357*, 678–688. [[CrossRef](#)]
22. Gabelman, A.; Hwang, S.-T. Hollow Fiber Membrane Contactors. *J. Memb. Sci.* **1999**, *159*, 61–106. [[CrossRef](#)]
23. Sabelfeld, M.; Geißen, S.-U. Effect of Helical Structure on Ozone Mass Transfer in a Hollow Fiber Membrane Contactor. *J. Memb. Sci.* **2019**, *574*, 222–234. [[CrossRef](#)]
24. Kaprara, E.; Kostoglou, M.; Koutsiantzi, C.; Psaltou, S.; Zouboulis, A.I.; Mitrakas, M. Enhancement of Ozonation Efficiency Employing Dead-End Hollow Fiber Membranes. *Environ. Sci.* **2020**, *6*, 2619–2627. [[CrossRef](#)]
25. Psaltou, S.; Kaprara, E.; Triantafyllidis, K.; Mitrakas, M.; Zouboulis, A. Heterogeneous Catalytic Ozonation: The Significant Contribution of PZC Value and Wettability of the Catalysts. *J. Environ. Chem. Eng.* **2021**, *9*, 106173. [[CrossRef](#)]
26. Psaltou, S.; Kaprara, E.; Mitrakas, M.; Zouboulis, A.I. Performance of Heterogeneous Catalytic Ozonation with Minerals in Degradation of p-Chlorobenzoic Acid (p-CBA) from Aqueous Solutions. *Proceedings* **2020**, *48*, 12. [[CrossRef](#)]
27. Kaprara, E.; Koutsiantzi, C.; Psaltou, S.; Zouboulis, A.; Mitrakas, M. Heterogeneous Catalytic Ozonation of Micropollutants in a Pilot Scale Continuous Flow System. *Environ. Sci. Proc.* **2020**, *2*, 24. [[CrossRef](#)]
28. Kaprara, E.; Belesakos, C.; Kollis, K.; Psaltou, S.; Zouboulis, A.; Mitrakas, M. Evaluation of Heterogeneous Catalytic Ozonation Process for the Removal of Micropollutants from Water/Wastewater: Application of a Novel Pilot-Scale Continuous Flow System. *Catalysts* **2023**, *13*, 899. [[CrossRef](#)]
29. Gottschalk, C.; Beuscher, U.; Hardwick, S.; Kobayashi, M.; Schweckendiek, J.; Wikol, M. Production of High Concentrations of Bubble-Free Dissolved Ozone in Water. *Solid State Phenom.* **1999**, *65–66*, 59–62. [[CrossRef](#)]
30. Kudlek, E. Decomposition of Contaminants of Emerging Concern in Advanced Oxidation Processes. *Water* **2018**, *10*, 955. [[CrossRef](#)]
31. Bridgewater, L.; American Public Health Association; American Water Works Association; Water Environment Federation. *Standard Methods for the Examination of Water and Wastewater*; American Public Health Association: Washington, DC, USA, 2012; ISBN 978-0875532356.
32. Ofrydopoulou, A.; Nannou, C.; Evgenidou, E.; Christodoulou, A.; Lambropoulou, D. Assessment of a Wide Array of Organic Micropollutants of Emerging Concern in Wastewater Treatment Plants in Greece: Occurrence, Removals, Mass Loading and Potential Risks. *Sci. Total Environ.* **2022**, *802*, 149860. [[CrossRef](#)]
33. Mandal, S. Reaction rate constants of hydroxyl radicals with micropollutants and their significance in advanced oxidation processes. *J. Adv. Oxid. Technol.* **2018**, *21*, 178–195. [[CrossRef](#)]
34. Lan, B.; Huang, R.; Li, L. Catalytic ozonation of p-chlorobenzoic acid in aqueous solution using Fe-MCM-41 as catalysts. *Chem. Eng. J.* **2013**, *219*, 346–354. [[CrossRef](#)]

35. Roshani, B.; McMaster, I.; Rezaei, E.; Soltan, J. Catalytic ozonation of benzotriazole over alumina supported transition metal oxide catalysts in water. *Sep. Purif. Technol.* **2014**, *135*, 158–164. [[CrossRef](#)]
36. El Najjar, N.H.; Touffet, A.; Deborde, M.; Journal, R.; Vel Leitner, N.K. Kinetics of paracetamol oxidation by ozone and hydroxyl radicals, formation of transformation products and toxicity. *Sep. Purif. Technol.* **2014**, *136*, 137–143. [[CrossRef](#)]
37. Zoumpouli, A.G.; Souza, F.S.; Petrie, B.; Feris, L.A.; Kasprzyk-Hordern, B.; Wenk, J. Simultaneous ozonation of 90 organic micropollutants including illicit drugs and their metabolites in different water matrices. *Environ. Sci. Water Res. Technol.* **2020**, *6*, 2465–2478. [[CrossRef](#)]

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