Thermal Treated Zeolite as Catalyst in Heterogeneous Catalytic Ozonation – Optimization of Experimental Conditions and Micropollutant Degradation

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Abstract: Raw and thermally pre-treated zeolite, denoted as zeolite-T, were examined as catalysts in the heterogeneous catalytic ozonation process. Their catalytic activity was evaluated by the degradation of p-chlorobenzoic acid (p-CBA) at initial concentration 4 μM, a typical biorefractory organic model compound. The results showed that the thermally pre-treated zeolite presented higher catalytic activity, than the raw material. Rates of 99.3%, 98% and 94.5% degradation of p-CBA were achieved within 3 min of reaction/oxidation time, by applying the zeolite-T/O_3, the zeolite/O_3 and the single ozonation (O_3) procedures, respectively, under comparable experimental conditions. After 15 min treatment time the concentration of p-CBA was found to be below the respective detection limit (0.025 μM) of the used analytical method (HPLC) for both catalytic processes, while the application of single ozonation reached to 0.16 μM residual concentration of p-CBA. The removal of p-CBA was also examined for different initial pH values commonly found in natural waters, as well as for different oxidation reaction temperatures. As optimum conditions were defined the pH value 8 and 25^{o} C, during which the production of hydroxyl radicals in the aqueous phase were found to be increased. Furthermore, the degradation of two other common micropollutants (i.e. benzotriazole and carbamazepine), which present different reaction rate constants with ozone (i.e. 20 $M^{-1}s^{-1}$ and $3*10^5$ $M^{-1}s^{-1}$, respectively) was additionally evaluated. It was found that all these micropollutants can be sufficiently removed by the catalytic ozonation system in the presence of zeolite-T. However, it is worth noting that carbamazepine can be also easily removed by the application of even simple ozonation and that the presence of catalyst just decreased the respective necessary oxidation time for sufficient removal. On the other hand, benzotriazole presented a lower ozone degradation rate, than the other micropollutants and during the early stage (i.e. after the 3rd min) of the oxidation reaction it was found to be removed by 96.5%.

Keywords: catalytic ozonation; micropollutants; zeolite; water treatment

1. Introduction

In recent years the relevant research, regarding water quality, focused(among other issues) on the presence and removal of micropollutants (MPs). These organic compounds are occurring in the aquatic environment in very small concentrations (in the range of μg/L or even lower). However, currently and due to the global socioeconomic development, the variety of such substances was increased with potential harmful effects for the human health (food chain) and the overall ecosystem [1]. These substances are usually designed to be refractories (i.e. not easily biodegradable) and as a result the conventional wastewater treatment plants in most cases are not able to eliminate sufficiently them [2]. The respectively applied micropollutants' treatment technologies can be divided into three groups, i.e. phase-changing technologies, biological treatment and Advanced Oxidation Processes (AOPs) [1]. This study focuses on a common advanced oxidation process and particularly, on the heterogeneous catalytic ozonation treatment technique. The heterogeneous catalytic ozonation, utilizing several minerals as catalysts, has been previously reported to remove efficiently different emerging organic pollutants via the acceleration of hydroxyl radicals production [3]. Minerals, such as zeolite [4], anatase [5], kaolin [6] and calcite [7], are shown satisfactory performances as catalysts in this process.

The aim of this study was to accelerate the catalytic activity of a commonly applied zeolite catalyst by appropriate modification, applying the simple and inexpensive method of thermal treatment, and to optimize the experimental conditions of respective heterogeneous catalytic ozonation with the use of thermally treated zeolite as catalyst. For that purpose a compound that can be practically removed only by hydroxyl radicals (p-CBA), was used as probe compound [8]. As a result, the enhancement of this material catalytic activity was indirectly evaluated by accelerating the production of hydroxyl radicals through the improved removal efficiency of p-CBA. Furthermore, the removal of two other micropollutants (benzotriazole, carbamazepine) with different oxidation relevant properties was also evaluated.

2. Materials and Methods

Zeolite was used as an efficient catalyst during the application of heterogeneous catalytic ozonation before and after its thermal treatment at 600° C. All the used chemicals were of analytical grade, except acetonitrile and phosphoric acid, which was used for the micropollutants' determination by HPLC and were HPLC-grade. Benzotriazole and carbamazepine were purchased from Sigma-Aldrich (USA), while carbamazepine was purchased from HPC (Germany) and they were used as model compounds. Their main physicochemical properties were previously reported by Psaltou et. al. [7]. Dipotassium phosphate (K_2HPO_4) and potassium phosphate monobasic (KH_2PO_4) was used for pH adjustments, when needed. All the aqueous solutions were prepared with distilled/deionized water. Batch adsorption, ozonation and catalytic ozonation experiments were conducted by following the procedure previously described by Psaltou et. al.[12]. The concentration of ozone was determined by the application of indigo colorimetric method [13], while the concentration of micropollutants was determined by HPLC (Thermo, USA), according to the protocol also described by Psaltou et. al. [7].

3. Results

3.1. Zeolite as Catalyst in Heterogeneous Catalytic Ozonation and the Selection of Optimal Conditions

In this research zeolite was studied as potential catalyst before and after its thermal treatment at 600° C (abbreviated as zeolite-T) for the removal of p-CBA. Relevant adsorption experiments were conducted for comparison reasons to elimate the possibility of zeolite or of zeolite-T to be acted as adsorbents. Both of these materials showed rather low uptake capacity for p-CBA at pH 7. However, the thermally treated zeolite presented higher adsorption capacity than the raw material, i.e. 68.9 μg p-CBA/g vs. 59.5 μg p-CBA/g, respectively. Fig. 1a shows the results of ozone decomposition during single or catalytic ozonation, by using zeolite and zeolite-T as catalysts. The presence of both materials increased the decomposition of ozone, when compared to single ozonation, although they presented similar decomposition rates. On the contrary, the p-CBA removal presented certain differences (Fig. 1b). The addition of catalysts was found to improve p-CBA degradation, but the highest catalytic activity was presented by zeolite-T, which removed up to 97.5% of the micropollutant after 1st min of reaction/oxidation time. Although, the decomposition of ozone by zeolite-T was similar to untreated zeolite, the contact of micropollutant with the surface of zeolite-T was enhanced (due to higher adsorption capacity) and the efficiency of p-CBA degradation was overall improved.

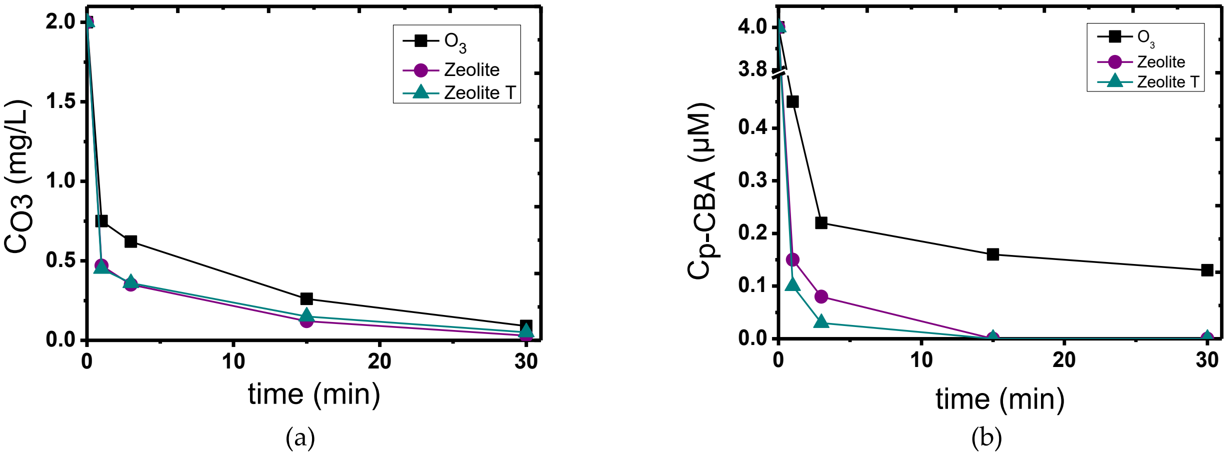


Figure 1. of single ozonation and of catalytic ozonationby using zeolite or zeolite-T as potential catalysts;(**a**) ozone decomposition; and (**b**) p-CBA degradation. Experimental conditions:$C_{p\text{-}CBA}$ 4 μM, C_{O_3} 2 mg/L, $C_{zeol.}$0.5 g/L, pH 7, Temprature 23±2° C.

The influence of experimental conditions was further studied with the qualified catalyst zeolite-T. The rate of ozone decomposition in the experimental conditions study can be divided into three categories according to the respective reaction rate constant. At pH 6 and 15° C ozone molecules are more stable [9] and hence, the decomposition rate of ozone was *low* (0.057 min^{-1} and 0.059 min^{-1}, respectively), while when the pH value or temperature raised to 8 and 35° C respectively, the ozone decomposition is favored and thus,it was significantly *higher*. In this study, in which three pH values and three temperature values were examined, the ozone decomposition at pH 7 and 25° C can be characterized as *moderate*. Table 1 shows the 1st order kinetic constants of ozone decomposition at different experimental conditions, when zeolite-T was added as catalyst in a heterogeneous catalytic ozonation system.

Table 1. 1st order kinetic constants of ozone decomposition under different experimental conditions using zeolite T as catalyst.

Conditions	k (min^{-1})
pH 6 and 25° C	0.057
pH 7 and 25° C	0.093
pH 8 and 25° C	0.252
15° C and pH 7	0.059
25° C and pH 7	0.093
35° C and pH 7	0.112

Since the initially examined micropollutant (p-CBA) cannot react directly with ozone molecules [8], it was not removed efficiently, when the ozone decomposition was low, as Fig.2 shows. However, when the pH value and the temperature were increased at 7 and 25° C respectively, then the micropollutant removal was increased and its residual concentration was 0.1 μM, even after the 1st min of oxidation reaction. When these two parameters increased further, the ozone decomposition was enhanced, but the p-CBA removal was not increased regarding both conditions change. At pH 8 the efficiency of oxidation system reached 98.3% after 1st min (residual concentration 0.068 μM), because the production of hydroxyl radicals was enhanced. However, at 35° C although the ozone decomposition was promoted, the ozone dissolution in the aqueous phase was simultaneously reduced [9]. Therefore, less oxidant was available in the ozonation system and this is probably the reason why the respective kinetic constant in this case was only 0.112 min^{-1}.

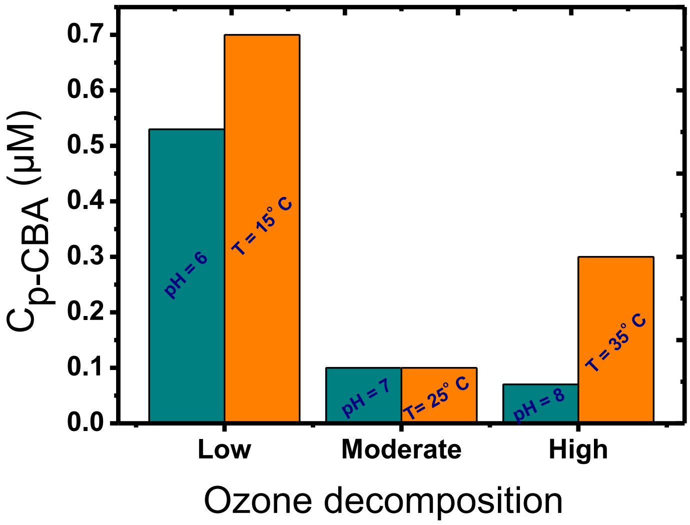
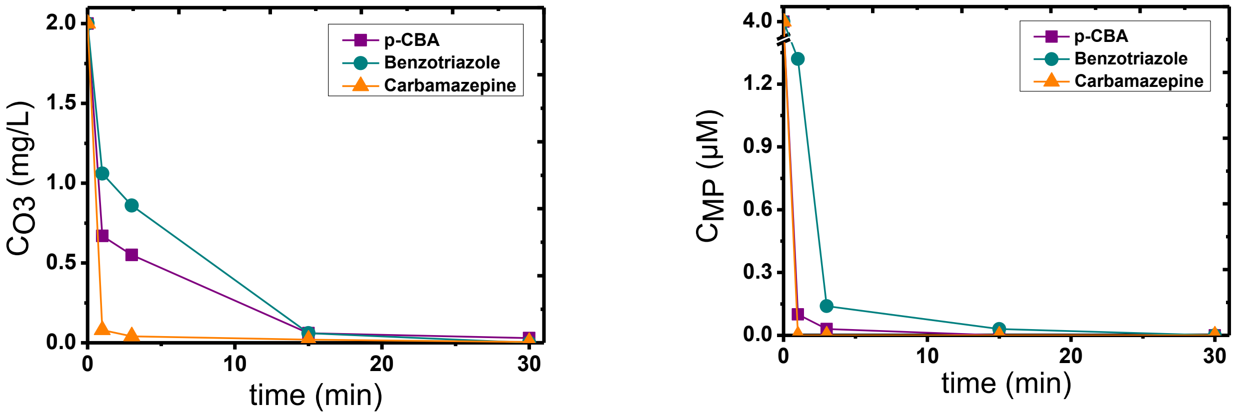


Figure 2. Influence of ozone decomposition rate during the removal of p-CBA, by using zeolite-T as catalyst. Experimental conditions:$C_{p\text{-}CBA}$ 4 μM, C_{O_3} 2 mg/L, $C_{zeol.}$ 0.5 g/L, reaction (oxidation) time 1 min.

3.2. Removal of Micropollutants by Catalytic Ozonation with the Addition of Zeolite-T

Fig.3 shows the evaluation of catalytic activity of zeolite-T against other common micropollutants, presenting different properties at 25° C. Due to the fact that the catalytic activity of zeolite-T is very high, even at pH 7, the micropollutants removal study was conducted at this pH value in order to detect any differences and not at pH 8, which was the optimum pH value. At pH 8 the micropollutants removal would be too fast and the differences in removal rates may not have been observed. Based on a relevant previous study [7] the removal of benzotriazole, carbamazepine and p-CBA, examined under the same experimental conditions was 66.3%, 97.3% and 88.8% at 1st min of single ozonation. As Fig. 3b shows, these removal rates were increased up to 67%, 100% and 97.5%, respectively, with the addition of zeolite-T in the ozonation system. Carbamazepine presents reaction rate constant with ozone equal to $3*10^5$ $M^{-1}s^{-1}$ [10] and reacts fast with the O_3 molecules; therefore, this compound can be easily removed even by the application of single ozonation. However, the addition of zeolite-T was found to reduce the respective oxidation time. Under these experimental conditions, the residual concentration of carbamazepine was under 5.9 μg/L even after the 1st min of the reaction. Furthermore, zeolite - cannot be characterized as an effective adsorbent, since it presents low adsorption capacity also against benzotriazole (114 μg/g) and carbamazepine (217 μg/g), which corresponds to 12% and 11.5% removal, respectively by applying only the adsorption process. Consequently, zeolite-T proved to be an efficient catalyst for the removal of all three examined micropollutants.



(a) (b)

Figure 3. of micropollutants during heterogeneous catalytic ozonationby using Zeolite-T as catalyst; (**a**) ozone decomposition, and (**b**) micropollutants removal. Experimental conditions:C_{MP} 4 μM, C_{O_3} 2 mg/L, $C_{zeol.}$0.5 g/L, pH 7, Temperature 23±2° C.

4. Discussion

The thermal treatment at 600° C was found to increase the catalytic activity of raw zeolite. Since p-CBA ozone reaction rate constant was lower than 0.15 $M^{-1}s^{-1}$ the examined ("model") compound cannot practically removed by oxidation with ozone molecules. The main oxidative species in an ozonation system is the (secondary) production of hydroxyl radicals. These species can react fast and unselectively with the present organic molecules. The reaction rate constant of p-CBA with the hydroxyl radicals is $5*10^9$ $M^{-1}s^{-1}$. Thus, the observed increase of p-CBA removal is corresponding to an increase of hydroxyl radicals production.

The two main factors that can influence decomposition of ozone are the pH value and the temperature. Ozone decomposition in aqueous phases is depeding highly upon the present pH value. The kinetic constant of ozone degradation for pH values under 8 is $1.4*10^5$ s^{-1}, while this value increases to 10^8 s^{-1}, when the pH value is equal or higher than 8 [11]. Since the degradation of p-CBA is accelerated by the higher production of hydroxyl radicals, the presence of catalyst further improved the oxidation efficiency of the treatment system. This improvement was more pronounced at the pH value 7, in which the micropollutant residual concentration was just 30% lower after the 1st min of oxidation reaction, while during the progress of this reaction the obtained percentage was still kept rather low. Although the pH study proved that higher pH values can result in better oxidation efficiency, this is not the case regarding the investigation of temperature. As Fig.2b shows, the optimum removal of p-CBA was achieved at 25° C. At 15° C, similarly with the pH 6 case, ozone molecules are more stable and the degradation of ozone into hydroxyl radicals is rather small. This type of micropollutants, such as p-CBA, which practically cannot be degraded by ozone molecules, were found to present lower removal efficiencies under those conditions. Respectively, when the raising of temperature, the dissolution of ozone in the aqueous phase becomes lower and the oxidation action is decreasing [9].

The removal of micropollutants,presenting different properties and reaction rate constants with ozone and hydroxyl radicals, was examined by using zeolite-T as catalyst. In the case of benzotriazole the addition of the catalyst did not accelerates further its removal from the 1st min, due to the lower ozone degradation. As Fig. 3a shows the behavior of ozone decomposition is depending also on the specific target compound. p-CBA, probably because H_2O_2 is co-produced during the reaction [8], can accelerate the decomposition of ozone even after the 1st min of oxidation, similarly to carbamazepine, which presents high ozone reaction rate constant ($3*10^5$ $M^{-1}s^{-1}$) [10], while benzotriazole does not accelerate that decomposition in the 1st stage of the oxidation reaction. After the 1st min the ozone concentration in the system in the presence of benzotriazole was 1.06 mg/L, while at the same time this concentration in the case of p-CBA presence was 0.67 mg/L. This lower ozone degradation had as a result the lower removal efficiencies of benzotriazole during the early stage of the reaction, whereas after the 3rd min of reaction, 96.5% removal efficiency was achieved.

5. Conclusions

The thermal treatment proved to be a successive method to enhance the catalytic activity of a solid material, such as zeolite, when applied as catalyst to improve the efficiency of heterogeneous catalytic oxidation. The removal of p-CBA was increased by 33% and 78% in zeolite-T/O_3 system, as compared to untreated zeolite/O_3 and to the single ozonation processes, respectively. The optimum conditions for the removal of p-CBA were found to be pH 8 and 25° C. Zeolite-T can be also characterized as an efficient catalyst for the removal of benzotriazole and carbamazepine. The residual concentration of carbamazepine under the applied experimental conditions was under the respective analytical determination limit (0.025 μM), even after the 1st min of reaction, while at the same time the benzotriazole concentration was 1.32 μM. The low removal of benzotriazole after the 1st min of oxidation time was due to the slower ozone decomposition during the early stage of this oxidation reaction. The research revealed that the decomposition of ozone is depending not only on the pH value and on the temperature of the treatment system, but also on the specific type of examined micropollutant in the ozonation system.

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