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Comparative study on heterogeneous and homogeneous catalytic ozonation efficiency in micropollutants' removal

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ABSTRACT

Catalytic ozonation was applied for the removal of small concentrations (4 μM) of micropollutants benzotriazole, carbamazepine, p-CBA from aqueous solutions at pH 7. These compounds present different physicochemical characteristics and different kinetic rate constants, when reacting with ozone or hydroxyl radicals in the ranges of <0.15–3×10^5, 5.2×10^9, and 8.8×10^9 M^{-1}s^{-1}, respectively. Calcite was used as heterogeneous catalyst and its catalytic activity evaluated, by applying (and optimized) different experimental conditions (i.e., pH, temperature, ozone concentration), concerning the removal efficiency of p-CBA. Study of micropollutants' removal showed all examined organic compounds can be sufficiently removed by application of catalytic ozonation either by use of calcite, or by presence of Co(II) or Fe(II) (applied as homogeneous catalysts), while the optimum catalyst between them was found to be calcite. Carbamazepine with $k_{O3} = 3 \times 10^5$ M^{-1}s^{-1} can be easily removed, even by application of single ozonation, while benzotriazole and p-CBA resulted in 50% and 68.2% higher removal after application of catalytic ozonation within 3 min of oxidation reaction, due to acceleration of hydroxyl radicals' production by presence of calcite in the ozonation system. The contribution of hydroxyl radicals in removal of all three micropollutants was evaluated by extraction of R_{ct} and f•OH parameters.

Key words: advanced oxidation processes, catalysts, catalytic ozonation, micropollutants, R_{ct} value, water treatment

HIGHLIGHTS

- Benzotriazole, carbamazepine and p-CBA were successfully removed by catalytic ozonation.
- Among examined catalysts calcite was defined as the best one.
- The removal of micropollutants is based on the mechanism of radicals' production.
- Benzotriazole removal was in best agreement with the 1st order kinetic model.
- The kinetic model of p-CBA depended on the applicable catalyst.

INTRODUCTION

Micropollutants is a common name given to organic compounds, occurring in the water environment at trace levels ($<$mg/L), and they are considered as contaminants of emerging concern (Sousa *et al.* 2018). This group of substances includes different types/classes of compounds, such as pharmaceuticals, personal care products, pesticides, hormones, perfluorinated compounds, disinfection by-products, etc. (Lei *et al.* 2015; Rodriguez-Narvaez *et al.* 2017). The production, use, and disposal of numerous (mainly organic) chemicals commonly employed in the industry, agriculture, medicine or even in everyday use products (e.g., shampoo, moisturizing cream, gel, etc.) has led to the wide spread of micropollutants in the aquatic environment. These chemicals may have potentially detrimental effects to both aquatic ecosystems, as well as to human health, such as carcinogenicity, mutagenicity, and teratogenicity (Lei *et al.* 2015; Sousa *et al.* 2018).

The application of conventional treatment processes, as well as the natural attenuation procedures, is not sufficiently capable for the efficient removal of most micropollutants from surface/ground/drinking water and wastewater sources. For this reason, there are several non-conventional micropollutants' removal technologies, which can be categorized into the following three groups: (1) phase-changing technologies, (2) biological treatment, and (3) advanced oxidation processes.

The most studied/published processes among them are the adsorption, membrane filtration, and ozonation processes (Rodriguez-Narvaez *et al.* 2017). Among the ozonation processes employed for micropollutants' degradation is catalytic ozonation. Catalytic ozonation can be divided into homogeneous (using dissolved common transition metal ions) and heterogeneous (applying appropriate solid materials). A variety of transition metals, such as Co(II), Fe(II), Mn(II), and Cu(II) have been already reported in the literature as potential catalysts for homogeneous catalytic ozonation processes (Pines & Reckhow 2002; Ni *et al.* 2003; Xiao *et al.* 2008; Psaltou *et al.* 2019). Also, several metals, but in the respective oxide forms, are frequently used in the heterogeneous catalytic ozonation processes (Roshani *et al.* 2014; Jeirani & Soltan 2016). Additionally, a number of minerals and carbons have also been examined as potential catalysts for the catalytic ozonation process (Nawrocki 2013; Chen *et al.* 2018).

Catalytic ozonation is based on the degradation of organic compounds via the decomposition of ozone mainly towards the production of hydroxyl radicals, which are powerful (2.7 V) and non-selective oxidant agents (Nawrocki 2013). Homogeneous catalytic ozonation can be carried out mainly through the following three pathways (Martins & Quinta-Ferreira 2014; Psaltou *et al.* 2019):

1. The presence of dissolved metal ions can decompose ozone; and, therefore, enhance the production of hydroxyl radicals, which can subsequently oxidize more effectively the organic compounds.
2. The added metal ions can create intermediate complexes with the target organic compounds; and, hence, favor their subsequent more efficient oxidation by the ozone effect.
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 improves the decomposition of ozone and the production of hydroxyl radicals. These nano-structures convert the homogenous catalytic ozonation into the heterogeneous one.

On the other hand, the heterogeneous catalytic ozonation can be carried out mainly through the following three pathways (Nawrocki & Kasprzyk-Hordern 2010):

1. Approach of ozone to the catalyst surface.
2. Organic molecules adsorb onto the catalyst surface.
3. Both ozone and organic molecule come in contact at the catalyst surface.

The efficiency of ozonation processes can be influenced by the effect of several parameters, such as the specific water matrix, the ozone dose, the pH value, the temperature, and the organic pollutants' type and concentration (Nawrocki & Kasprzyk-Hordern 2010; Nawrocki 2013). The micropollutants in the ozonation processes can be categorized, based mainly on the reaction rate constant with ozone, into three groups: (1) ozone-resistant compounds ($k_{O3} < 10\ M^{-1}s^{-1}$), which are not significantly oxidized by the direct reaction with ozone, (2) moderately ozone-reactive compounds ($10\ M^{-1}s^{-1} < k_{O3} < 10^4\ M^{-1}s^{-1}$), which are oxidized by both ozone and hydroxyl radicals, and (3) high ozone reactive compounds ($k_{O3} > 10^4\ M^{-1}s^{-1}$), which are mainly oxidized by the presence of ozone (Hübner *et al.* 2015; Guo *et al.* 2018).

Calcite is a low-cost, raw material with high commercial availability and it can be used without further modification. In previous research (Psaltou *et al.* 2020a, 2020b), it was pointed out that it can be used as a catalyst with high removal efficiency, especially for the case of p-CBA, which cannot be removed by its oxidative reaction with ozone molecules. Therefore, it is considered as an interesting alternative for application in heterogeneous catalytic ozonation systems, although its activity in different experimental conditions or against other micropollutants has not been yet clearly evaluated. There are several factors that affect the catalytic ozonation processes. Among them, the most important are considered the pH and temperature, which highly influence the stability of ozone in water (Nawrocki & Kasprzyk-Hordern 2010). The aim of this study is to investigate these experimental conditions in the catalytic ozonation process and to evaluate the catalytic activity of calcite, by studying the removal of low concentration (4 µM) of certain typical micropollutants, belonging in the three aforementioned broad ozone-reactant categories. Among these, the catalytic efficiency of calcite (heterogeneous catalyst) was compared with that of Co(II) and Fe(II), two well-known homogeneous catalysts (Rivas *et al.* 2001; Pines & Reckhow 2002; Psaltou *et al.* 2019). To fulfill this goal, three different micropollutants were used: benzotriazole, i.e., a moderately ozone-reactive compound (Roshani *et al.* 2014), carbamazepine, i.e., an easy-reactive with ozone compound (Rosal *et al.* 2008), and p-CBA, i.e., an ozone-resistant compound (Lan *et al.* 2013). p-CBA was also used as a typical/probe compound for the indirect evaluation of hydroxyl radicals' production, confirming the way that the examined experimental conditions affect their production during the catalytic ozonation process. Also, p-CBA was used to define the dose of

ozone, another important parameter in the micropollutant experiments. For the first time, the mechanistic aspects of the oxidation reactions evaluated by the calculation of R_{ct} and f.OH parameters and by the kinetic models were also compared for different micropollutants and applying the same experimental conditions, hence enabling the comparison of the respective mechanisms.
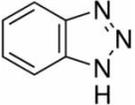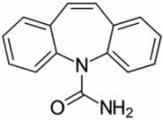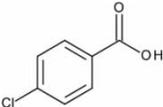
EXPERIMENTAL

Materials and methods

All used chemicals were of analytical grade, except for HPLC-grade acetonitrile (Chem-Lab, Belgium) and phosphoric acid (Sigma-Aldrich, USA). Benzotriazole, carbamazepine and p-CBA (Sigma-Aldrich, USA) were used as typical/model organic compounds at the initial concentration of 4 μM. In Table 1 the main physicochemical characteristics of the examined micropollutants, as well as the kinetic constants of their reactions with ozone or with hydroxyl radicals, are shown.

All solutions were prepared in distilled water. Based upon preliminary experiments (Psaltou et al. 2020a, 2020b), calcite (a widely found mineral) was selected as solid catalyst for the heterogeneous catalytic ozonation experiments. $CoCl_2 \cdot 6H_2O$ (PRS Panreac, Spain) and $FeSO_4 \cdot 7H_2O$ (Chem-lab, Belgium) were used as sources for the dissolved metal cations, applied as homogeneous catalysts. K_2HPO_4 and KH_2PO_4 (Chem-Lab, Zedelgem, Belgium) were used for the adjustment of pH values. Furthermore, tert-butanol (TBA) was used to quench effectively the produced hydroxyl radicals, due to decomposition of ozone during the ozonation process.

The ozonation experiments were performed in batch mode. Ozone was generated using a corona discharged ozone generator (Ozonia-Triogen Model TOGC2A) with pure oxygen as feed gas. The initial concentration of ozone was 2 mg/L, except for the experiments that examined the influence of ozone dose in the removal efficiency of heterogeneous catalytic ozonation, where 1 and 3 mg/L were also examined as initial ozone concentrations. The concentration of calcite was 0.5 g/L, while the concentration of dissolved metal ions was 1 mg/L. The pH was adjusted by the addition of phosphate buffer (ionic strength: 0.005 M). The catalyst was introduced into the dark vessel right before the addition of ozone solution. The catalytic ozonation contact time depended on the target pollutant. The longest reaction time was with p-CBA, which lasted for 30 min. In the ozonation experiments, where calcite was used as catalyst, the samples were filtered through 0.45 μm membrane (nylon) filter before the analytical determination. The oxidation reaction was stopped by the addition of the appropriate amount of indigo solution (50 μL). The single ozonation experiments were conducted in the same way, without the addition of any catalyst. The adsorption experiments were also performed in batch mode, similar to the catalytic ozonation experiments, but without the addition of ozone. The amount of adsorbed micropollutants (μg/g) was calculated based on Equation (1),

Table 1 | Micropollutants used in this study as model compounds and their properties (adapted from Psaltou et al. 2020a, 2020b)

Micropollutant	Structure	MW[a]	pK$_a$	PSA[b] (Å^2) (PubChem n.d.)	k$_{O_3}^c$ (M^{-1}s^{-1})	k·OH[d] (M^{-1}s^{-1})
Benzotriazole		119.1	9.04	41.6	20	7.6×10^9
Carbamazepine		236.3	16	46.3	3×10^5	8.8×10^9
p-CBA		156.6	4.07	37.3	< 0.15	5.2×10^9

[a]Molecular weight.
[b]Polar surface area.
[c]Reaction rate constant with ozone.
[d]Reaction rate constant with •OH.

regarding sorption capacity:

$$q_t = \frac{[(C_0 - C_t)*V]}{W} \tag{1}$$

where q_t is the adsorption capacity (μg/g), C_0 is the initial concentration of micropollutant (μg/L), C_t is the residual concentration of the micropollutant (μg/L) at a specific time, V is the volume of the solution (L), and W is the weight of the catalyst (g).

Analytical techniques

The residual concentration of micropollutants was determined by HPLC (Thermo, USA) with UV detector at 254 nm (Thermo, UV2000). The mobile phase consisted of 10 mM phosphoric acid and acetonitrile, in percentages shown in Supplementary Material, Table S1. The detection limit for the examined micropollutants was 0.025 μM. The respective calibration curves are shown in Supplementary Material, Figure S1. The concentration of ozone was determined by the application of the indigo method (Clesceri *et al.* 1989); the color change of the indigo solution was measured at 600 nm by spectrophotometer (Lange, DR3900). The measured physicochemical properties of calcite were the specific surface area (6.3 m²/g), the pore size distribusion (0.038 mL/g) (Brunauer–Emmett–Teller (BET) method) and the point of zero charge (PZC = 9.7) with the application of immersion technique (Bourikas *et al.* 2003). The pH of aqueous solutions was measured by pH meter (Jenway, model 3540).

RESULTS AND DISCUSSION

Based upon preliminary experiments (data not shown), calcite was selected as solid catalyst for the heterogeneous catalytic ozonation experiments. Therefore, in this study, the influence of the main experimental parameters and the optimization of conditions, regarding catalytic activity and removal efficiencies against micropollutants, presenting different physicochemical properties, was investigated. Calcite is a widely found mineral with a chemical formula of $CaCO_3$. The surface area and pore size were 6.3 m²/g and 0.038 mL/g, respectively. The point of zero charge of calcite was found to be 9.7.

Influence of experimental conditions on the catalytic activity of calcite

There are several factors that can affect the efficiency of heterogeneous catalytic ozonation process. Among them, the pH value and the temperature can highly influence the stability of ozone dissolved in water. Also, the concentration of ozone can be crucial for the efficiency of ozonation systems. The influence of experimental conditions on the catalytic activity of calcite was evaluated, based on the removal efficiency of p-CBA. This is an organic molecule that cannot be practically removed by oxidation from the presence of ozone ($k_{O3} < 0.15$ M^{-1}s^{-1}); therefore, its removal depends on its oxidation by the presence of hydroxyl radicals, which are the main product of ozone decomposition.

The pH value is a very important aspect of the ozonation process because it can highly influence the decomposition of ozone and the subsequent production of hydroxyl radicals (see also Text S1, Supplementary Material). As the pH is increasing, the decomposition of ozone accelerates (Supplementary Material, Figure S2(a)). Figure 1(a) shows the removal of p-CBA, when calcite was added in the ozonation system as catalyst for the pH values 6, 7, and 8 (a typical pH range for drinking water and post-treated effluents of municipal wastewater treatment plants). As expected, the relatively higher removal of pollutant was observed at pH 8, although in all these pH values the efficiency of catalytic ozonation was higher than that of the single ozonation process (Supplementary Material, Figure S3(a)). At pH 8, p-CBA was almost totally removed, already within the 3rd min of reaction time. Respectively, at pH 7 the p-CBA was removed by 97.8% at the same duration, while the concentration of p-CBA was under the analytical detection limit (0.025 μM) at the 15th min of the oxidation process. In contrast, at pH 6, the removal of p-CBA reached 89.7% at the 3rd min of the oxidation process, while at the end of the oxidation reaction (after 30 min) the removal efficiency was increased to 98.3%. The lower efficiency at this (slightly acidic) pH value of 6 can be attributed to the lower production of hydroxyl radicals, since the p-CBA practically reacts only with them.

Furthermore, the ozone molecules are more stable in the aqueous solutions of lower temperature; therefore, in this case the ozone decomposition reactions and the respective production of radicals are slower (Psaltou *et al.* 2020a). Thus, the removal efficiency of p-CBA was decreased by reducing the solution temperature (Figure 1(b)). At 15 °C, the production of hydroxyl radicals was decreased, and the p-CBA molecules removed by 89.5% after 30 min oxidation time. Although a rise in the temperature can increase the decomposition of ozone and the respective chemical reaction rates, it can also simultaneously
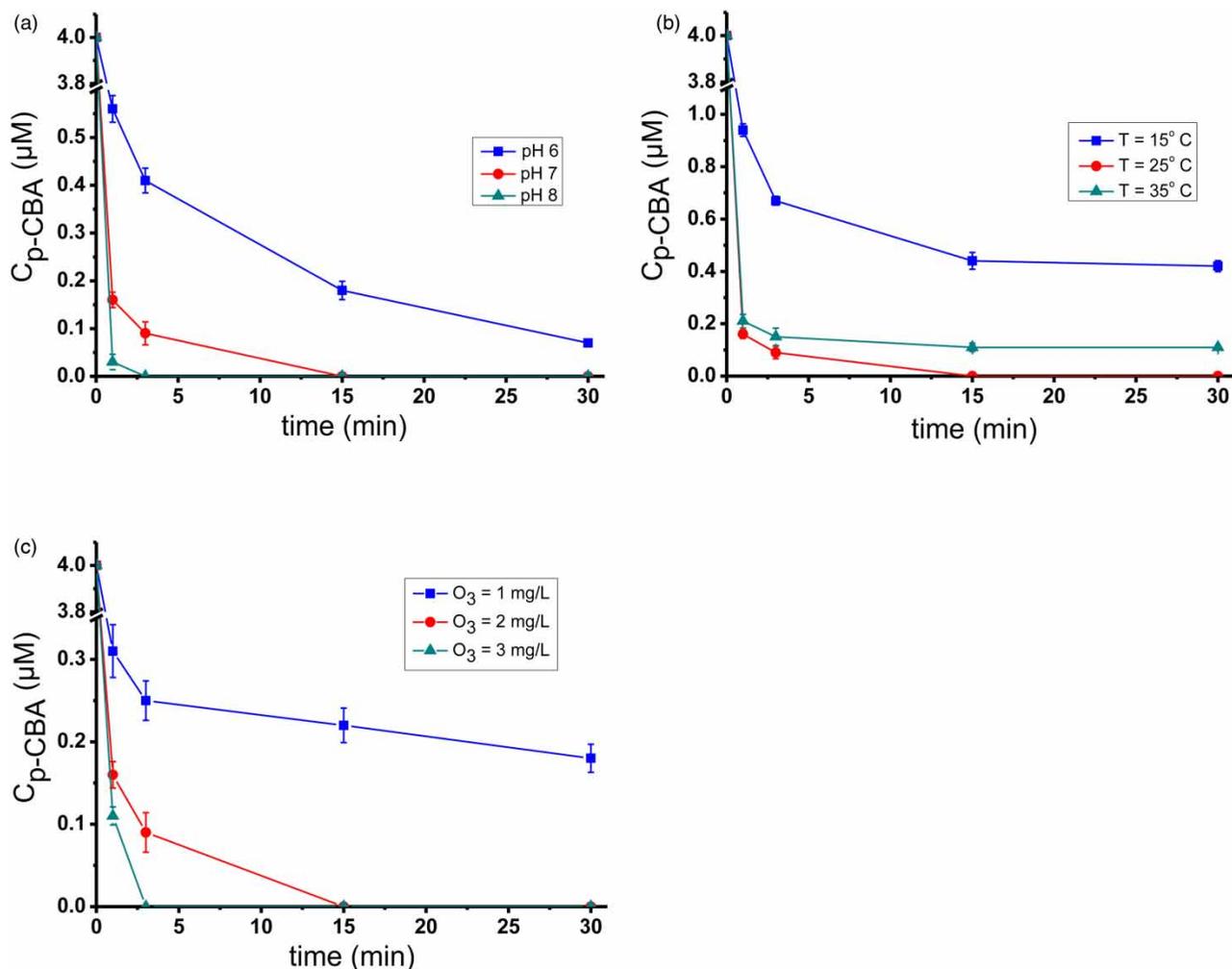
Figure 1 | Influence of (a) pH value, (b) temperature, and (c) ozone concentration on p-CBA removal by the application of catalytic ozonation. Experimental conditions: C_{O3} 2 mg/L, C_{p-CBA} 4 μM, $C_{calcite}$ 0.5 g/L, pH 7, T 23 $\pm$ 2 °C – unless the figure legend suggests otherwise. (Data are the averages of the values obtained in independent experiments conducted in triplicate and the error bars represent the standard deviation.)

decrease the concentration of dissolved ozone in water. Thus, by increasing the temperature of the system, e.g., from 15 °C to 25 °C, the reaction rate of p-CBA removal accelerated, while the further increase of temperature to 35 °C can lead to lower dissolved ozone concentration in the water matrix and, hence, to lower p-CBA removal rate. Furthermore, the adsorption efficiency of micropollutants is decreasing at the elevated temperatures (see also Supplementary Material, Table S2), reducing in turn the efficiency of heterogeneous catalytic ozonation process. The influence of temperature on the concentration of ozone during these experiments is clearly shown in Supplementary Material, Figure S3b. In this study, with the use of calcite as catalyst, the optimum temperature for the removal of p-CBA is 25 °C. The removal of p-CBA after the 3rd min of reaction/ oxidation time reached 97.8%. Similar observations were also reported by Luo *et al.* (2018).

Ozone dosages also affect in large extent the efficiency of the ozonation processes. Three different ozone dosages (1, 2, and 3 mg/L) were examined, and the results are shown in Figure 1(c). With the use of 2 and 3 mg/L ozone, the p-CBA was almost totally removed after 15 min or after 3 min of reaction/oxidation time, respectively. The removal rate of this micropollutant after 3 min of reaction, when 1 mg/L ozone was added to the ozonation system, was 93.4%, while the removal efficiency after 30 min of the process was 95.5%, i.e., the removal was slightly increased, because in this case the concentration of ozone was rather small for the respective duration of the reaction, and it was almost totally consumed after 15 min of the process (Supplementary Material, Figure S2(c)).

The recycling capacity of calcite was tested by applying ten consecutive cycles. After each catalytic ozonation process, the catalyst was removed from the treated solution by filtration and washed with distilled water. The catalyst was used in the next

catalytic ozonation experiment after drying at 50 °C. Supplementary Material, Figure S4 shows that after ten cycles the catalytic activity of calcite remained almost constant proving that it is a stable catalyst capable of being used in continuous catalytic ozonation processes.

Removal of micropollutants by catalytic ozonation

The second part of this study is the evaluation of catalytic activity of calcite for the removal of micropollutants, presenting different properties and ozone reactivities. Also, the efficiency of calcite as catalyst was compared with that of two well-known homogeneous catalysts and, in particular, with Co(II) and Fe(II) dissolved cations (Rivas et al. 2001; Pines & Reckhow 2002; Psaltou et al. 2019). Although pH 8 was found to be the optimum pH value for the removal of p-CBA in the O_3/calcite system, pH 7 was selected for the following experiments, as being more appropriate for the study of micropollutants' removal, because this is the average value in the drinking water treatment effluents and in the treated wastewaters and, also, because the decomposition of ozone at pH 8 is too fast (producing radicals) and as a result, even the single ozonation process under these conditions is considered as an AOP process (Miklos et al. 2018). Also, the fast removal rates, due to the excess of oxidant species, when 3 mg/L O_3 is applied, overshadow the contribution of catalysts, hence 2 mg/L was selected as the ozone initial concentration in the micropollutants' removal study.

The evaluation of adsorption capacity, regarding a solid catalyst, is considered as very important in the catalytic ozonation process, due to the following reasons: (1) research studies have shown that heterogeneous catalytic ozonation is a synergistic process, during which, adsorption may also contribute via the improved contact between the pollutant and the catalyst (Valdés et al. 2012; Shahamat et al. 2014), and (2) a solid material can be characterized as catalyst when the efficiency of the catalytic system is higher than the efficiencies' sum of adsorption and of single ozonation (Xu et al. 2019); i.e., the solid material should act mainly as a catalyst and not as an adsorbent agent. Table 2 shows the adsorption capacity of calcite against benzotriazole, carbamazepine, and p-CBA. The opposite charge between the solid material (IEP) and the organic compound (pK_a) favors the affinity between them during the adsorption process. The isoelectric point (IEP) of calcite is about 8 (Fuerstenau & Han 2003); hence, this is positively charged at the reaction pH 7.

On the contrary, benzotriazole and carbamazepine are almost neutrally charged because they are not ionized at pH 7, while the p-CBA is negatively charged. p-CBA is a low adsorbing organic chemical compound, as other researchers have also observed (Pines & Reckhow 2003). Between the neutrally charged compounds, carbamazepine, presenting a higher PSA (polar surface area), seems to be adsorbed at a higher degree onto calcite than benzotriazole which has PSA equal to 41.6 $Å^2$. PSA has also been used to predict the adsorption of drugs and it is the surface sum of oxygen, nitrogen, and bonded-hydrogen atoms (Palm et al. 1996; Schaftenaar & de Vlieg 2012). p-CBA, having the lowest PSA among the examined organic compounds, adsorbed in lower degree than the other micropollutants onto the catalyst surface. The process of adsorption plays an important role in the promotion of catalytic effect but cannot be used for efficiency comparisons in the respective studies regarding the removal of micropollutants, which present different activity against ozone. Therefore, the calcite adsorption experiments were performed in this study to verify its affinity with the micropollutants.

Supplementary Material, Figure S5 shows the results of ozone decomposition during the single ozonation and the catalytic ozonation (using calcite, Co(II), and Fe(II) as catalysts) of the three different micropollutants (benzotriazole, carbamazepine, and p-CBA) at pH 7. All the examined catalysts have been found to increase the decomposition of ozone, as compared to single ozonation, independently of the target micropollutant. However, the presence of each organic compound in the oxidation system leads to a different ozone decomposition rate. Carbamazepine, presenting ozone reaction rate constant equal to $3 \times 10^5 \, M^{-1}s^{-1}$ (Rosal et al. 2008), reacts very fast with the ozone molecules and, therefore, in this case, the consumption of ozone was high, both in single and in catalytic ozonation processes, reaching 94.5 and 97% after only 1 min of reaction/oxidation time for the O_3 and O_3/calcite systems, respectively; noting that in both homogeneous systems the decomposition of ozone reached 95% for the same time. On the other hand, in the presence of p-CBA, presenting the

Table 2 | Adsorption loading of micropollutants ($C_0 = 4 \, \mu M$) onto calcite ($C_{cat.} = 0.5$ g/L) at t = 30 min

Parameter	Benzotriazole	Carbamazepine	p-CBA
q (μg MP/g calcite)	59.6	104.0	55.3

lowest reaction rate constant with ozone among the examined micropollutants (<0.15 M^{-1}s^{-1}), the decomposition of ozone was much slower, reaching about 96% after 30 min of reaction/oxidation time. Almost the same consumption was observed for the benzotriazole oxidation system, but after 15 min of the respective process time.

The removal of micropollutants presented the same behavior as the decomposition of ozone. Figure 2 shows the results of micropollutants' removal during the application of single and of catalytic ozonation processes with the use of calcite, Co(II), and Fe(II), examined as catalysts. The concentration of p-CBA decreased generally in parallel with the decreasing ozone concentration during the single or catalytic ozonation. The p-CBA cannot be removed efficiently by the application of direct ozonation ($k_{O3} < 0.15$ M^{-1}s^{-1}), whereas it presents high reactivity with the hydroxyl radicals ($k_{OH} = 5 \times 10^9$ M^{-1}s^{-1}, Lan et al. 2013). However, the p-CBA degraded quickly even after the 1st min, following the application of both processes, and then, the removal rate became smaller until the termination of this reaction. As shown in Figure 2(b), carbamazepine, presenting high reactivity with ozone (Table 1), was quickly degraded during the ozonation process, regardless of the presence of catalysts. Furthermore, benzotriazole was efficiently removed by the application of both single ozonation and catalytic ozonation processes, and its concentration was under the detection limit (0.025 μM) after the 15th and the 3rd min of the reaction/oxidation time, respectively. After the 3rd min, the removal efficiency of benzotriazole in the O$_3$/calcite, O$_3$/Co(II), and O$_3$/Fe(II) catalytic ozonation systems was 50%, 35.7%, and 27.2%, respectively higher, than that of the single ozonation application.
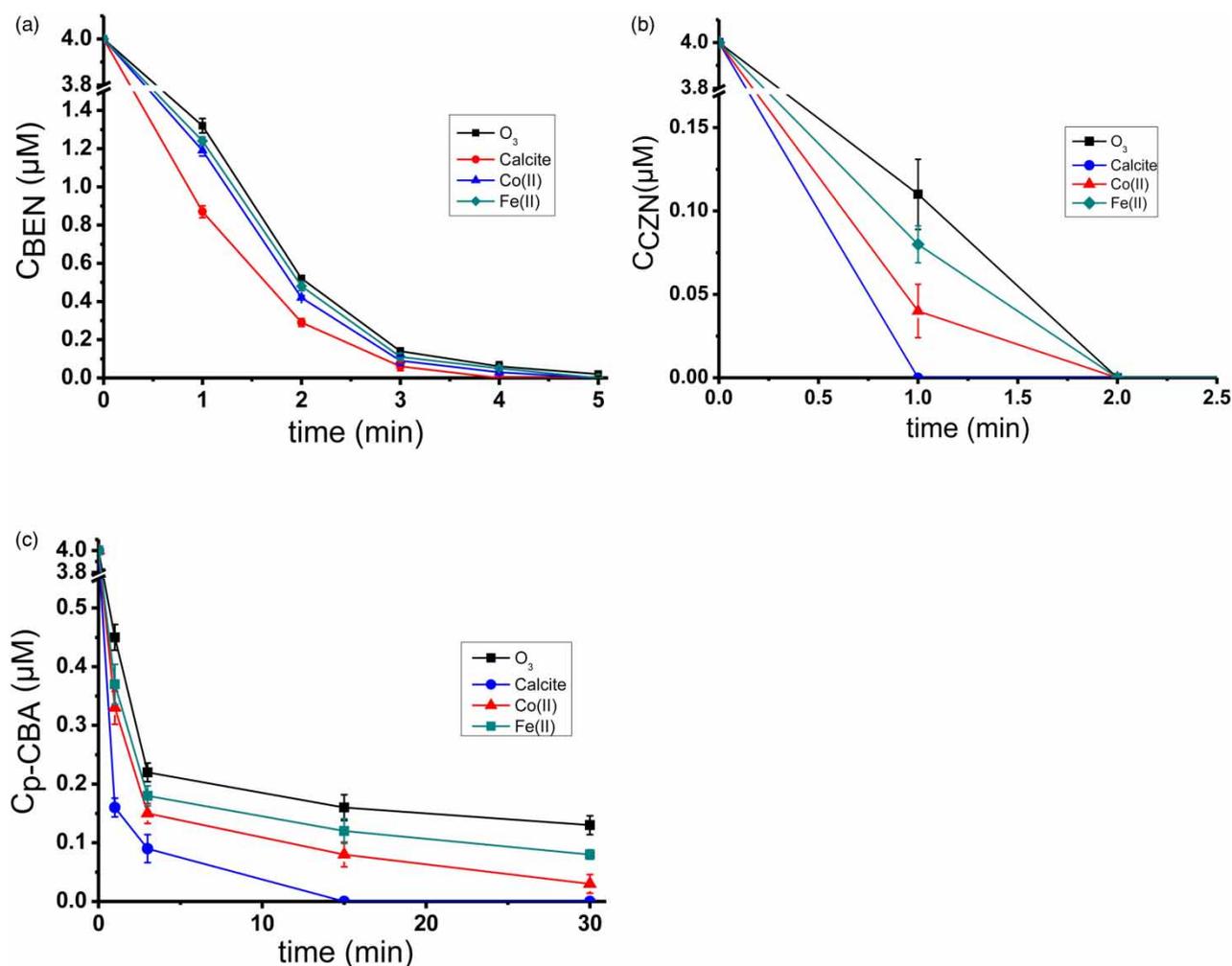

Figure 2 | Degradation of (a) benzotriazole, (b) carbamzepine, and (c) p-CBA by the application of catalytic ozonation in comparison with single ozonation. Experimental conditions: C$_{O3}$ 2 mg/L, C$_{MP}$ 4 μM, C$_{calcite}$ 0.5 g/L, C$_{metal\ ions}$ 1 mg/L, pH 7, T 23 ± 2 °C. (Data are the averages of the values obtained in independent experiments conducted in triplicate and the error bars represent the standard deviation.)

The formation of ˙OH was also investigated by the addition of a well-known radical scavenger, tert-butyl alcohol (TBA). The reaction rate constant of TBA with ozone and hydroxyl radicals is $3.0 \times 10^{-3}\,M^{-1}s^{-1}$ and $6.0 \times 10^{8}\,M^{-1}s^{-1}$, respectively (Alver & Kılıç 2018). The concentration of TBA should be in excess of the substrate and its concentration was calculated by the equation suggested by Wang et al. (2016). The addition of TBA in all examined ozonation systems indicates that the removal of these micropollutants is based on the mechanism of radical production, during which hydroxyl radicals are the main species (Figure 3). The higher inhibition effect was observed for the case of p-CBA, which is practically removed only by the presence of hydroxyl radicals. The optimum catalyst for the p-CBA removal was calcite (Figure 2(c)); the inhibition effect in this system was above 97.6%. The concentration of p-CBA was under the analytical detection limit ($0.025\,\mu M$) after the 3rd min of the reaction/oxidation time, while in the presence of TBA at the 30th min of the process, the removal efficiency was only 17.7%. On the other hand, carbamazepine with the highest ozone reactivity ($3 \times 10^{5}\,M^{-1}s^{-1}$) compared to the examined micropollutants, was removed by 71% in the presence of TBA even in the system of single ozonation, while the addition of the catalysts increased its removal efficiency (Figure 3(b)).

Aqueous ozone solutions of neutral or basic pH values are unstable, due to the formation of ˙OH by the HO^{-} and the reaction of ˙OH with ozone molecules as Equation (2) shows:

$$^{\bullet}OH + O_3 \rightarrow HO_2^{\bullet} + O_2 \qquad\qquad (2)$$
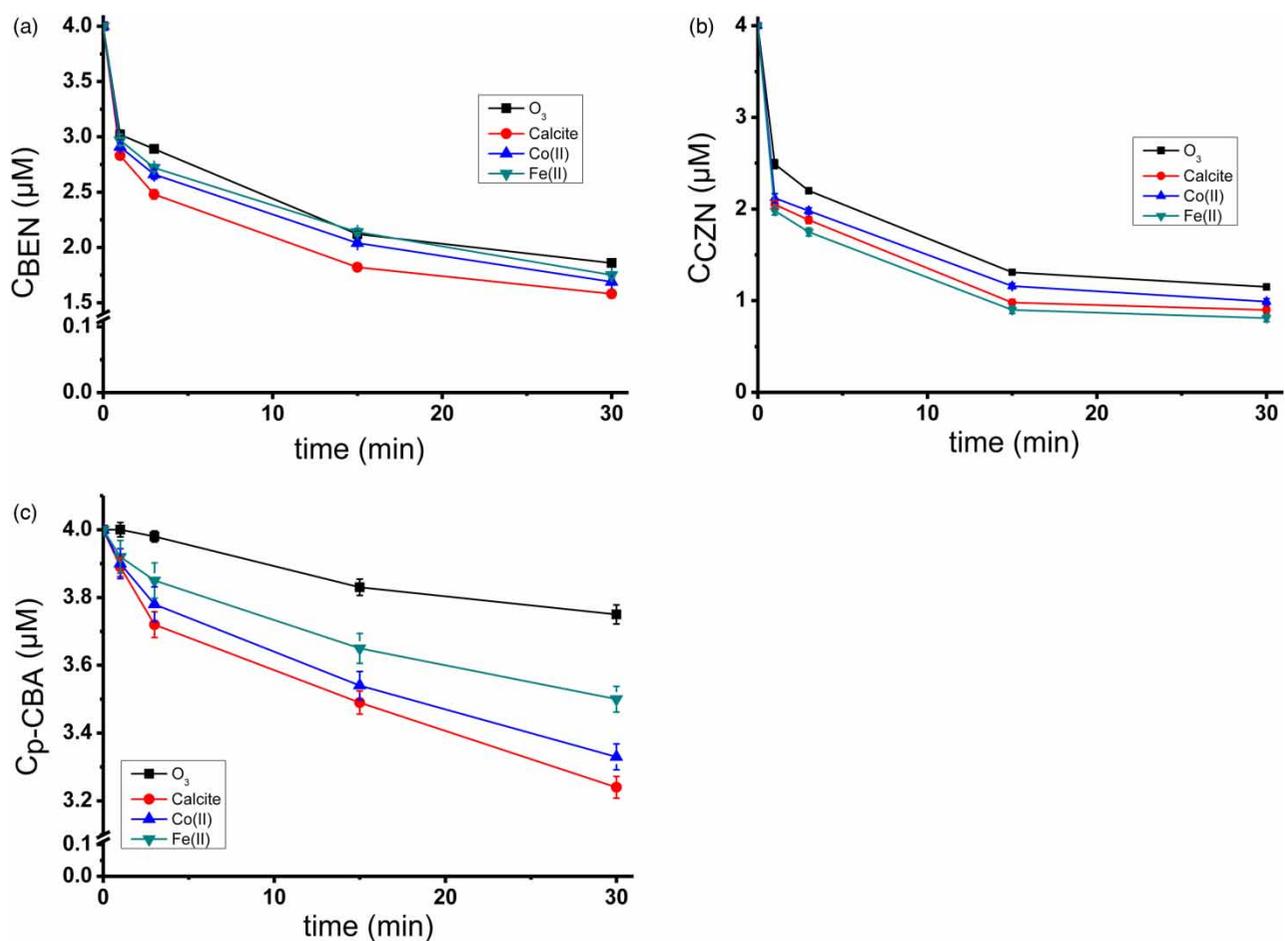
Figure 3 | Influence of TBA on the degradation of (a) benzotriazole, (b) carbamzepine, and (c) p-CBA by the application of catalytic ozonation in comparison to single ozonation. Experimental conditions: C_{O3} 2 mg/L, C_{MP} 4 μM, $C_{calcite.}$ 0.5 g/L, $C_{metal.\ ions}$ 1 mg/L, TBA 0.3 mM, pH 7, T 23 ± 2 °C. (Data are the averages of the values obtained in independent experiments conducted in triplicate and the error bars represent the standard deviation.)

This reaction is very fast and exothermic. The reaction rate constant of ozone with hydroxyl radicals is equal to 3×10^9 M^{-1}s^{-1}. In the absence of a scavenger, the reaction turns into a chain reaction in which ozone is decomposed towards O_2. Therefore, the addition of TBA increases the stability of ozone in aqueous solutions (von Sonntag & von Gunten 2012). In the present study, TBA slowed down the decomposition of ozone and the production of $^\cdot$OH was rather limited and quenched by its presence. However, carbamazepine and benzotriazole, presenting reaction rate constants with ozone equal to 3×10^5 M^{-1}s^{-1} and 20 M^{-1}s^{-1}, respectively, are capable of reacting with ozone molecules and be degraded by them. Therefore, in the presence of TBA, the removal efficiency of ozonation systems was mainly due to the oxidative action of ozone (see also Table 4). In the O_3/calcite + TBA system the removal efficiency of carbamazepine reached 79.8% after 30 min of the oxidation process, while under the same conditions the removal efficiency of benzotriazole was 60.5% (Figure 3(a)).

However, in the absence of TBA the decomposition of ozone is determined by the target compound, as Supplementary Material, Figure S4 shows. When the p-CBA is added to the system, the decomposition of ozone becomes much slower and 30 min are needed for the ozone concentration to be under 0.1 mg/L, while in the case of benzotriazole and carbamazepine, the decomposition of ozone is occurring during 15 and 1 min, respectively. Therefore, the removal efficiency is largely based on the respective ozone decomposition capacity. The addition of catalyst can enhance to some extent the ozone decomposition and accelerate the production of $^\cdot$OH, but did not change ozone decomposition profile. Table 3 shows the duration for the termination of ozone decomposition, according to the target compound.

The R$_{ct}$ concept

The R$_{ct}$ parameter allows the quantitative comparison of ozonation efficiency in the respective oxidation systems, considering the ozone transformation into the more powerful hydroxyl radicals. This was calculated by using the model of Elovitz & von Gunten (1999) (Equations (3)–(6)). Higher values of R$_{ct}$ indicate that a greater fraction of ozone is converted into $^\cdot$OH:

$$\frac{-d[p-CBA]}{dt} = k_{\bullet OH\,p-CBA} * [p-CBA][\bullet OH] \tag{3}$$

$$ln\left(\frac{[p-CBA]_t}{[p-CBA]_0}\right) = -k_{\bullet OH\,p-CBA} * R_{ct} \int [O_3 dt] \tag{4}$$

$$R_{ct} = \frac{\int [\bullet OH]dt}{\int [O_3]dt} \tag{5}$$

From Equation (4) a straight line was obtained (Supplementary Material, Figure S6) and the R$_{ct}$ value is calculated from its slope. In addition, once the R$_{ct}$ value was calculated, the fraction of a micropollutant (M) when degraded by $^\cdot$OH can also be estimated by the f$_{OH}$ parameter, which can be calculated from the application of Equation (6) (Guzman-Perez et al. 2011):

$$f_{\bullet OH} = \frac{k_{\bullet OH}[\bullet OH][M]}{k_{O3}[O_3][M] + k_{\bullet OH}[\bullet OH][M]} = \frac{k_{\bullet OH}R_{ct}}{k_{O3}R_{ct} + k_{O3}} \tag{6}$$

Table 3 | Ozone decomposition[a] duration, according to each target compound; experimental conditions: C_{O3} 2 mg/L, C_{MP} 4 μM, $C_{cal.}$ 0.5 g/L, $C_{metal\ ions}$ 1 mg/L, TBA 0.3 mM, pH 7, T 23 $\pm$ 2 °C

	Duration of ozone decomposition (h)			
Target pollutant	Single ozonation	Calcite	Co(II)	Fe(II)
Benzotriazole	0.50	0.33	0.33	0.33
Benzotriazole + TBA	2.9	1.8	2.1	2.1
Carbamazepine	0.03	0.03	0.03	0.03
Carbamazepine + TBA	2.6	1.8	2.1	2.1
p-CBA	0.67	0.5	0.58	0.58
p-CBA + TBA	3.7	3.5	3.5	3.7

[a]Below detection limit of 0.01 mg O_3/L.

Table 4 shows that calcite and Co(II) present higher R_{ct} values independently from the examined micropollutant. However, for the case of carbamazepine, the R_{ct} and f·OH could not be calculated in the absence of TBA due to the very fast reaction occurring for this micropollutant with the oxidative agents of ozonation systems. Calcite presented the highest R_{ct} values, proving to be the optimum catalyst of this study, which can convert ozone in a higher degree into its more oxidative by-product, i.e., the hydroxyl radicals. The addition of TBA stabilized ozone molecules and the decrease in R_{ct} parameter corresponds to the reduction of ozonation systems' efficiency, proving that the removal of all examined micropollutants is mainly based on radical mechanism. Meanwhile, the ozonation systems of benzotriazole presented a specific R_{ct} value, similarly to the observations of other researchers (Sánchez-Polo *et al.* 2006; Guzman-Perez *et al.* 2011), while in the case of p-CBA, the oxidation reaction consists of two stages therefore presenting for the relevant catalytic system two R_{ct} values. The first, which was the faster stage occurring with higher hydroxyl radicals' participation, lasted around 2 min (1–3 min), while the second stage lasted until the end of the oxidation reaction (i.e., at 30 min). In the catalytic system of calcite only the first stage can be calculated, due to its higher oxidation efficiency, resulting in the removal of p-CBA even from the first minutes of the reaction. Similar observations were also reported by Aghaeinejad-Meybodi *et al.* (2021) regarding the catalytic ozonation of fluoxetine.

The f$_{OH}$ parameter is another factor that can help the evaluation of hydroxyl radicals' participation in the oxidation systems. From Table 4 it becomes obvious that p-CBA is a molecule that practically can be only removed by hydroxyl radicals, even in the presence of TBA. The lower f·OH value was observed in the single ozonation system and was equal to 0.9. The presence of hydroxyl radicals is very important also for the removal of benzotriazole. The major part of micropollutant reacted and was degraded by them, while the contribution of ozone molecules for oxidation purposes was rather small. However, when TBA was introduced into the ozonation systems turning ozone into the dominant species, the contribution of oxidative agents was reversed. The highest f·OH value in this case was 0.4 and observed for the O_3/calcite system. The presence of ozone is very important for the oxidation of carbamazepine. When TBA was introduced into the system the oxidation of this micropollutant took place almost entirely by the ozone molecules in the single, as well as in the catalytic ozonation systems.

The kinetic models of micropollutants removal

In the relevant literature, several kinetic models have been proposed for the removal of micropollutants by the application of catalytic ozonation (Yong *et al.* 2005; Sumegová *et al.* 2013; Chen *et al.* 2018). However, the variety of the examined micropollutants, catalysts, and experimental conditions makes difficult the comparisons between these studies and the extraction of generalized conclusions. The kinetic study performed in this research, regarding the removal of micropollutants by the use of

Table 4 | R_{ct} and f·OH values of micropollutants' removal during the application of single and catalytic ozonation in the absence or presence of TBA Experimental conditions: C_{O3} 2 mg/L, C_{MP} 4 μ*M*, $C_{cal.}$ 0.5 g/L, $C_{metal\ ions}$ 1 mg/L, C_{TBA} 0.3 mM, pH 7, T 23 ± 2 °C

Micropollutant	Catalyst	In the absence of TBA		In the presence of TBA	
		R_{ct}	f·$_{OH}$	$R_{ct}(\times 10^{-9})$	f·$_{OH}$
Benzotriazole	/	9.9×10^{-8}	0.974	1.7	0.390
	Calcite	10.7×10^{-8}	0.976	1.8	0.400
	Co(II)	10.4×10^{-8}	0.975	1.6	0.380
	Fe(II)	9.1×10^{-8}	0.972	1.5	0.360
Carbamazepine	/	/	/	1.8	$5.4*10^{-5}$
	Calcite	/	/	2.6	$7.7*10^{-5}$
	Co(II)	/	/	2.2	$6.5*10^{-5}$
	Fe(II)	/	/	2.2	$6.5*10^{-5}$
p-CBA	/	4.4×10^{-8} (1–3 min)	0.999	0.3	0.900
		3.4×10^{-9} (3–30 min)	0.991	0.3	0.900
	Calcite	5.6×10^{-8} (1–3 min)	0.999	0.7	0.959
	Co(II)	5.3×10^{-8} (1 × 3 min)	0.999	0.5	0.955
		9.0×10^{-9} (3–30 min)	0.994	0.5	0.955
	Fe(II)	4.8×10^{-8} (1–3 min)	0.999	0.6	0.941
		4.6×10^{-9} (3–30 min)	0.997	0.6	0.941

calcite, Co(II), and Fe(II) as potential catalysts, revealed that the best-fitted kinetic models are dependent on the examined micropollutant (see also Supplementary Material, Text S2). Sumegová *et al.* (2013) observed that in the removal of methylene blue the order of the applicable kinetic model was changed according to the used catalyst. The removal of the pollutant followed first order kinetic model in the single ozonation and in the catalytic ozonation using granular activated carbon (GAC) as catalyst, while with the addition of zeolite the oxidation systems was in best agreement with the second order kinetic model. However, no adsorption experiments were conducted to confirm whether GAC did act also (or not) as an adsorbent, or simply as an oxidizing agent.

In the present study, benzotriazole is in good agreement with the first order kinetic model, while in the case of p-CBA the kinetic order, regarding its degradation, is more complex. When calcite or Co(II) are used as catalysts, the p-CBA abatement showed good correlation with the second order kinetic model. On the other hand, when Fe(II) was used as catalyst, and for the application of single ozonation process, the p-CBA removal was in best agreement with the pseudo-second order kinetic model. The kinetic model of carbamazepine cannot be plotted, due to the fast degradation of this micropollutant.

The first order kinetic model is applied in the oxidation reactions, where the rate is based on the concentration of one reagent (Stavropoulos 2014). This model leads to the conclusion that benzotriazole, due to the excess concentration of ozone, was removed quickly (Table 3) and almost entirely by the hydroxyl radicals (Table 4), according to the oxidation reactions, taking place in the bulk solution. From the calculation of the respective reaction rate constants, it is obvious that calcite, presenting a reaction rate constant equal to $0.020 \, s^{-1}$ (Supplementary Material, Figure S7), is the optimum catalyst for the removal of benzotriazole, while Fe(II) cannot be considered as catalyst in this case. The second order kinetic model refers to the removal of contaminants, based upon the physicochemical interactions between the existing phases that can share or exchange electrons, and the controlling step in this case is the velocity of respective chemical reaction (Ferreiro *et al.* 2019; AlGburi *et al.* 2020). In particular, the pseudo-second order kinetic model is usually valid for the treatment systems presenting rather low initial concentrations of the examined pollutants, as well as low removal rate efficiencies of them. In these systems there is an equilibrium concentration representing their removal limit (Stavropoulos 2014). The equilibrium concentration of p-CBA, when Fe(II) was used as catalyst, was 0.11 µM, while in the single ozonation system it was 0.14 µM (Supplementary Material, Table S3) and they were both achieved after the application of 30 min reaction/oxidation time. Therefore, the catalytic process of p-CBA removal (i.e., by the O_3/calcite and O_3/Co(II) systems), presenting high removal rates for p-CBA was in best agreement with the second order kinetic model, whereas in the case of non-catalytic processes they present a removal limit and showed good correlation with the pseudo-second order kinetic model (Supplementary Material, Table S5). The second order models revealed that, unlike benzotriazole, the p-CBA is assisted by the interactions occurring in the catalyst surface, regarding its oxidation by the hydroxyl radicals.

In the experiments performed to elucidate the mechanism, where TBA was added to quench the hydroxyl radicals produced from the decomposition of ozone, all the kinetic constants of micropollutants' degradation present good correlation with the pseudo-second order kinetic model (Supplementary Material, Table S4), because the addition of TBA stabilizes ozone molecules and quenched the production of hydroxyl radicals, hence increasing the duration of ozone decomposition, as Table 3 shows. The inhibition of the catalytic effect can lead to a removal limit which can be calculated by the pseudo-second order kinetic model. The increase of the oxidation duration and the participation of both ozone and hydroxyl radicals can lead to reactions both in the bulk solutions and solids' surface. The kinetic values of the respective models (as extracted from the plots of Supplementary Material, Figure S8) for the application of single ozonation and of catalytic ozonation in the presence of calcite, Co(II), and Fe(II), are presented in Table 5. The kinetic constants independently from the target compound and the kind or the presence of catalysts in the ozonation systems were almost equal. This indicates that the degradation of examined micropollutants (benzotriazole, carbamazepine, and p-CBA) follows the mechanism of radicals' production and the hydroxyl radicals' absence can decrease in large extent the respective oxidation rates. The kinetic models that have been calculated from experiments conducted under the same experimental conditions are most affected by the target-compound and the way that this can influence ozone decomposition, rather than the nature of the catalyst.

CONCLUSIONS

The efficiency of calcite as catalyst during the heterogeneous catalytic ozonation process was evaluated by applying different experimental conditions. It was found that this mineral can act as catalyst (enhancing the production of ˙OH) in the pH, temperature, and ozone concentration ranges 6–8, 15–35 °C, and 1–3 mg/L, respectively. Calcite was found capable of increasing

Table 5 | Kinetic models of micropollutants' degradation during the application of single or of catalytic ozonation in the absence/presence of TBA

		In the absence of TBA	In the presence of TBA
Micropollutant	**Catalyst**	**1st order kinetic constant (s^{-1})**	**Pseudo-2nd order kinetic constant ($\times 10^{-6}$ M^{-1}s^{-1})**
Benzotriazole	/	0.017	0.014
	Calcite	0.020	0.017
	Co(II)	0.022	0.013
	Fe(II)	0.018	0.013
Micropollutant	**Catalyst**	**2nd order kinetic constant ($\times 10^{-6}$ M^{-1}s^{-1})**	**Pseudo-2nd order kinetic constant ($\times 10^{-6}$ M^{-1}s^{-1})**
Carbamazepine	/	/	0.018
	Calcite	/	0.024
	Co(II)	/	0.024
	Fe(II)	/	0.019
p-CBA	Calcite	0.076	0.018
	Co(II)	0.018	0.019
Micropollutant	**Catalyst**	**Pseudo-2nd order kinetic constant ($\times 10^{-6}$ M^{-1}s^{-1})**	**Pseudo-2nd order kinetic constant ($\times 10^{-6}$ M^{-1}s^{-1})**
p-CBA	/	0.153	0.040
	Fe(II)	0.157	0.025

Experimental conditions: C_{O3} 2 mg/L, C_{MP} 4 µM, $C_{cal.}$ 0.5 g/L, $C_{metal\ ions}$ 1 mg/L, C_{TBA} 0.3 mM, pH 7, T 23 ± 2 °C.

the degradation rate of all the examined micropollutants (benzotriazole, carbamazepine, p-CBA), as compared to the application of single ozonation and it is a more efficient catalyst than the Co(II) and Fe(II) (examined as homogeneous catalysts). However, the removal efficiency of calcite, regarding the different micropollutants, depended on the specific physicochemical properties of examined organic compounds. Carbamazepine, presenting 3×10^5 M^{-1}s^{-1} reaction rate constant with ozone, is a highly ozone-reactive micropollutant and it can be easily removed, regardless the presence of catalyst, in the ozonation system, while from the f.OH the high contribution of ozone in its degradation was confirmed. Benzotriazole is a moderately ozone-reactive compound ($k_{O3} = 20$ M^{-1}s^{-1}) which can be degraded by the application of both single and catalytic ozonation, due to the oxidative action of the hydroxyl radicals. However, the catalytic ozonation decreased the required removal time. On the other hand, p-CBA is an ozone-resistant organic compound and its concentration cannot be eliminated by the application of single ozonation, as in the previous cases of carbamazepine and benzotriazole. However, p-CBA, presenting a reaction rate constant with the hydroxyl radicals equal to 5×10^9 M^{-1}s^{-1}, was efficiently removed by the acceleration of hydroxyl radicals' production, due to the addition of catalysts. The kinetic model regarding the removal of organic compounds is dependent on the examined micropollutant. Benzotriazole is in best agreement with the first order kinetic model, presenting a constant R_{ct} value during its reaction. On the contrary, the p-CBA is in best agreement with the second order kinetic model, when calcite and Co(II) were used as catalysts, whereas it presents optimum fit with the pseudo-secnd order kinetic model, when using the O_3 and O_3/Fe(II) treatment systems. Furthermore, p-CBA independently of the catalytic system presented a two-stage reaction, one faster than the other, as two different R_{ct} values were observed during its oxidative reaction.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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