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Transition Metal Ions as Ozonation Catalysts: An Alternative Process of Heterogeneous Catalytic Ozonation

Savvina Psaltou [1], Konstantina Sioumpoura [2], Efthimia Kaprara [2], Manassis Mitrakas [2] and Anastasios Zouboulis [1],*

[1] Laboratory of Chemical and Environmental Technology, Department of Chemistry, Aristotle University, 54124 Thessaloniki, Greece; spsaltou@chem.auth.gr
[2] Laboratory of Analytical Chemistry, Department of Chemical Engineering, Aristotle University, 54124 Thessaloniki, Greece; ksioumpou@cheng.auth.gr (K.S.); kaprara@auth.gr (E.K.); mmitraka@auth.gr (M.M.)
* Correspondence: zoubouli@chem.auth.gr; Tel.: +30-2310-997794

Abstract: The aim of this study is to elucidate the mechanism of micropollutants' removal in drinking water by the application of catalytic ozonation, using transition metals as appropriate catalysts. For that purpose, the degradation of 500 μg/L of p-chlorobenzoic acid (p-CBA) and benzotriazole with the addition of 2 mg/L of ozone in the presence of 1 mg/L of Co(II) or Fe(II) and at pH 7.8 were examined. It was found that in distilled water experiments, both metal ions can be characterized as catalysts, enhancing the ozonation process; however, in the natural water matrix, only iron presented higher removal rates of examined organic pollutants, when compared to single ozonation. The metal ions present catalytic activity, when they can form precipitates, hence converting the initially homogeneous process of catalytic ozonation towards a heterogeneous one. However, when 2 mg/L of ozone was applied in natural water experiments, Co(II)—unlike Fe(II)—could not be oxidized into its trivalent form, hence it cannot precipitate as $Co(OH)_3$. Therefore, under these experimental conditions, this metal was not found to present any catalytic activity. Nevertheless, the addition of phosphates (PO_4^{3-}) in concentrations higher than 100 mg/L can increase the oxidation ability of the $Co(II)/O_3$ system, due to the resulting sufficient formation of $Co_3(PO_4)_2$ precipitates. Although cobalt can enhance the $^{\bullet}OH$ production (and therefore, the ozonation procedure) under these conditions, the relatively highly added concentration of phosphate ions makes the treated water non-potable, resulting in the application of further treatment to remove the excess phosphates. Therefore, only Fe(II) can be considered as a sufficient catalyst to enhance the ozonation processes.

Keywords: catalytic ozonation; transition metals; p-CBA; benzotriazole; phosphates; water treatment; potable water

Citation: Psaltou, S.; Sioumpoura, K.; Kaprara, E.; Mitrakas, M.; Zouboulis, A. Transition Metal Ions as Ozonation Catalysts: An Alternative Process of Heterogeneous Catalytic Ozonation. *Catalysts* **2021**, *11*, 1091. https://doi.org/10.3390/catal11091091

Academic Editor: Jacek Grams

Received: 23 August 2021
Accepted: 8 September 2021
Published: 10 September 2021

1. Introduction

Homogeneous catalytic ozonation is not a widely investigated process. Few research papers have been published regarding this treatment technique and there are even fewer studies dealing with the respective mechanism(s). Although several metal ions have been used for improved removal of micropollutants by the application of ozonation processes, the variety of the experimental conditions that have been applied so far makes comparisons between the relevant publications almost impossible [1–4]. The ozonation processes are generally greatly influenced by the pH of the water to be treated, because ozone is more stable at the acidic pH region, while as the pH values are increased, the ozone decomposition rate also increases [5]. Commonly, the preliminary experiments of homogeneous catalytic ozonation use distilled water, aiming for the elimination of the inhibition effects caused by the several constituents of natural waters, in order to make each parameter of the process easier to study. The pH values, when they are not in the acidic region [6], are too difficult to keep stable when using distilled water, and for that reason, buffer solutions are commonly used for the proper pH adjustment [3–8]. The natural water contains already certain buffer capacity [9]; therefore, the effect of oxidation reactions on the resulting pH value is considered as rather negligible. Hence, the decomposition of ozone and the subsequent production of hydroxyl radicals are not greatly influenced by the fluctuations of initial pH values. In the respective experiments, where there is concern about the adjustment of pH, the most frequently used buffer solution to stabilize pH at the range 6–8 (i.e., for the values typically found in most wastewaters and drinking water sources) is the phosphate buffer [1,3]. However, its effect in the homogeneous catalytic ozonation process has not yet been properly evaluated.

The homogeneous catalytic ozonation is a process studied to remove micropollutants from aqueous solutions, mostly at acidic pH values [2,8–10]. Relevant research at the (typical for waters/wastewaters) pH range 6–8 is quite rare and does not present promising results. Ni et al. [2] investigated the influence of various metallic ions for the degradation of 2-dichlorophenol at various pH values. However, when the pH increased from the acidic region to the slightly alkaline region (7–9), the effect of metal ions was almost diminished. Furthermore, the description of experimental procedures has not been properly clarified. Pines and Reckhow [3] used Co(II) as a catalyst for the removal of oxalate. The adjustment of the pH value was performed by the addition of 5 mM of phosphate (i.e., containing around 475 mg/LPO_4^{3-}) buffer solution. The efficiency of this system was increased as the pH value decreased from 6.7 to 5.3, which was attributed to the higher formation of $CoHPO_4$ at pH 6.7. Khan and Jung [1] used phosphoric acid or potassium phosphate buffer for pH adjustment. They observed that Fe(II) concentration was reduced immediately in the reaction system, due to its oxidation towards Fe(III). However, Fe(III) is not considered as a good homogeneous catalyst, as Fe(II)is; therefore, this metal ion showed better catalytic activity at pH 2, where the oxidation to the trivalent form is prohibited. On the other hand, Rivas et al. [7] found that the increase of the pH value from 5 to 9 had a positive effect on simazine removal, when Mn(II) and Fe(II) cations were used as catalysts. The same relevant observations were reported in our previous study [11] for distilled water with the use of Fe(II) and Co(II) as catalysts for the removal of p-CBA.

The few published papers not based on real water conditions and the controversial results reported create a lack of understanding of the respective mechanisms governing the catalytic ozonation processes. A previous survey [11] showed that Fe(II) and Co(II) can be characterized as catalysts for the removal of p-CBA from deionized water. Therefore, in this study, their catalytic activity was evaluated in natural potable water and not under simulated conditions. The main aim of the research is to elucidate the contribution of metal ions' precipitation in the catalytic ozonation mechanism and to explore the role of phosphate ions, regarding the increased catalytic activity with the use of certain common transition metal ions applied as catalysts. For that purpose and for comparison reasons, two micropollutants with different ozone reactivities were used; in particular, p-CBA and benzotriazole. Benzotriazole is a moderate ozone reactive compound with a reaction rate constant with ozone and with hydroxyl radicals ($^{\bullet}OH$) equal to 20 M^{-1} s^{-1} and 7.6×10^9 M^{-1} s^{-1}, respectively [12]. On the contrary, p-CBA presents very low reaction kinetic constant with ozone ($k_{O3} < 0.15$ M^{-1} s^{-1}), which means that practically, this organic compound cannot react with it, and thus, its removal is due to its reaction with the produced $^{\bullet}OH$ ($k_{\bullet OH} = 5.2 \times 10^9$ M^{-1} s^{-1}) [13,14]. Therefore, p-CBA was used in the study for the indirect evaluation of $^{\bullet}OH$ production by the ozonation systems.

2. Results and Discussion

2.1. Catalytic Ozonation with Fe(II) and Co(II) as Catalysts—The Role of Aqueous Matrix

The catalytic activity of Fe(II) and Co(II) against p-CBA at pH 7.8 in deionized and dechlorinated natural potable water is presented in Figure 1a,b respectively, and the results are compared to those of single ozonation. Both Co(II) and Fe(II) can be characterized as catalysts when the reaction is taking place in deionized water, as Figure 1a shows, and that can occur independently of the pH value, as previous research has shown [11]. However, in water matrixes, also containing several scavenging compounds, such as in the dechlorinated natural potable water, the addition of Co(II) presented a negative result, regarding the p-CBA removal. In deionized water, ozone decomposed very fast (under 15 min), as shown in Supplementary Figure S1a, while in natural potable water, when Co(II) was introduced into the system, the reaction of ozone decomposition lasted for 100 min, instead of 60 min during the single ozonation and catalytic ozonation with the use of Fe(II) as a catalyst (Supplementary Figure S1b). Furthermore, the amount of ozone decomposed is not correlated with the amount of removed p-CBA in the same manner for all the examined reactions.

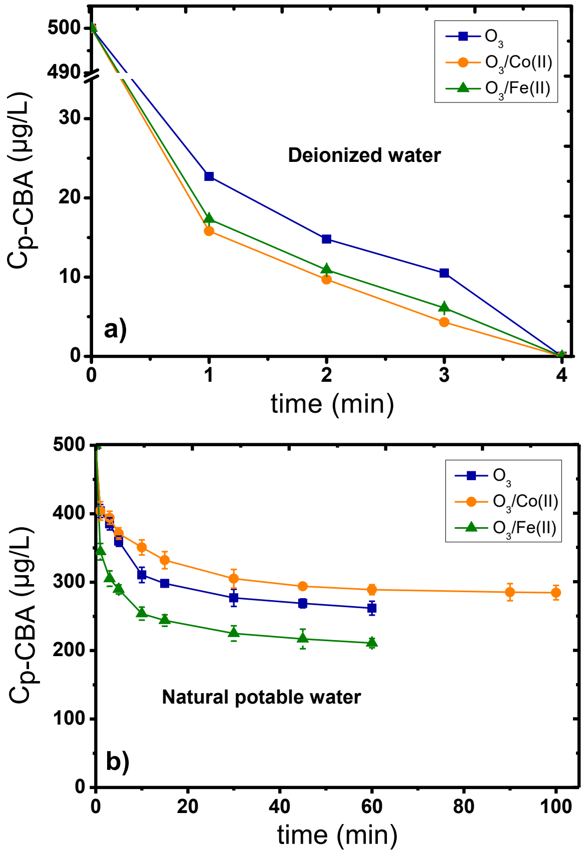

Figure 1. Catalytic ozonation of p-CBA with the use of Fe(II) and Co(II) as catalysts in (**a**) deionized water, and (**b**) dechlorinated natural potable water. Experimental conditions: initial p-CBA concentration 500 μg/L, ozone concentration 2 mg/L, catalyst concentration 1 mg/L, pH 7.8, temperature 23 ± 2 °C.

Hydrogen peroxide (H_2O_2) can be produced during the ozonation reactions, and the amount of H_2O_2 depends on the scavenging degree of the water matrix. In deionized water, the production of H_2O_2 is higher, as Pi et al. [15] observed, while this production reduces with the increase of the scavengers' presence in the aqueous solution. H_2O_2 is a strong oxidizing agent that can accelerate the production of hydroxyl radicals and enhance the oxidation result [16]. The use of $CoCl_2$ inhibits the production of H_2O_2 [17], and therefore, the rate of chain reactions, considering the decomposition of ozone, was reduced. In this study, it was observed that although in low-scavenger water, Co(II) can be considered as a catalyst, when the same metal ion was used under the same experimental conditions in the natural water matrix, the oxidation reaction was inhibited. The removal efficiency of p-CBA in the O_3/Co(II) system was lower, even than that of single ozonation. In the single O_3 process with natural water as a water matrix, the removal of p-CBA reached 48% after 60 min of oxidation time, while for the same duration in the O_3/Co(II) and O_3/Fe(II) catalytic ozonation processes, the removals were 44% and 58%, respectively. Therefore, in the drinking water, between these two metals, only Fe(II) can be characterized as a catalyst for the p-CBA removal by ozonation.

The same results were obtained from the benzotriazole removal study (Figure 2), which is a micropollutant of moderate ozone reactivity, in contrast to p-CBA, which (as previously mentioned) is practically unable to react with ozone [12]. In deionized water, benzotriazole can be easily removed even by the application of single ozonation, while the presence of both Fe(II) and Co(II) can slightly increase the oxidation efficiency of ozonation(Figure 2a). On the contrary, in the experiments with dechlorinated natural potable water, only Fe(II) presented catalytic activity against benzotriazole, and its removal rate reached 98% after 20 min of the oxidation process.

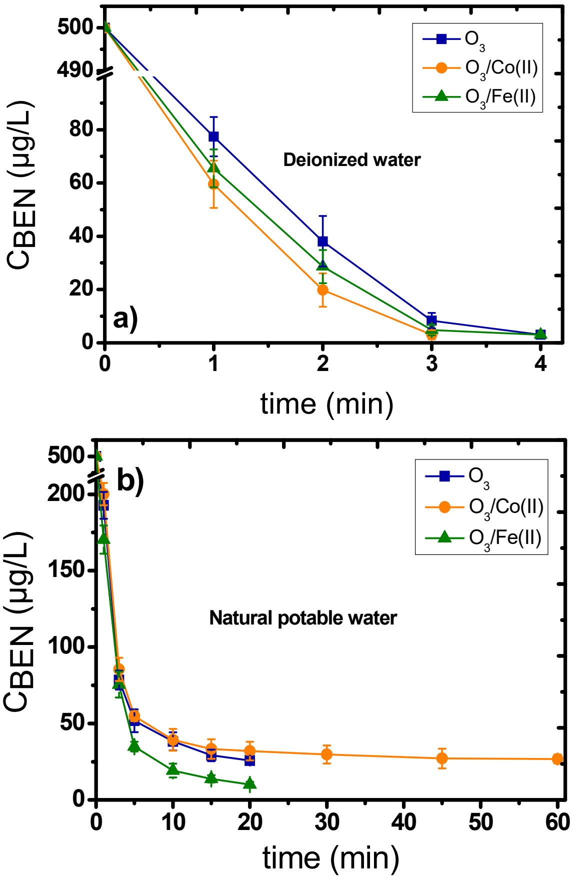

Figure 2. Catalytic ozonation of benzotriazole with the presence of Fe(II) and Co(II) as catalysts, using (**a**) deionized and (**b**) dechlorinated natural potable water. Experimental conditions: initial benzotriazole concentration 500 µg/L, ozone concentration 2 mg/L, catalyst concentration 1 mg/L, pH 7.8, temperature 23 ± 2 °C.

Additionally, the presence of Co(II) resulted in the extension of ozone decomposition reaction time to 60 min, as shown in Supplementary Figure S2. Furthermore, after 20 min of oxidation, the removal of benzotriazole reached 94% (i.e., lower than the application of single ozonation), while the removal efficiency increased only to 95% after 60 min of treatment. The decomposition of ozone after 10 min of oxidation reaction slowed down, and its rate was reduced from 0.114 to 0.047 min^{-1} (see Supplementary Table S1). Therefore, the extra reaction time cannot be considered as beneficial for the removal of the micropollutants, as was also observed for the case of p-CBA (Figure 1). The parameters of the first-order kinetic model of ozone decomposition during single or catalytic ozonation, regarding the oxidation of benzotriazole, are presented in Supplementary Table S1 and extracted from the plots of Supplementary Figure S3.

There are three main proposed mechanisms regarding the oxidation of micropollutants by the application of homogeneous catalytic ozonation [11,18]:

1. The presence of dissolved metal ions can decompose ozone, enhancing the production of $^{\bullet}OH$, which can subsequently more effectively oxidize the organic compounds/pollutants.
2. The added metal ions can create intermediate complexes with the micropollutants; hence, subsequently favoring their more efficient oxidation by the ozone molecules.
3. The oxidation of dissolved metals under the presence of highly oxidative conditions can lead to the formation of oxides/oxy-hydroxides at the nano-scale range (1–5 nm), which can further improve the decomposition of ozone and the subsequent production of the more oxidative $^{\bullet}OH$ agents.

In the study of Psaltou et al. [11], the third pathway mechanism was reported for the first time. In the experiments in dechlorinated natural potable water, when Fe(II) was used as a catalyst, it precipitated during the first minutes of reaction (Supplementary Table S2); however, in the case of Co(II), the results were different. The concentration of cobalt in the filtered solution after the oxidation reaction was 1 mg/L, i.e., the same as the initial one. When cobalt or iron are oxidized towards the respective trivalent forms in the aqueous solutions, they can precipitate as $Co(OH)_3$ and $Fe(OH)_3$ respectively, according to the reactions 1 and 2. Reaction 1 can occur even without the presence of ozone, by using oxygen (from the atmosphere) as the oxidation agent [19].

$$2Fe(II) + O_3 + 3H_2O \rightarrow 2Fe(OH)_3\downarrow \quad (1)$$

$$2Co(II) + O_3 + 3H_2O \rightarrow 2Co(OH)_3 \quad (2)$$

Therefore, the absence of any solid phases (precipitates) in the treated solution containing cobalt suggests that Co(II) was not oxidized towards its trivalent form. Figure 3 shows the remaining cobalt concentration in the solutions after treatment, according to the initial ozone concentration. When 1 or 2 mg/L were added in the ozonation system, no precipitation was observed, while an increase of initial ozone concentration up to 3 mg/L seems capable to oxidize Co(II) into Co(III), according to reaction 2. After the filtration (using a 0.22 µm filter), the residual concentrations of Co(II) in the aqueous solution under treatment, when 3, 5, 8 and 10 mg/L O_3 were applied, were found to be 0.73, 0.69, 0.54 and 0.39 mg/L, respectively. Therefore, under such conditions, even the addition of 10 mg/L of ozone was not capable to completely oxidize Co(II), and subsequently, to remove it as a precipitate.

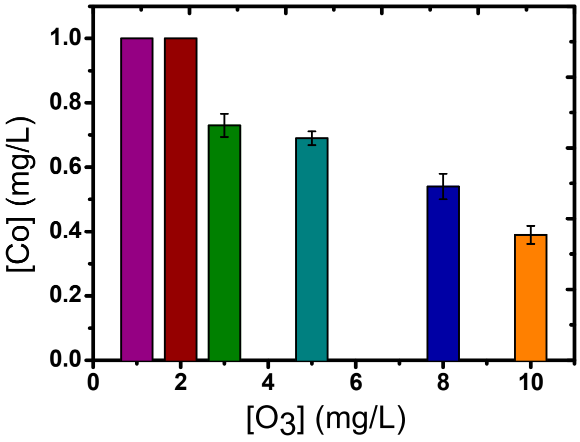

Figure 3. Concentration of soluble cobalt, according to the applied ozone dose after 90 min of oxidation reaction for the case of p-CBA. Experimental conditions: catalyst concentration 1 mg/L, pH 7.8, temperature 23 ± 2 °C.

It is worth noting that ozonation has also been applied as a technique for the oxidation and precipitation of cobalt [20,21]. Tian et al. [20] used the ozonation process for cobalt chloride solutions. However, the precipitation of cobalt is highly related to the applied experimental conditions. As Rekab et al. [22] observed, in the dark, cobalt begins to precipitate at pH 9, and only when irradiation (light) is applied can be precipitated at lower pH values. In the present study, 1 mg/L of Co(II) was not precipitated at pH 7.8, unlike Fe(II), nor even after 1 day (Supplementary Table S2). Furthermore, while the addition of Fe(II) increased the removal of p-CBA and of benzotriazole by 19% and 61% respectively, the addition of Co(II) lowered the oxidation activity of ozone, as Figures 1b and 2 show, by 11% and 19% after 60and 20 min of the oxidation reaction, respectively. Consequently, due to the ability of Fe(II) to precipitate easily in the water solutions, as $Fe(OH)_3$ after oxidation towards Fe(III),this metal ion can be characterized as a catalyst. The ozone molecules can react with the formed iron solid phases (precipitates), resulting to the acceleration of $^\bullet$OH production, proving that the third mechanism has occurred.

2.2. The Influence of Phosphate Ions Regarding the Catalytic Activity of Co(II)

The absence of scavenger compounds enhances the oxidation rate of ozonation systems [23,24], and the other difference between the two examined matrixes (i.e., deionized and tap water) was the presence of phosphate ions. In this study, the experiments using deionized water were performed with the addition of phosphate buffer for the adjustment of pH to 7.8.

Cobalt in its trivalent form occurs in the aqueous solutions as Co(OH)(II), as presented in Supplementary Figure S4, and as Yuan et al. [25] observed. At pH 7.8, the Co(III) can be precipitated in water with or without the presence of phosphates, and its soluble form remains as the trivalent one, unaffected by the presence of PO_4^{3-} in the solution. On the other hand, the divalent form of cobalt reacts with phosphates. Figure 4 shows the distribution of respective aqueous species in the experimental conditions of the study, when cobalt is in the divalent form, according to the concentration of phosphate ions in the solution. The data of cobalt species distribution were obtained from the Visual MINTEQ v.3 software. The percentage of $CoHPO_4$ increases with the increase of phosphate concentration in the treatment system. When the concentration of PO_4^{3-} is higher than 150 mg/L, the percentage of $CoHPO_4$ is higher than that of Co(II) in the solution at pH 7.8. Simultaneously, in the presence of phosphates, Co(II) can also be precipitated, according to reaction 3, and a lower concentration of Co(II) remains in the solution [26]:

$$3Co(II) + 2PO_4^{3-} \leftrightarrow Co_3(PO_4)_2\downarrow \tag{3}$$

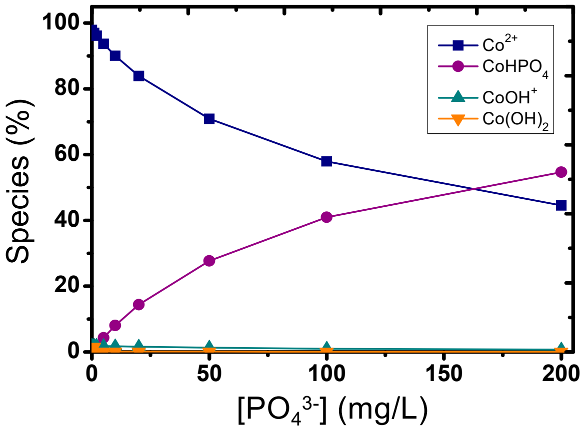

Figure 4. The soluble species of Co(II), according to the concentrations of PO_4^{3-} in the solution. Initial Co(II) concentration 1 mg/L and pH 7.8 (data obtained with the application of Visual MINTEQ version 3.0 software).

When Co(II) is fully oxidized towards Co(III), the addition of phosphates into the solution should present a negative effect on the oxidation reaction and on the catalytic activity of cobalt [27]. The kinetic curves of ozone decomposition in the presence of phosphate ions and for different initial concentrations, ranged between 1 and 200 mg/L, are shown in Figure 5a. These results are compared to those of the Co(II)/O_3 oxidation system, but without the addition of PO_4^{3-}. According to MINTEQ software (version 3.0), and for the studied conditions, the phosphate ions occur in the aqueous solution mainly as HPO_4^{2-}, but the $H_2PO_4^-$ ions can also be identified. From these experiments, it was observed that the increase of phosphate ions' concentration decelerates ozone decomposition (Figure 5a). According to Hoigné et al. [28], the reaction rate constants of hydro- and dihydro-phosphate ions with the hydroxyl radicals are 2×10^4 M^{-1} s^{-1} and 1.5×10^5 M^{-1} s^{-1} respectively, according to reactions 4 and 5. The p-CBA organic compound reacts faster with the hydroxyl radicals (the respective constant is 5.2×10^9 M^{-1} s^{-1} [14]); thus, the phosphate ions can be considered as scavengers for ozone decomposition, although not very strong ones.

$$HO^\bullet + H_2PO_4^- \rightarrow HO^- + H_2PO_4^\bullet \tag{4}$$

$$HO^\bullet + HPO_4^{2-} \rightarrow HO^- + HPO_4^{\bullet-} \tag{5}$$

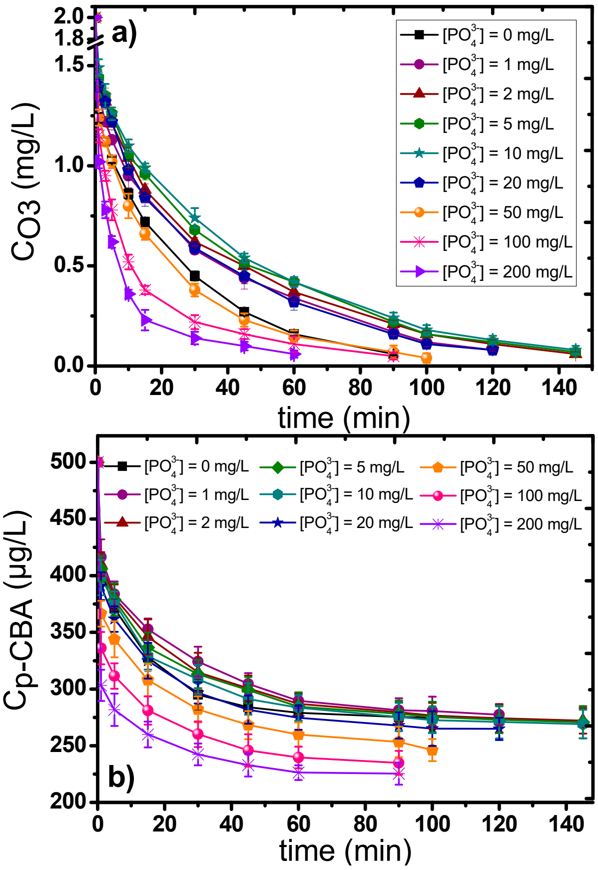

Figure 5. Influence of PO_4^{3-} concentration on (**a**) ozone decomposition, and (**b**) p-CBA removal in the Co(II)/O_3 catalytic ozonation process. Experimental conditions: initial p-CBA concentration 500 µg/L, ozone concentration 2 mg/L, catalyst concentration 1 mg/L, pH 7.8, temperature 23 ± 2 °C.

The results of Figure 5a can lead to the conclusion that the presence of HPO_4^{2-}, as well as of $H_2PO_4^-$ (but to a smaller extent), increase ozone stability up to the 10 mg/L concentration, while in higher concentrations, the decomposition of ozone is accelerated. Similar findings were reported in the study of Morozov and Ershov [27].

Furthermore, as Figure 5b shows, the catalytic activity of cobalt was also influenced by the concentration of phosphates in the aqueous solution. When the concentration of phosphates ranged between 1 and 10 mg/L, the removal efficiency of the treatment process was less than or equal to single ozonation. However, further increases in phosphate concentration can improve the efficiency of oxidation.

Additionally, the formation of precipitate was observed in these experiments. The only precipitate that can be formed between Co(II) and PO_4^{3-} is $Co_3(PO_4)_2$, according to the Visual MINTEQ version 3.0 software. The formation of $Co_3(PO_4)_2$ depends on the concentration of phosphates, and its production is increased by the increase of phosphate ions' concentration. When the phosphate ions were added into the system in relatively lower concentrations, less precipitate was formed. The ions remained free in the solution, because even $CoHPO_4$ (i.e., the respective soluble form) can be formed at the lower percentages, as shown in Figure 4. However, following the addition of higher PO_4^{3-} concentrations, the cobalt precipitation was increased. Additionally, the observed precipitation procedure is being continued and increased over time. However, in the presence of phosphates, $Co(OH)_3$ can also be formed, due to the fact that the presence of phosphates favors to some extent the oxidation of Co(II) into its trivalent form, in comparison to the results of Figure 3. Therefore, Figure 6a shows the percentage of Co(II) oxidized by ozone and precipitated as $Co(OH)_3/Co_3(PO_4)_2$, while Figure 6b shows the residual Co(II) concentration, as a result of the solubility product constant (K_{sp}). Nevertheless, the increase of phosphates' concentration implies a decrease in the solubility of Co(II). After a period of 24 h in an oxidizing environment, the oxidation rate of Co(II) is increased in comparison to the 90 min examined ozonation period. The rest of the soluble Co(II) concentration is reduced according to phosphates' concentration. However, the soluble concentration at 200 mg/L was the same as the corresponding concentration in the ozone-free system, which is directly related to the respective K_{sp} value.

At concentrations of 50–200 mg/L, there are also water-soluble phosphate ions. This leads to the conclusion that $Co_3(PO_4)_2$ presented very good catalytic action, which overshadows the inhibiting action of the water-soluble phosphates. However, only when the concentration of phosphates was over 100 mg/L could the process be characterized as catalytic, and its removal efficiency was higher than that of single ozonation. In the highest examined PO_4^{3-} concentration, the removal of p-CBA reached 55% after 90 min of the oxidation process. Similar results were reported by Eberhardt et al. [29] for the peroxone process, where the reaction of Co(II) with H_2O_2 caused only a trace amount of H_2O_2 decomposition. However, the rate of its decomposition increased dramatically in the presence of phosphate buffer solutions and at the pH range 7–8.8. Cobalt can enhance the $^{\bullet}OH$ production in the presence of phosphates, due to the formation of solid phases, however the relatively high added concentration of those ions makes the treated water non-potable, resulting in a need for further post-treatment processes (remove the excess concentrations).

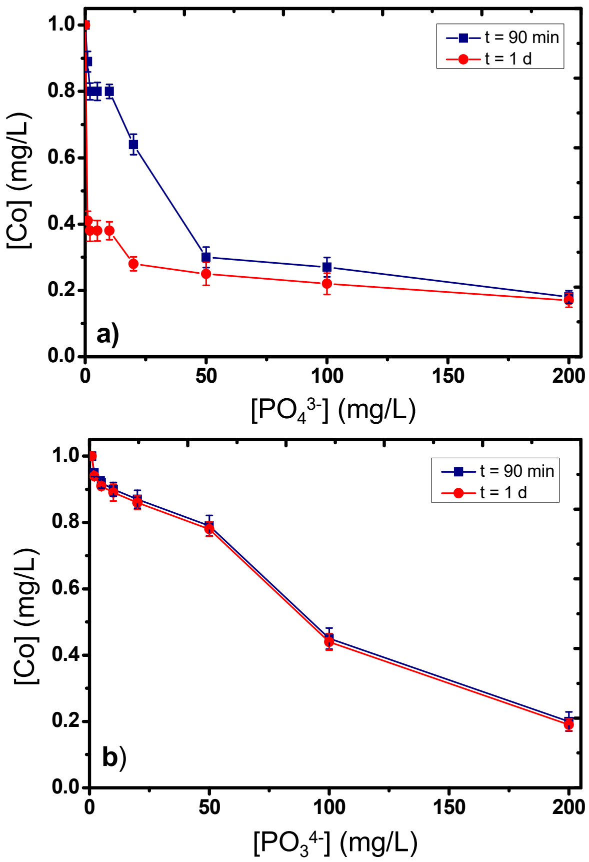

Figure 6. Concentration of soluble cobalt, according to phosphates' addition during (**a**) O_3 oxidation, and (**b**) O_3absence. Experimental conditions: ozone concentration 2 mg/L (when applied), catalyst concentration 1 mg/L, pH 7.8, temperature 23 ± 2 °C.

3. Materials and Methods

3.1. Materials

Benzotriazole and p-chlorobenzoic acid (p-CBA) were used as typical probe organic compounds (micropollutants) for the study of catalytic ozonation experiments, purchased from Sigma-Aldrich (St. Louis, MO, USA). A stock solution of 50 mg/L was prepared by dissolving p-CBA/benzotriazole into deionized water. Ozone was produced from pure oxygen (99.9%), using the corona discharged method in the laboratory ozonator Ozonia Triogen, Model TOGC2A. $CoCl_2$•$6H_2O$ and $FeSO_4$•$7H_2O$ (Chem-Lab, Zedelgem, Belgium) were dissolved in deionized water to produce stock solutions, containing 100 mg/L of Co(II) and Fe(II), respectively. Acetonitrile and phosphoric acid, HPLC-grade, were purchased from Chem-Lab (Zedelgem, Belgium) and Sigma-Aldrich (St. Louis, MO, USA), respectively. Indigo stock solution and reagent were prepared by potassium indigo trisulfonate (TCI, Tokyo, Japan), based on the method described in the Standard Methods Handbook [30].

3.2. Ozonation Procedure

Single and catalytic ozonation experiments were conducted in 250 mL dark glass vessels in batch mode and at ambient temperature. The aqueous solution of substrates was placed into the vessel before starting the reaction. Two different aqueous matrixes were used for the evaluation of the performance of examined metal ions in the catalytic ozonation experiments: (1) deionized, and (2) dechlorinated natural/tap water, whose physicochemical characteristics are presented in Table 1. The pH of natural water was 7.8, without the need for further adjustment, while the pH of deionized water was adjusted to the same value with the proper addition of KH_2PO_4/K_2HPO_4 buffer solution. The examined metal ion was introduced, and the reaction was initiated by the addition of an appropriate amount of dissolved (in deionized water) ozone. The solution was continuously stirred with a magnetic bar at 250 rpm to ensure a homogeneous mixture, avoiding the escape of high ozone concentration into the gaseous phase. The initial ozone concentration was 2 mg/L, and the duration of the reaction depended on the water matrix, the metal ion and the micropollutant that have been examined. Samples were received during different time intervals, according to each reaction, and the oxidation step was quenched by the addition of small amounts of indigo stock solution. For the evaluation of phosphate ions' presence in the catalytic activity of the ozonation systems, 8 different concentrations of phosphates were used in the range of 1–200 mg PO_4^{3-}/L, and the experiments were conducted as previously described with the addition of phosphates into the vessel before the addition of ozone. Additionally, blank experiments (without the addition of ozone) were performed in the same manner. The data presented in the figures are the average values obtained during independent experiments, conducted in triplicate, and the error bars represent the standard deviation.

Table 1. Major characteristics of the dechlorinated natural potable water used for the experiments.

Constituent	**pH**	**DOC (mg/L)**	**Conductivity (μS/cm)**	**NO^{3-} (mg/L)**	**PO_4^{3-} (mg/L)**
Value	7.8	0.5	790	0.18	0.14

3.3. Analytical Determinations

The aqueous dissolved ozone concentration was determined by the application of the common indigo method [30]. The adsorption measurements were performed at 600 nm with a UV-Vis spectrophotometer (Hach Lange, Manchester, UK, model DR3900). The pH was measured using the Crison (Barcelona, Spain, model MM41) pH meter. The p-CBA and benzotriazole concentrations were measured by HPLC with a Thermo apparatus (Thermo Fisher Scientific, Waltham, MA, USA). A 4.6 × 250 mm reversed phase column (AGILENT, model Eclipse Plus C18) was used, and the mobile phase was a mixture of 60:40%v/v and 70:30%v/v 10 mM phosphoric acid/acetonitrile, respectively. The injection volume was 25 μL, the flow rate was 0.8 mL/min and the wavelength of the UV absorbance detector was 254 nm. The respective calibration curves are presented in Supplementary Figure S5. Cobalt and iron concentrations were determined by the Flame Atomic Absorption Spectrometry method (Perkin-Elmer AAS Analyst 800 instrument, Waltham, MA, USA). The samples were filtered through a 0.22 μm filter and the filtrates were acidified at $pH \leq 2$, with the addition of 6 N HCl. The NO_3^- and PO_4^{3-} were measured spectrophotometrically by the appropriate Hach Lange LCK kits with the use of the Lange model DR3900 spectrophotometer (Hach, Loveland, CO, USA), while Total Organic Carbon (TOC) and conductivity were measured by a TOC-V_{CSH} Total Organic Carbon Analyzer (Shimadzu, Kyoto, Japan) and CON 6+meter (Oatkon, Vernon Hills, IL, USA), respectively.

4. Conclusions

Water matrix is a crucial factor in the catalytic ozonation processes, especially when metal ions are used as catalysts. Co(II) and Fe(II) presented sufficient catalytic activity in deionized water, but in the dechlorinated natural potable water matrix, only Fe(II) could be characterized as an effective catalyst. In natural potable water, the removal of p-CBA and benzotriazole by the O_3/Fe(II) process reached 57% and 98% in 60 and 20 min, respectively. Fe(II) precipitates as $Fe(OH)_3$ even from the first minutes of the respective reaction, while 2 mg/L O_3 is not a dose capable of oxidizing Co(II) towards its trivalent form, hence it does not permit the formation of the $Co(OH)_3$ precipitate. Co(II) presented catalytic activity in the natural potable water, but only in the presence of phosphates, due to the creation of $Co_3(PO_4)_2$ solid forms, converting the homogeneous catalytic ozonation into a heterogeneous one, as in the case of iron. The presence of low PO_4^{3-} concentrations act as scavengers, by reducing the oxidation capacity of the ozonation system, while at concentrations higher than 10 mg/L, the formation of $Co_3(PO_4)_2$ can accelerate the production of $^{\bullet}OH$. Although phosphates can convert Co(II) into a catalyst for the removal of micropollutants from drinking water/wastewater effluents, the necessary presence of them in such high concentrations makes the treated water not appropriate for consumption, requiring post-treatment before its further use or disposal into the aquatic environment.

Supplementary Materials: The following information is available online at https://www.mdpi.com/article/10.3390/catal11091091/s1, Figure S1: Ozone decomposition during the catalytic ozonation of p-CBA, with the use of Fe(II) and Co(II) as catalysts in (a) deionized water, and (b) dechlorinated natural potable water. Experimental conditions: initial p-CBA concentration 0.5 mg/L, ozone concentration 2 mg/L, catalyst concentration 1 mg/L, pH 7.8, temperature 23 ± 2 °C; Figure S2: Ozone decomposition during the catalytic ozonation of benzotriazole with the use of Fe(II) and Co(II) as catalysts in dechlorinated natural potable water. Experimental conditions: initial benzotriazole concentration 0.5 mg/L, ozone concentration 2 mg/L, catalyst concentration 1 mg/L, pH 7.8, temperature 23 ± 2 °C; Figure S3: First-order kinetic model of ozone decomposition during the ozonation of benzotriazole in dechlorinated natural potable water. Experimental conditions: initial benzotriazole concentration 0.5 mg/L, ozone concentration 2 mg/L, catalyst concentration 1 mg/L, pH 7.8, temperature 23 ± 2 °C; Figure S4: Soluble species of Co(III) for the initial metal ion concentration of 1 mg/L in different pH values in aqueous solutions; Figure S5: Linear response for the determination of (a) p-CBAand (b) benzotriazole concentrations (by HPLC) in the concentration range 0–600 μg/L; Table S1: Parameters of first-order kinetic model of ozone decomposition during ozonation of benzotriazole in dechlorinated natural water. Experimental conditions: initial benzotriazole concentration 0.5 mg/L, ozone concentration 2 mg/L, catalyst concentration 1 mg/L, pH 7.8, temperature 23 ± 2 °C; Table S2: Iron and cobalt concentrations in different time intervals with and without the addition of ozone.

Author Contributions: Conceptualization, S.P., M.M. and A.Z.; methodology, S.P. and M.M.; validation, S.P., M.M. and A.Z.; formal analysis, S.P. and E.K.; investigation, S.P. and K.S.; resources, M.M. and A.Z.; data curation, S.P. and E.K.; writing—original draft preparation, S.P.; writing—review and editing, E.K., M.M. and A.Z.; visualization, S.P.; supervision, M.M. and A.Z.; project administration, A.Z.; funding acquisition, A.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship, and Innovation, under the call RESEARCH-CREATE-INNOVATE (project code: T1EDK-02397).

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European Social Fund

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Partnership Agreement
2014 - 2020

Co-financed by Greece and the European Union

Conflicts of Interest: The authors declare no conflict of interest.

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