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Evaluation of Heterogeneous Catalytic Ozonation Process for the Removal of Micropollutants from Water/Wastewater: Application of a Novel Pilot-Scale Continuous Flow System

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Abstract: The present study evaluates the removal of micropollutants from water/wastewater contaminated sources through the application of a heterogeneous catalytic ozonation process, using a pilot-scale continuous operation unit, composed of a membrane module for the diffusion and effective dilution of ozone into the liquid phase to be treated and a plug flow reactor/continuous stirred tank reactor (PFR/CSTR) contact reactor system in series, where the catalyst is recirculated in dispersion mode. The solid materials tested as catalysts are natural and calcined zeolite, Bayoxide and alumina, whereas the examined micropollutants, used in this case as probe compounds, are p-chlorobenzoic acid (p-CBA), atrazine, benzotriazole and carbamazepine. A high-performance liquid chromatography system was used to determine the removal of micropollutants. In the case of p-CBA, an ozone-resistant compound, the addition of catalyst was found to significantly enhance its degradation rate, leading to >99% removal under the optimum defined conditions, i.e., in terms of catalyst concentration, pH, temperature, and process time. On the other hand, in the case of atrazine, a different ozone-resistant compound, the introduction of examined catalysts in the ozonation process was found to reduce the degradation of micropollutant, when compared with the application of single ozonation, indicating the importance of specific affinity between the pollutant and the solid material used as catalyst. Benzotriazole, a moderately ozone-reactive compound was degraded by more than 95% under all experimental conditions and catalysts tested in the pilot unit, while carbamazepine, a highly ozone-reactive compound, was completely removed even during the first stage of treatment process (i.e., at the membrane contactor). When increasing the pH value (in the range 6–8) and the contact time, the performance of catalytic ozonation process also improved.

Keywords: micropollutants; emerging contaminants; heterogeneous catalytic ozonation; pilot unit; continuous flow operation

1. Introduction

The presence of micropollutants (also termed as emerging contaminants or contaminants of emerging concern) in aquatic environments is constantly increasing and this trend is not predicted to be avoided, since these contaminants originate from several widely used chemical products, which are indispensable for the present quality of life in modern societies [1,2]. Personal care products (PCPs), hormones, flame retardants, industrial additives, endocrine-disrupting chemicals (EDCs), pharmaceuticals, nanomaterials, and pesticides are common examples of these substances, often detected in water resources or wastewaters and in variable concentration levels, ranging from ng/L up to μg/L [3–6].

All micropollutants have a potentially negative impact on living organisms and on the course of environmental processes [7]. Endocrine disruption and both carcinogenic and mutagenic effects on animals and humans have been demonstrated for many compounds [7,8]. The risks of continuous environmental exposure and the constant rise of micropollutant presence in water bodies has substantially raised the awareness of the scientific community and water/wastewater treatment stakeholders, emphasizing the need to design novel remediation techniques that are more effective, simpler, relatively inexpensive, and more environmentally friendly [9].

To date, various treatment techniques have been designed and implemented to eliminate both insoluble contaminants and soluble pollutants, including physical, chemical, and biological processes, that are utilized in water or wastewater treatment [10–12]. However, most of these conventionally applied processes mainly act as barriers to prevent the wider spread of micropollutants, i.e., by simply separating them from the waste streams and transferring the problem to a following treatment step; therefore, they are considered rather insufficient [13]. Alternatively, the application of specific advanced (usually applied in hybrid/combined mode) treatment processes, such as activated carbon adsorption [14–16], nanofiltration [17], reverse osmosis [18], or membrane bioreactors [19,20], as well as several advanced oxidation processes (AOPs) are able to achieve the increased and more consistent removal (due to mineralization) of dangerous micropollutants [21].

Although the high adsorption capacity of activated carbons is widely recognized, there are some drawbacks, namely their rather rapid saturation and occasionally the difficult regeneration for reuse purposes [9]. Nano-filtration presents relatively higher installation costs and the limited retention of micropollutants, meaning that it is quite difficult to separate soluble constituents from the contaminated aqueous systems [11]. Reverse osmosis, although widely used, e.g., in water reuse applications, due to its high pollutant removal efficiency, requires high energy and pressure to facilitate effective deionization, as well as the subsequent treatment of concentrates [11]. On the other hand, the application of membrane bioreactors can effectively remove a wide range of micropollutants, including compounds that are resistant to convenient activated sludge processes [21,22]. However, the performance of membrane bioreactors, especially when treating micropollutants, can be easily affected by several operational factors, such as the sludge age and concentration, the existence of subsequent anoxic and anaerobic compartments, as well as the temperature, pH, salinity, membrane fouling, and specific composition of wastewater matrix [23,24].

Ozonation and other advanced oxidation processes are considered to be effective ReDox technologies that prevail over conventional treatments, due to their higher degradation/oxidation rates for the treated pollutants and being non-selective processes, especially when applied to micropollutants [21]. However, the high ozonation efficiency may also present undesirable side effects, such as the formation of potentially harmful by-products [10]. To further reduce parent compounds, as well as oxidation by-products, the ozonation process can be improved through the addition of an appropriate catalyst (catalytic ozonation) [10,21,25]. The catalytic ozonation can be divided into homogeneous, when using dissolved (common) transition metal ions, and heterogeneous, when applying appropriate solid materials as catalysts [26], categories. The catalytic ozonation Is based on the degradation of organic compounds through the improved decomposition of ozone, mainly towards the production of hydroxyl radicals, which are very powerful, (2.7 V) and non-selective oxidizing agents [27]. Depending on their behavior towards the ozonation processes, the target micropollutants can be categorized into three main groups, based on the corresponding reaction rate constants with ozone, i.e., (1) ozone-resistant compounds, (2) compounds with moderate ozone reactivity, and (3) compounds that are highly reactive with ozone [28].

The previous relevant studies of the authors revealed that the introduction of a solid material into an ozonation system can potentially enhance the degradation of micropollutants, depending on several factors potentially affecting their removal, such as the physicochemical characteristics of catalyst [29–31], the specific affinity with the contami-

nant [26,29], the solution matrix [21,31], etc. The present research examines the effect of the catalyst's concentration on the removal of micropollutants in a pilot-scale unit, where the catalyst (being in dispersion mode) is recirculated in the treatment system, consisting (in series) of a plug flow reactor (PFR) and a continuous stirred tank reactor (CSTR).

The examined solid materials are natural or calcined zeolite (Zeolite-T), Bayoxide and alumina, and the tested micropollutants, used as typical probe compounds, are p-chlorobenzoic acid (p-CBA) (ozone-resistant) [32], atrazine (ozone-resistant) [33], benzotriazole (BTA) (moderately ozone-reactive) [34], and carbamazepine (highly ozone reactive) [35]. Other main process parameters, such as the pH and temperature of the liquid phase, and process time are also evaluated under this heterogenous catalytic ozonation system.

2. Results and Discussion

The results of heterogeneous catalytic ozonation experiments carried out in the pilot unit employed for the removal of micropollutants are presented and evaluated in the following sub-sections.

2.1. Effect of Catalysts' Concentrations on the Removal of Micropollutants

Figure 1 depicts the effect of the catalysts' concentrations on the removal of micropollutants in the case of Zeolite-T (calcined zeolite) application.
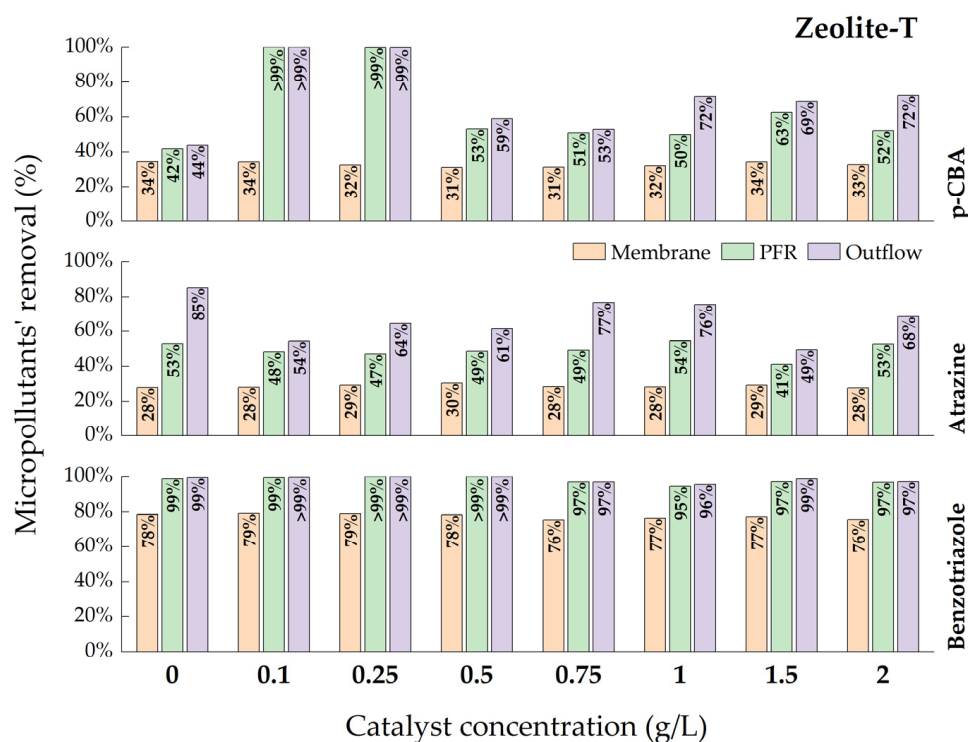

Figure 1. Effect of catalyst concentration on the removal of micropollutants. Experimental conditions: catalyst—Zeolite-T; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; pH—7; T—25 °C; t_{PFR}—8 min.

As can be seen, the performance of pilot unit, expressed as % removal of the respective micropollutant (MP), is found to increase with the addition of each subsequently applied treatment step. Even after the first stage of this combined treatment process (i.e., after the contact membrane unit), where the effective dissolution of ozone in the liquid phase takes place, a significant percentage of micropollutant degradation can be achieved, reaching an average of 33% for p-CBA, 29% for atrazine, and 78% for benzotriazole, respectively. The introduction of the catalyst into the system offers the appropriate surface for the enhanced contact of ozone with the dissolved micropollutants, improving their oxidation. In addition, it is expected to favor the decomposition of ozone and the higher formation of hydroxyl radicals (●OH), which are able to react more effectively with the micropollutants, increasing

their degradation rate. Especially in terms of p-CBA, which cannot be effectively removed through the application of direct ozonation (as the respective k_{O3} is <0.15 $M^{-1}s^{-1}$) [29], the higher formation of hydroxyl radicals seems to be particularly important, because these are mainly responsible for its oxidation and removal. As a result, the removal of p-CBA in the heterogeneous catalytic ozonation ranges between 42% up to >99% after the PFR reactor and from 44% up to >99% at the exit of pilot unit, indicating a mechanism of catalytic ozonation that includes the adsorption of ozone onto the catalytic surface and the subsequent production of hydroxyl radicals. From the experimental results, it is also apparent that the catalyst concentration can affect the ozonation of micropollutants, leading to the conclusion that there is an appropriate ratio of catalyst to micropollutant concentration, at which point the available catalytic surface maximizes the contact of the micropollutant with the ozone (or with radicals), without itself (the catalyst) consuming or influencing the concentration of ozone (or radicals).

In the case of p-CBA, the optimal concentration of Zeolite-T, when applied in the pilot unit to treat 2 μM of micropollutant, lies between 0.1 and 0.25 g/L.

In the case of atrazine, the achieved degradation rates in the catalytic ozonation system reach 77%; however, the application of single ozonation appears to be better, regarding the removal of this organic compound, as it presents higher degradation rate (85%). The inhibition of atrazine removal during ozonation through the presence of a solid material (alumina, calcite, dolomite, goethite, pearlite, PET, zeolite) was also noticed by the authors during previous relevant studies [21,36,37], implying that in order for a material to act as an efficient catalyst in the heterogeneous catalytic ozonation process, especially in the case of ozone-resistant compounds, it must not only be able to increase the production of hydroxyl radicals but also be able to bring the pollutant into a closer encounter with these radicals in order for it to be efficiently oxidized [37], i.e., to present higher (or at least good) affinity both with the micropollutant and with the ozone/radicals. Namely, although ozone is adsorbed on the surface of the catalyst, promoting the formation of hydroxyl radicals, atrazine molecules are not adsorbed on the catalytic surface, indicating that the mechanism of this organic pollutant's degradation mainly includes its oxidation in the liquid phase. A certain improvement, regarding the removal of atrazine, was only observed in the presence of SiO_2, suggesting that this organic molecule can bind (probably via weak hydrogen bonds) to the Si surface, but not with the other examined materials/catalysts, as the relevant previous research has also reported [38–40].

The effect of catalyst concentration on the ozonation of benzotriazole is not as notable as in the case of p-CBA. Benzotriazole is a moderate ozone reactive compound with a reaction rate constant with ozone equal to 20 $M^{-1}s^{-1}$, i.e., much higher than that of p-CBA [41]. Specifically, it can react much faster with ozone; therefore, a significant percentage of this micropollutant can be removed even after the first stage of the process, i.e., by the membrane used to diffuse/contact the ozone into/within the liquid phase to be treated. This percentage can reach up to 79%, while after the PFR reactor the removal rates range between 95% up to >99%. At the outlet of the pilot unit and for catalyst concentrations up to 0.5 g/L, complete degradation of benzotriazole can be achieved, while a further increase in the amount of Zeolite-T appears to present a rather negative effect, which, however, can be considered as statistically insignificant to the catalytic ozonation process.

A complete removal of carbamazepine was achieved even after the first treatment stage of the process, i.e., by the gas–liquid membrane contactor. The rapid degradation of this micropollutant is explained by its almost instantaneous reaction with ozone, as indicated by the value of respective high reaction rate constant ($k_{O3} = 3 \times 10^5$ $M^{-1}s^{-1}$). Similar observations can be seen for all the experimental conditions examined at the pilot unit; therefore, the removal of carbamazepine specifically will not be further discussed.

The effect of catalyst concentration on the removal of micropollutants in the case of Bayoxide material/catalyst application is presented in Figure 2.
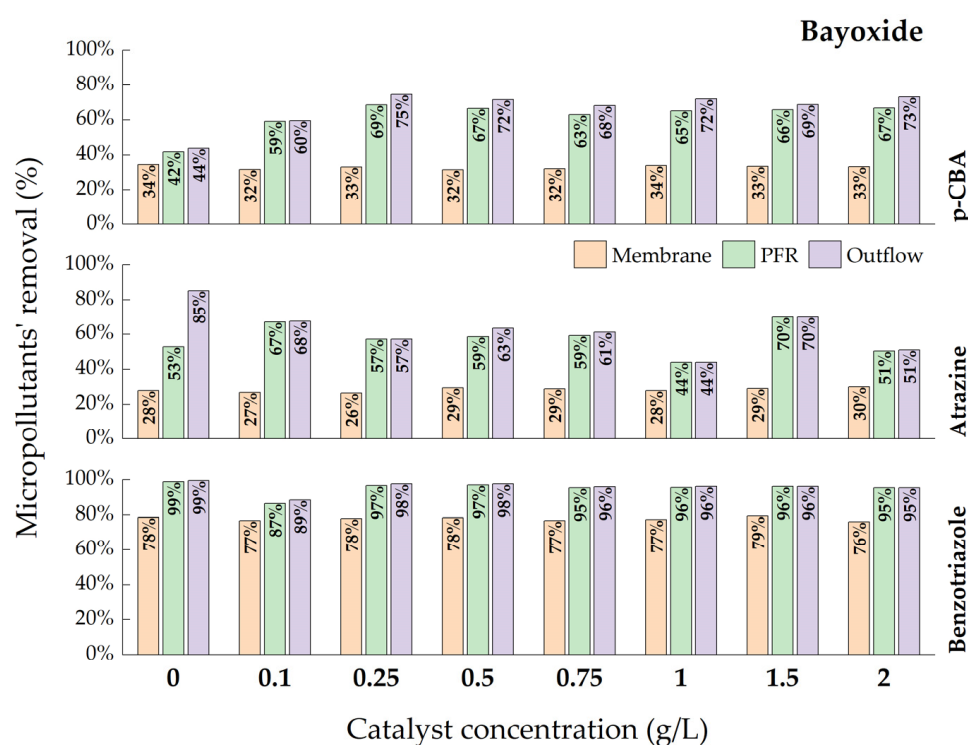
Figure 2. Effect of catalyst concentration on the removal of micropollutants. Experimental conditions: catalyst—Bayoxide; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 µM; pH—7; T—25 °C; t_{PFR}—8 min.

In the case of p-CBA, the experimental results indicate that the introduction of Bayoxide material into the treatment system favors its removal. About 34% of this compound is degraded via direct ozonation in the membrane module, while the enhanced contact of micropollutant with ozone onto the surface of the catalyst can significantly increase its oxidation, leading to a total removal rate, ranging between 60% up to 75%, depending on the concentration of catalyst utilized in the treatment system. Namely, the concentration of the catalyst influences the degradation of the micropollutant, showing improved removal rates for a concentration greater than, or equal to, 0.25 g/L. Similar behavior was also observed during the respective batch mode experiments of heterogeneous catalytic ozonation for the removal of p-CBA in the presence of Bayoxide, where the optimum catalyst dose at pH 7 was determined to be 0.3 g/L [42].

Considering the removal of atrazine, an 85% removal efficiency is achieved through the application of single ozonation, surpassing that of heterogeneous catalytic ozonation, as in the previous case of zeolite use and for similar reasons as aforementioned. About 28% of atrazine is removed in the first stage of the process (contact membrane), while the efficiency of catalytic system can reach up to 70% for a Bayoxide concentration of 1.5 g/L.

The removal of benzotriazole is insignificantly affected by the presence of Bayoxide, being rather easily and directly oxidized even only by the presence of ozone, as similarly observed during the application of Zeolite-T (Figure 1).

Similar results were obtained for atrazine and benzotriazole with the addition of alumina (Figure 3). However, p-CBA oxidation was enhanced, as alumina concentration increased, extending to 85% micropollutant removal for a catalyst concentration of 2 g/L.

The residual ozone concentration at the end of each experimental procedure and for any examined experimental condition was less than, or equal to, 0.02 mg/L, suggesting a very sufficient overall ozone consumption (around 99%).
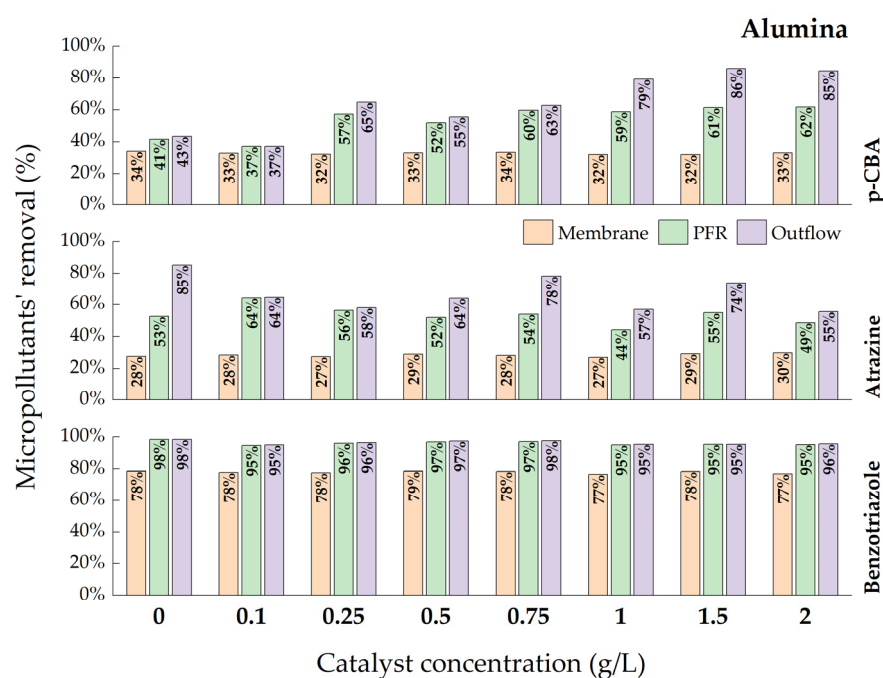
Figure 3. Effect of catalyst concentration on the removal of micropollutants. Experimental conditions: catalyst—alumina; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; pH—7; T—25 °C; t_{PFR}—8 min.

2.2. Effect of Solution pH on the Removal of Micropollutants

The influence of solution pH on micropollutants removal was also examined in the catalytic ozonation pilot unit. The experimental results, regarding the application of zeolite, Bayoxide and alumina materials applied as potential catalysts, are presented in Figures 4–6, respectively. As can be observed in all these diagrams, the pH value significantly affects the ozonation of micropollutants, as it favors the faster decomposition of ozone and the production of hydroxyl radicals [43]. For the examined pH values of 6–8, the expected increase in micropollutant removal via increasing pH is verified, with the maximum achieved at pH 8. At this pH value, p-CBA and benzotriazole are almost completely removed, even after the first stage of this treatment process (i.e., the membrane module), while atrazine is degraded to a much lower percentage (around 40%). This is likely due to the formation of a $CaCO_3$ deposit in the hollow fiber membrane contactor, causing it to act similarly to the catalytic ozonation PFR; in this case, the $CaCO_3$ is considered to be the catalyst material.

2.3. Effect of Solution Temperature on the Removal of Micropollutants

The effect of solution temperature on the removal of micropollutants was studied regarding the case of p-CBA ozonation, when catalyzed by the Zeolite-T material (Figure 7). As revealed by the experimental results, a decrease in temperature from 25 °C to 15 °C weakens the efficiency of catalytic ozonation, due to the higher stability of ozone molecules in the aqueous solutions of lower temperatures, subsequently resulting in slower ozone decomposition reactions and a lower radical production rate. The above should also lead to a reduction in catalytic ozonation performance with temperature drop from 35 °C to 25 °C. However, the opposite case occurs. As shown in Figure 7, a decrease in temperature from 35 °C to 25 °C, leads to an increase in the performance of heterogeneous catalytic ozonation (Figure 7). This was also observed in relevant previous research [44], and it can be associated with two effects when increasing temperature, i.e., (i) the decrease in dissolved ozone concentration, due to the increase in ozone escape into the gas phase, and (ii) the decrease in micropollutant adsorption onto the catalyst surface [44]. The increase in temperature from 15 °C to 25 °C leads to an increase in micropollutant degradation reaction kinetics, exceeding the corresponding increase in ozone escape into the gas phase, while at 35 °C, the higher escape of ozone into the gas phase results in lower p-CBA removal

rates. Thus, under the experimental conditions applied in the pilot unit, the optimum temperature for the removal of p-CBA through the application of heterogeneous catalytic ozonation is 25 °C.
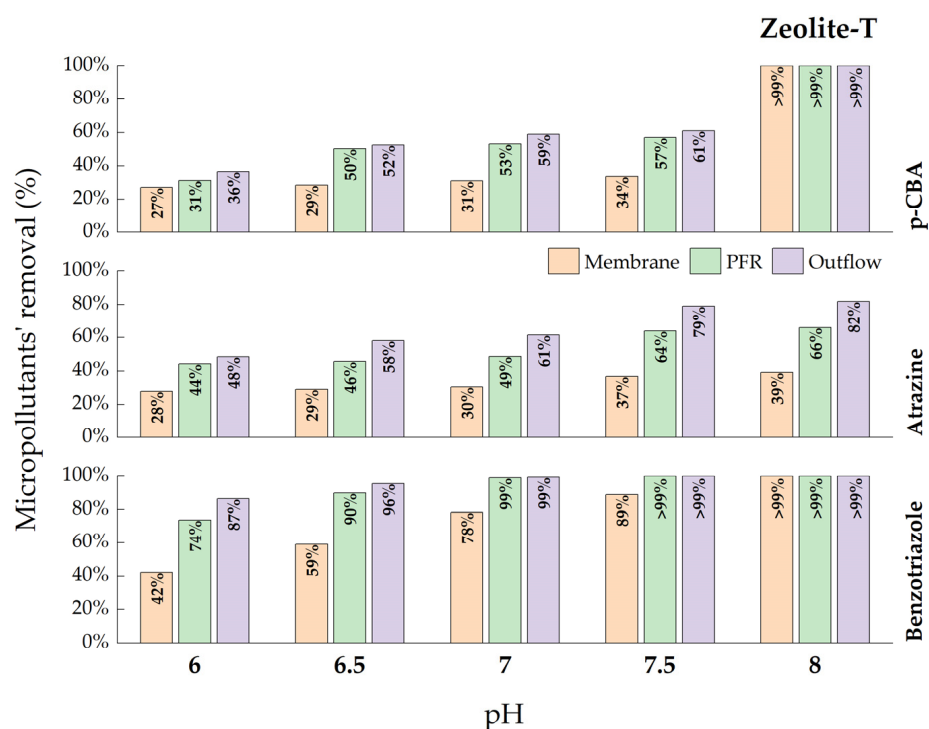

Figure 4. Effect of solution pH on the removal of micropollutants. Experimental conditions: catalyst—Zeolite-T; $C_{catalyst}$—0.5 g/L; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; T—25 °C; t_{PFR}—8 min.
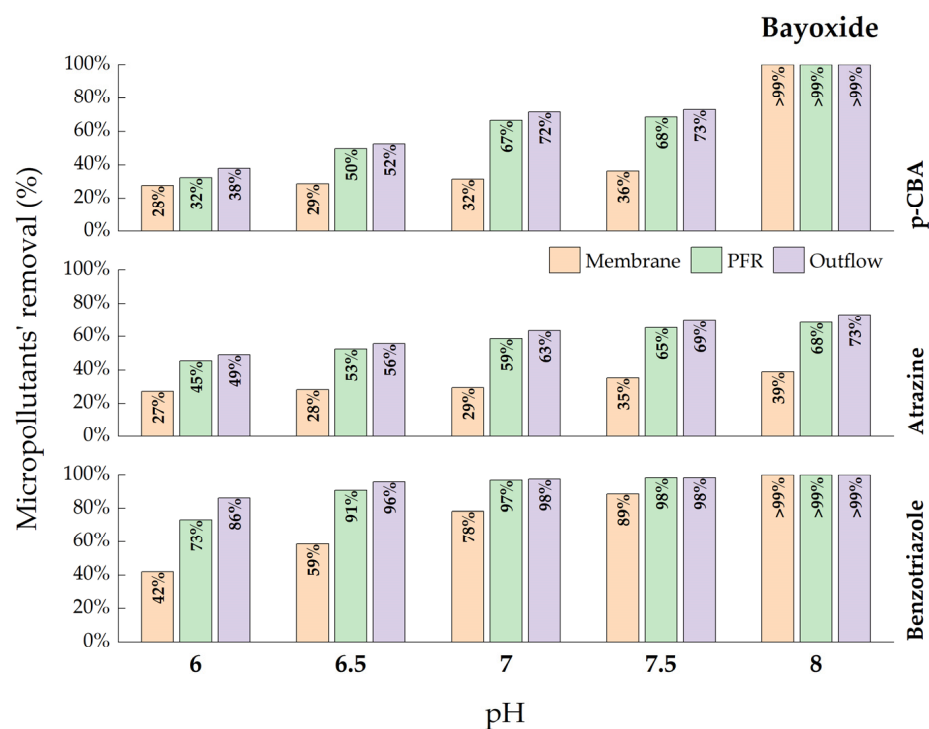

Figure 5. Effect of solution pH on the removal of micropollutants. Experimental conditions: catalyst—Bayoxide; $C_{catalyst}$—0.5 g/L; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; T—25 °C; t_{PFR}—8 min.
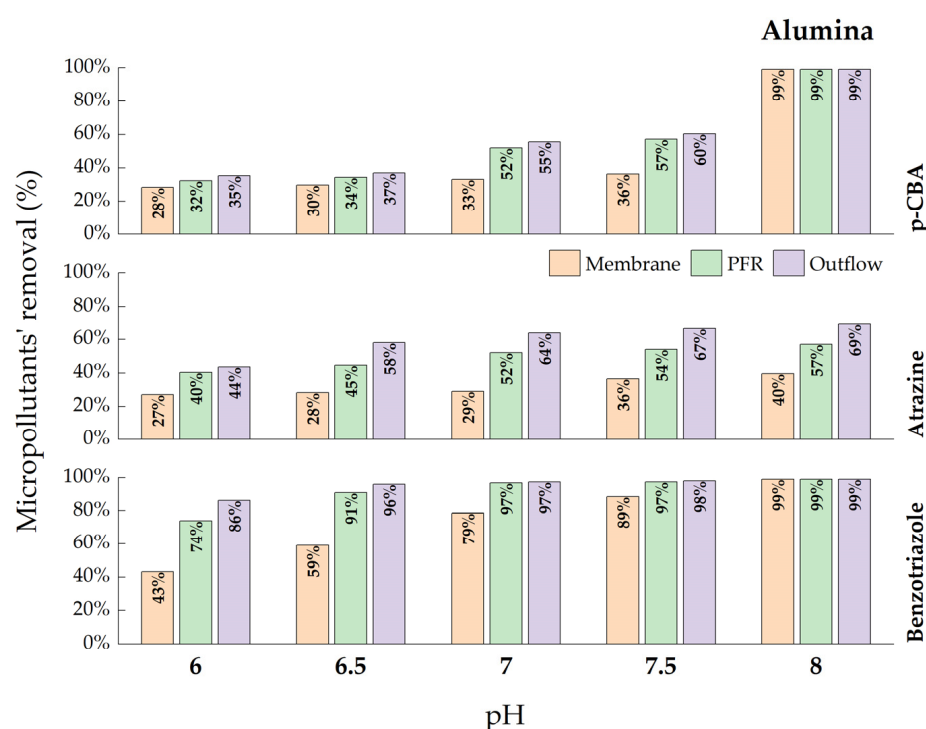
Figure 6. Effect of solution pH on the removal of micropollutants. Experimental conditions: catalyst—alumina; $C_{catalyst}$—0.5 g/L; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; T—25 °C; t_{PFR}—8 min.
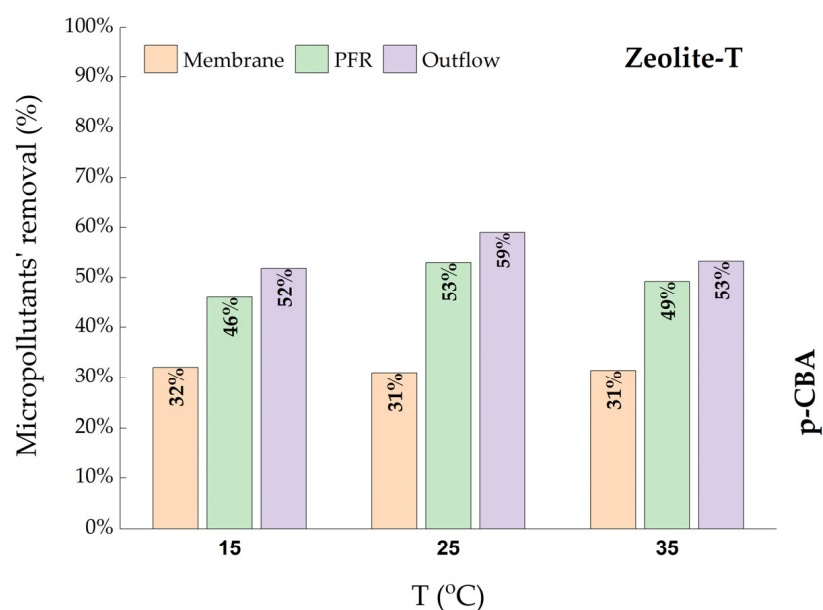

Figure 7. Effect of solution temperature on the removal of micropollutants. Experimental conditions: catalyst—Zeolite-T; $C_{catalyst}$—0.5 g/L; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; pH—7; t_{PFR}—8 min.

2.4. Effect of Contact/Treatment Time on the Removal of Micropollutants

The effect of different contact (treatment) time on the removal of micropollutants was studied for treatment times corresponding to the range of 6–10 min in the PFR reactor, considered as typical treatment times in relevant systems. The experimental results for the application of zeolite, Bayoxide, and alumina as catalysts are presented in Figures 8–10, respectively. As expected, higher contact times can upgrade the application of catalytic ozonation, at least up to the examined level of 10 min. This was also the case when the heterogeneous catalytic ozonation of micropollutants was examined in a pilot-scale unit

by applying the catalyst in fixed-bed mode (i.e., in a column filled with granules of the respective catalyst) [21]. P-CBA removal achieved higher rates with Zeolite-T application, reaching up to 88% after 10 min of contact time in the PFR reactor. The corresponding value for atrazine was 76%, while benzotriazole was completely removed via all (three) catalysts examined.
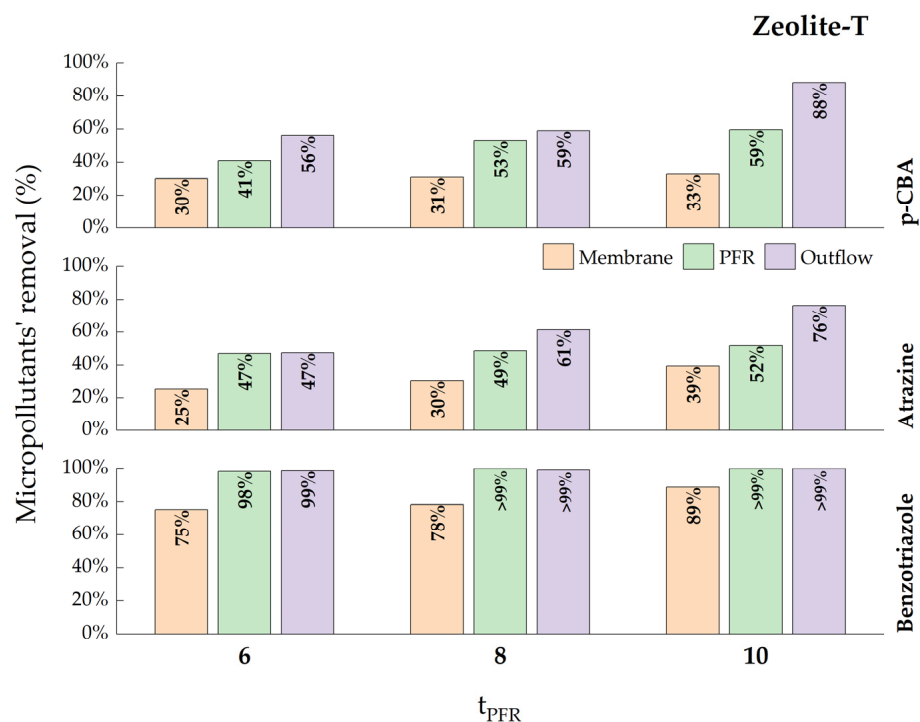

Figure 8. Effect of contact time on the removal of micropollutants. Experimental conditions: catalyst—Zeolite-T; $C_{catalyst}$—0.5 g/L; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; pH—7; T—25 °C.
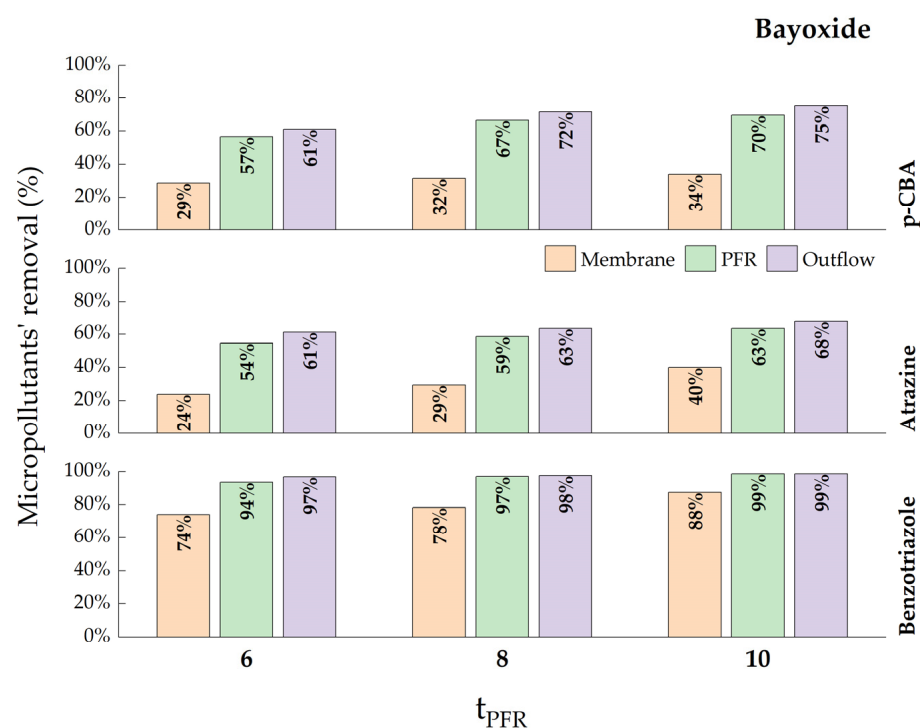

Figure 9. Effect of contact time on the removal of micropollutants. Experimental conditions: catalyst—Bayoxide; $C_{catalyst}$—0.5 g/L; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; pH—7; T—25 °C.
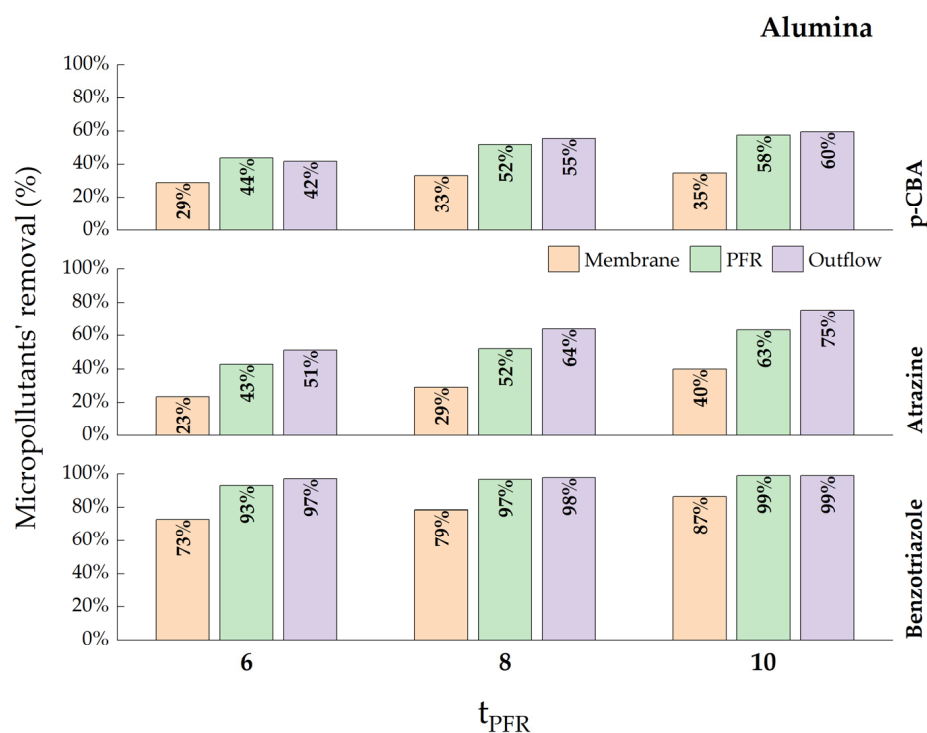
Figure 10. Effect of contact time on the removal of micropollutants. Experimental conditions: catalyst—alumina; $C_{catalyst}$—0.5 g/L; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; pH—7; T—25 °C.

2.5. Effect of Calcination on a Material's Catalytic Ability regarding the Ozonation of Micropollutants

To evaluate the influence of thermal treatment (calcination) on a material's catalytic action, catalyst concentration effect experiments on the removal of micropollutants were repeated by applying raw zeolite (i.e., not subjected to calcination) to the pilot unit. The respective results are presented in Figure 11.
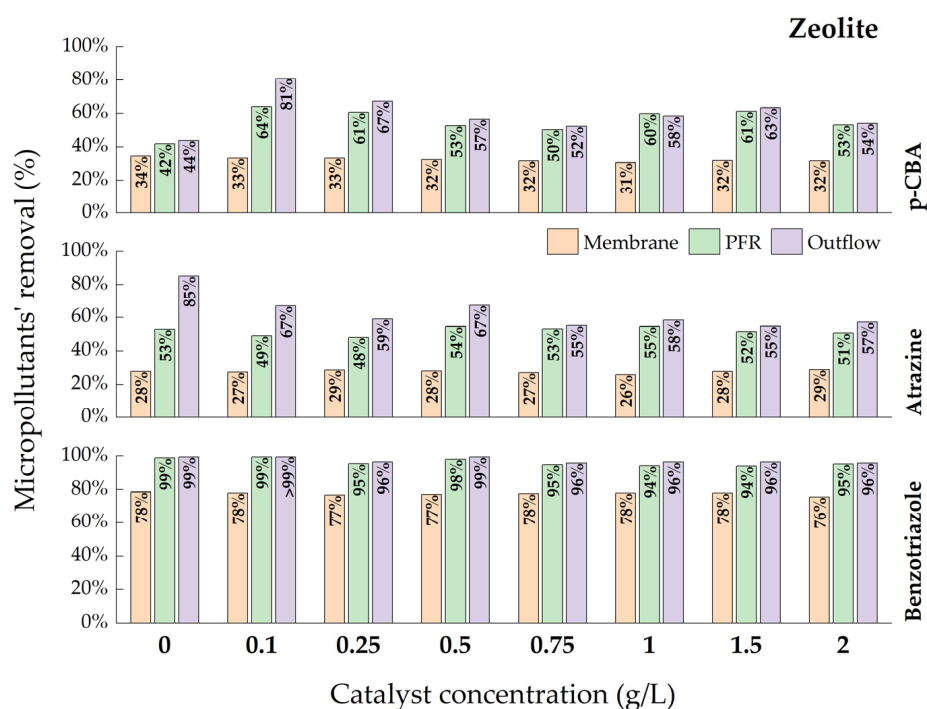

Figure 11. Effect of catalyst concentration on the removal of micropollutants. Experimental conditions: catalyst—raw Zeolite (not calcined); $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 μM; pH—7; T—25 °C; t_{PFR}—8 min.

When compared to calcinated zeolite (Figure 1), the raw zeolite presents lower performance in the catalytic ozonation of micropollutants, as also observed during the respective batch mode experiments [31]. This can be attributed to the increase in zeolite's Point-of-Zero Charge (PZC) value by the application of thermal treatment (see Table 2). A PZC value around the pH value of the solution is expected to favor the efficient contact of ozone molecules with the catalyst surface and, therefore, can accelerate its decomposition, leading to the production of more hydroxyl radicals [30,44]. According to the experimental results, as in the case of Zeolite-T application, the appropriate range of catalyst concentration, aiming to maximize the p-CBA removal, is between 0.1 and 0.25 g/L, with the 0.1 g/L being the optimal concentration. In this case, micropollutant removal reaches 64% after the PFR reactor and more than 80% at the pilot unit outlet. The catalytic ozonation of benzotriazole degradation with the use of raw zeolite follows a similar pattern to that of Zeolite-T use with an average removal rate of around 99% for catalyst concentrations up to 0.5 g/L and insignificantly lower values (96%) obtained for higher catalyst/micropollutant mass ratios. The single ozonation process seems to prevail over the catalytic one regarding the degradation of atrazine, which is similar to the case of Zeolite-T application, at least when using the treatment system examined in this study.

2.6. Comparison of Catalytic with Single Ozonation Process

To better understand the contribution of materials used as catalysts for the improvement of micropollutants' ozonation, the performances of single and catalytic ozonation are comparatively presented. Figure 12 compiles the experimental results obtained from the pilot unit, operating via (i) single ozonation and (ii) catalytic ozonation, with the catalyst's granules placed either in a column (i.e., fixed-bed operation) [21] or with the catalyst in dispersion mode, i.e., in a PFR/CSTR series system (in the present research) under comparable experimental conditions.
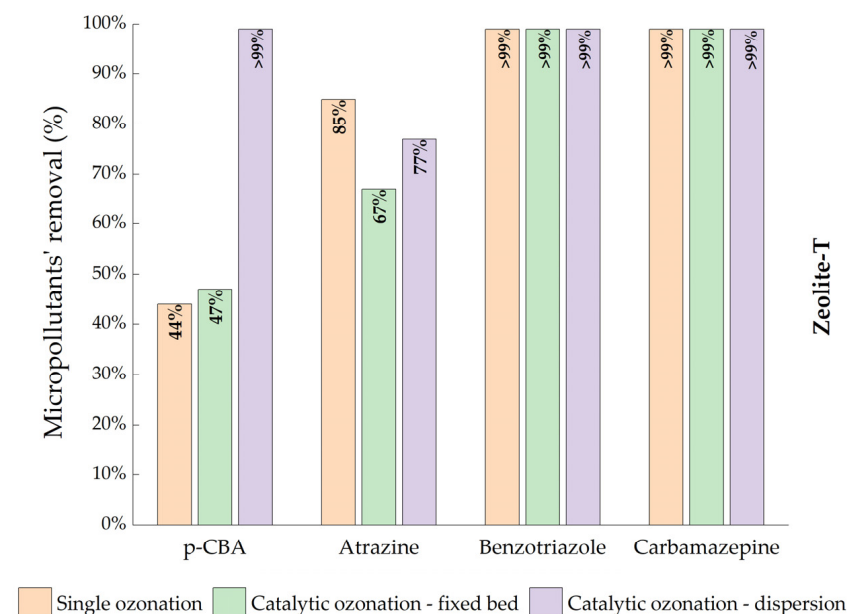

Figure 12. Removal of micropollutants by applying single or catalytic ozonation. Experimental conditions: catalyst—Zeolite-T; $C_{0,catalyst}$—optimal; $C_{0,ozone}$—2 mg/L; $C_{0,MP}$—2 µM; pH—7; T—25 °C.

As presented in this diagram, carbamazepine and benzotriazole can be completely removed by any of the three ozonation procedures applied in the pilot unit. These micropollutants demonstrate high reaction rate constants with ozone and are easily degraded by its presence, even in the absence of a catalyst. The addition of a catalyst to this system is found to increase the removal rate of p-CBA, when compared to the case of single ozonation, although by less than 5% when the catalyst is applied in column mode. Nevertheless,

in the case of the process evaluated in the context of this research, i.e., by applying the (recirculated) catalyst in suspension, the complete degradation of p-CBA can be achieved at the appropriate catalyst/micropollutant mass ratio. The application of the catalyst in suspension leads to an atrazine removal rate of 77%, improving the performance of the pilot unit operating as fixed-bed catalytic ozonation process by 10%. However, in the case of the examined catalyst (Zeolite-T), the presence of the material does not favor the decomposition of atrazine.

3. Materials and Methods

3.1. Experimental Set-Up

The heterogenous catalytic ozonation experiments were performed in a pilot-scale continuous flow unit, comprising a membrane contactor, used for the effective dilution of ozone into the contaminated water, and a recirculation system, consisting of PFR and CSTR sub-units, where the catalyst was applied in dispersed mode. The process parameters examined during the experimental procedure include the concentration of catalyst, the solution pH and temperature, and the treatment time of process (in terms of contact time in the PFR). Samples were collected after the contact membrane unit, as well as after the PFR and from the outlet of pilot unit, and the residual ozone and micropollutants concentrations were properly measured. Each experiment was performed in three replicates, and the average values are presented in the figures. The mean variation of concentration measurements was approximately within the 5% range, and the respective error bars are not presented in the figures.

The pilot unit (Supplementary Materials, Figure S1) is schematically illustrated in Figure 13 and described in more detail in the following section.
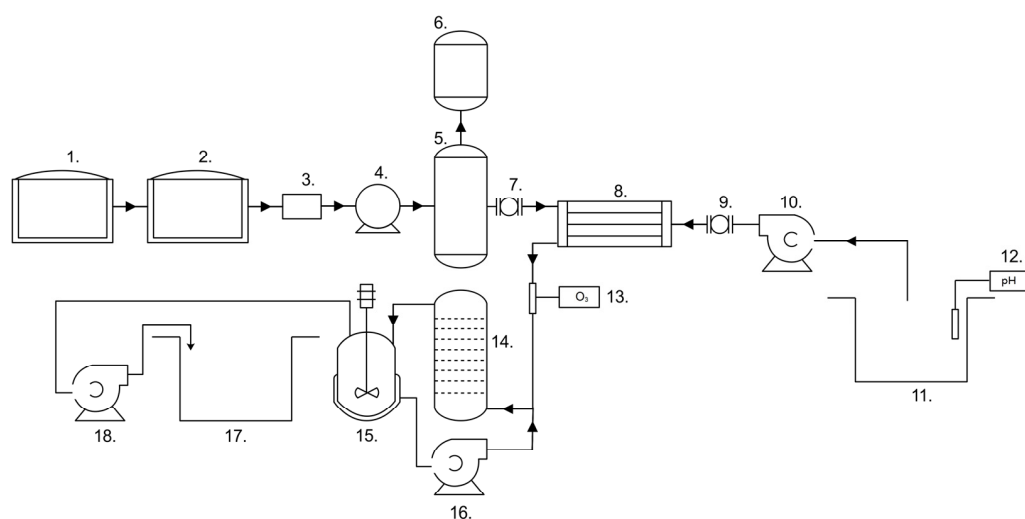

Figure 13. Flow diagram of the experimental set-up used for the catalytic ozonation experiments. 1. oxygen concentrator, 2. ozone generator, 3. ozone gas analyzer, 4. compressor, 5. ozone storage tank, 6. ozone destructor, 7. gas flow meter, 8. membrane contactor, 9. water flowmeter, 10. gear pump, 11. water tank, 12. pH meter, 13. dissolved ozone meter, 14. PFR, 15. CSTR, 16. (dispersed) catalyst recirculation pump, 17. treated water tank, 18. filtration pump.

The oxygen concentrator (model Nuvo Mark 5) with a production capacity of 95% O_2 was used to produce oxygen (from the air) that was subsequently introduced into the ozone generator (model TOGC2A, Ozonia Triogen, Goor, The Netherlands). The mass concentration of produced ozone gas was measured with an ozone analyzer (model BMT 964, BMT MESSTECHNIK GMBH, Stahnsdorf, Germany). The compressor (model 5KCR46JN0707X, Marathon Electric, Wausau, WI, USA) supplied the gas to an ozone storage tank, connected with an appropriate ozone destructor. The volumetric flowrate of ozone gas, entering the membrane sub-unit, was controlled via a needle valve and

measured using a 65 mm rotameter (model FL-3607ST, Omega, Taiwan). To achieve the maximum efficiency of ozone dissolution into the water solution to be treated, the ozone gas was introduced to the shell side and the liquid phase to the lumen side of the membrane unit [45]. The gear pump (model GB-P25.JVS.A.B1, Cole Parmer, Vernon Hills, IL, USA) forced the solution of micropollutants through the membrane hollow fibers, while the flowmeter (model EK-4AA, Lytola Instruments, Muurame, Finland) provided an accurate value of liquid flowrate. The dissolved ozone meter (model Dulcometer D1C, ProMinent, Heidelberg, Germany) with the corresponding sensor was located after the membrane unit, aiming to measure the dissolved ozone concentration, and the measured values were verified using the standard indigo method. The outflow of the membrane module was fed to the PFR reactor (dimensions: D = 1 cm, L = 32 cm), which was connected in series with the CSTR reactor (dimensions: D = 30 cm, H = 28 cm), equipped with a Heidolph stirrer (model RZR 2021). The examined catalyst was added to the CSTR and transferred to the PFR via a recirculation peristaltic pump (model 77200-50, Cole Parmer, Vernon Hills, IL, USA). Another peristaltic pump (model 77200-60, Cole Parmer) routed the PFR overflow to the treated water tank through a zeolite filter that ensured the separation of treated water from the catalyst, which was further recirculated.

3.2. Materials and Reagents

3.2.1. Ozone

The dissolution of ozone gas into the liquid phase was achieved by using a hollow fiber membrane contactor provided by Markel Corporation (Plymouth, PA, USA). The specifications of this membrane module are listed in Table 1. The pilot unit was set to provide a dissolved ozone concentration of 2 mg O_3/L.

Table 1. Specifications of the hollow fiber membrane module used for the dissolution of ozone into the liquid phase.

Specification	Value
Fiber ID (mm)	0.68
Fiber OD (mm)	1.2
Fiber length (m)	0.2
Number of fibers	590
Effective contact area (m^2)	0.33
Material	Polytetrafluoroethylene

3.2.2. Catalysts

Three commercially available solids were examined as potential catalysts, either as raw materials or after proper modification (i.e., calcination for the case of zeolite), in fine powdered form (with particle diameter < 63 μm). More specifically, alumina was obtained from Honeywell Fluka™ (Morris Plains, NJ, USA), Bayoxide (consisting mainly of goethite) from LANXESS (Cologne, Germany), and natural zeolite (Clinoptilolite) from the Metax-ades area (Alexandroupoli, Thrace region, Greece). The ability of zeolite to act as catalyst for the ozonation of micropollutants was also tested after its preliminary calcination at 600 °C (by applying the method proposed by Psaltou et al. [44]), and the modified material is abbreviated as Zeolite-T. Table 2 summarizes the main physicochemical characteristics of the solid materials examined as catalysts in the pilot unit for the heterogeneous catalytic ozonation process.

3.2.3. Micropollutants

The examined organic compounds used as model (typical) micropollutants, were atrazine, benzotriazole, carbamazepine, and p-CBA. All of these were of analytical grade, purchased from Sigma-Aldrich, USA. The solutions of micropollutants to be treated were prepared in natural-like water, according to the National Sanitation Foundation (NSF standard). For the preparation of 10 L of NSF water, 2.520 g $NaHCO_3$, 1.470 g $CaCl_2$

$2H_2O$, 1.283 g $MgSO_4 \cdot 7H_2O$, 0.706 g $NaSiO_3$ $5H_2O$, 0.1214 g $NaNO_3$, 0.0221 g NaF, and 0.0018 g $NaH_2PO_4 \cdot H_2O$ were dissolved in distilled water [46]. The initial concentration of micropollutant solution was set to 2 μM and the pH values to a range of 6–8, adjusted by the addition of either HCl or NaOH (1 N). Table 3 illustrates the main physicochemical characteristics of tested micropollutants, as well as the kinetic constants of their reactions with either ozone or hydroxyl radicals.

Table 2. Main physicochemical characteristics of solid materials examined as catalysts for the heterogeneous catalytic ozonation process.

Materials	Main Physicochemical Characteristics		
	PZC	S_{BET} (m^2/g)	Pore Volume (mL/g)
Zeolite	6.8	21	0.164
Zeolite-T	7.1	16.4	0.149
Alumina	7	150	0.512
Goethite	7.8	135	0.265

Table 3. Micropollutants used in this study as model (typical) organic compounds and their properties (adapted from Psaltou et al. 2020 [36]).

Micropollutant	MW	Log D at pH 8	pK$_a$	k_{O3} (M^{-1}s^{-1})	$k_{\bullet OH}$ (M^{-1}s^{-1})
Atrazine	215.7	2.20	3.2	6	2.4×10^9
Benzotriazole	119.1	1.21	9.04	20	7.6×10^9
Carbamazepine	236.3	2.77	16	3×10^5	8.8×10^9
p-CBA	156.6	−1.15	4.07	0.15	5×10^9

3.3. Analytical Methods

3.3.1. Ozone Determination

The dissolved ozone concentrations were determined by using the (classical) indigo method [47]. The color change of the indigo solution was detected via the U-5100 Hitachi spectrophotometer.

3.3.2. Analytical Determination of Micropollutants

The micropollutant concentrations were determined using a high-performance liquid chromatography system (HPLC Thermo Fisher Scientific Inc., model of UV Spectrum UV2000, Waltham, MA, USA) at 254 nm, equipped with a 4.6 mm × 250 mm reversed phase column (model AGILENT, model Eclipse Plus C18, Santa Clara, CA, USA). The mobile phase was consisted of 10 mM HPLC-grade phosphoric acid (Sigma-Aldrich, St. Louis, MO, USA) and HPLC-grade acetonitrile (Chem-lab, Belgium) in the percentages shown in Table 4. The detection limit of micropollutants was 0.025 μM.

Table 4. The proportion of mobile phase applied for the detection of micropollutants by HPLC.

Micropollutant	10 mM H$_3$PO$_4$, % *v/v*	ACN, % *v/v*
Atrazine	5	50
Benzotriazole	75	25
Carbamazepine	60	40
p-CBA	60	40

4. Conclusions

The increasing presence of micropollutants in water resources has led to the increasing chemical pollution of the aquatic environment, posing a threat to human and animal health. Conventional treatment processes, despite acting as the principal barriers to micropollutants' spread, are insufficient, emphasizing the need to design novel remediation

techniques. Heterogeneous catalytic ozonation can be considered as one of these, presenting the advantages of strong oxidation, less ozone dosage, and especially, its potentially greater effectiveness in the mineralization of organic matter.

This research examines the potential of certain solid materials to act as catalysts during the application of heterogenous catalytic ozonation for the oxidation of micropollutants, applying a continuous flow pilot-scale unit, comprising a membrane contactor, used for the effective dilution of ozone in water, and a catalyst recirculation system, consisting of PFR and CSTR sub-units in series, where the catalyst is used in dispersed mode. The experimental results revealed an increased performance of the pilot unit with the addition of each subsequent treatment stage. Even after the first stage of the process (i.e., after the membrane module), significant percentages of micropollutants degradation rates were achieved, reaching an average of 33% for p-CBA and 29% for atrazine (ozone-resistant compounds), 78% for benzotriazole (moderate ozone-reactive compound), and the complete degradation of carbamazepine (highly ozone-reactive compound).

The introduction of the catalyst into the system enhanced the oxidation of micropollutants not only by offering the appropriate surface for the (more) effective contact with ozone but also by favoring the formation of hydroxyl radicals ($\bullet$OH), being stronger oxidation agents than ozone and, hence, are able to react more efficiently to the micropollutants, increasing their degradation rate. Especially for p-CBA, which cannot be effectively removed through the application of direct ozonation, it was shown that the addition of a suitable catalyst at the appropriate concentration can lead to more than 99% removal. In the case of atrazine, on the other hand, the addition of the catalyst to the ozonation process (at least concerning those examined in the context of this research) was found to reduce the removal rate, when compared to single ozonation, indicating the importance of affinity between the contaminant and the solid material used as a catalyst. Benzotriazole, a moderately ozone-reactive compound, was easily degraded under the tested experimental conditions. By increasing the pH value from 6 to 8, the process performance significantly improved, whereas the application of higher contact (treatment) times also upgraded the efficiency of catalytic ozonation, at least up to the level of 10 min in the tested PFR sub-unit.

In conclusion, the findings of this study indicate that heterogenous catalytic ozonation can be efficiently used for the removal of micropollutants, leading to the complete degradation of these organic contaminants when applying the appropriate process parameters to the fully scalable pilot unit demonstrated in the present research.

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