

Article

The Effect of Thermal Treatment on the Physicochemical Properties of Minerals Applied to Heterogeneous Catalytic Ozonation

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Received: 30 October 2020; Accepted: 14 December 2020; Published: 15 December 2020



Abstract: In order to enhance the efficiency of heterogeneous catalytic ozonation, the effect of thermal treatment on three commonly used and inexpensive minerals, i.e., zeolite, talc and kaolin (clay), which present different physicochemical properties as potential catalysts, has been examined for the removal of para-chlorobenzoic acid (p-CBA). p-CBA is considered a typical micro-pollutant, usually serving as an indicator (model compound) to evaluate the production of hydroxyl radicals in ozonation systems. The catalytic activity of selected solid catalysts was studied for different pH values (6, 7 and 8) and different temperatures (15 °C, 25 °C and 35 °C). The mechanism of radicals' production was also verified by the addition of tert-butyl alcohol (TBA). The respective thermal behavior study showed that the point of zero charge (PZC) of these minerals increased with the increase of applied treatment temperature, as it removed crystalline water and hydroxyls, thus improving their hydrophobicity. Circa-neutral surface charge and the presence of hydrophobicity were found to favor the affinity of ozone with solid/catalytic surfaces and the subsequent production of hydroxyl radicals. Therefore, zeolite and talc, presenting PZC 7.2 and 6.5 respectively, showed higher catalytic activity after thermal treatment, while kaolin with PZC equal to 3.1 showed zero to moderate catalytic efficiency. The degradation level of p-CBA by oxidation was favored at 25 °C, while the pH value exerted positive effects when it was increased up to 8.

Keywords: heterogeneous catalytic ozonation; PZC; p-CBA; minerals; thermal treatment; micropollutants removal

1. Introduction

Nowadays, persistent organic compounds (POPs) are considered chemical compounds of great environmental concern [1]. Several classes of them occur in aquatic ecosystems [2] but with rather low concentrations, ranging from ng/L–μg/L (they are thus termed as micropollutants). They are very stable compounds and cannot be easily degraded or removed by the application of conventional biological wastewater treatment technologies [1]. Although their quantities are still quite low, they can constantly accumulate in fragile ecosystems, and there is a high probability of side effects in living organisms throughout the food chain [2]. Municipal wastewater treatment plants have been identified as one of the main sources of pollution from micropollutants. The treated wastewaters may contain several compounds of emerging concern, released into water bodies and eventually ending up in marine environments [3].

Among the available degradation techniques that have been examined for the removal/oxidation/destruction of micropollutants is the process of ozonation. This treatment method is based on the oxidation of organic compounds through the presence of ozone molecules, as well as through the secondary formation of hydroxyl radicals. Hydroxyl radicals are produced in this case by ozone self-decomposition and present higher oxidative potential than the application of single ozonation. Additionally, their ability to react unselectively with different organic molecules makes them an (almost) ideal oxidizing agent for Advanced Oxidation Processes (AOPs). However, in order to further increase the efficiency of this oxidation system, it is important to accelerate the production of hydroxyl radicals. The addition of an appropriate catalyst can enhance ozone decomposition, leading to a catalytic ozonation process, which is a promising treatment technique for the removal of refractory organic compounds, such as micropollutants, from water and wastewater sources. In heterogeneous catalytic ozonation, appropriate solid materials are commonly used as catalysts, improving hydroxyl radical's production [4].

In this procedure, the effective contact between ozone molecules and the catalyst surface is very important, and to some extent it can be estimated by the respective Point-of-Zero-Charge (PZC) of the solid material [5]. PZC is generally described as the pH, where the net charge of the particle surface is equal to zero [6]. The overall charge of hydroxyl groups on the surface of a solid is responsible for the adsorption and subsequent decomposition of ozone. Hydroxyl groups can be negatively, positively or even neutrally charged according to the relevant solution's pH [5]. Based on several publications, it has been concluded that the desired decomposition of ozone into hydroxyl radicals is favored when the material/catalyst surface is neutrally charged [5,7–12]. Due to its structure, the ozone molecule presents both nucleophilic and electrophilic properties. The (electrophilic) hydrogen atoms and the (nucleophilic) oxygen atoms of hydroxyl groups can simultaneously react with ozone molecules, creating a ring when the hydroxyls are in a natural state. However, this ring is unstable and can easily break down into superoxide radicals ($O_2^{\bullet-}$), hence promoting the production of hydroxyl radicals. When hydroxyl groups are positively or negatively charged, the interaction of the surface with ozone molecules decreases and mass transfer between them is inhibited [5].

Wang et al. [7] and Zhu et al. [8] prepared two different magnesium nano-oxides (nano-MgO) with point-of-zero-charge values 10.2 and 7.2, respectively, and used them as catalysts for the removal of phenol and quinolone via the application of a heterogeneous catalytic ozonation process. However, both solid materials showed similar behavior due to their degradation/dissolution in water during the process. The contribution of adsorption to the overall process can be considered as rather negligible. Higher catalytic activity was observed when the catalyst's surface was neutrally charged (i.e., at $pH=PZC$). In other relevant studies, pumice has been used as a catalyst, either as a raw material or after its modification. Its point-of-zero-charge was 6-7, either as pumice [9] or after iron silicate [10] or iron [11] deposition in its structure. These studies also concluded that at pH 6-7, pumice presented the best catalytic action because it was neutrally charged. Zhao et al. [12] also tested Cu-cordierite material for the removal of nitrobenzene by catalytic ozonation. Nitrobenzene is a compound that practically cannot be removed by oxidation with molecular ozone, similar to the p-CBA used in this study. Due to the fact that the PZC was 6.94, it exhibited the highest catalytic activity at circa-neutral pH value, where the surface of the catalyst was also neutrally charged.

Sui et al. [13] used ferric oxy-hydroxide ($FeOOH$) as a catalyst for the removal of oxalic acid, with the adsorption of this pollutant in the catalyst surface being rather negligible. This research differed because the ozone decomposition and the subsequent production of hydroxyl radicals were found to be enhanced in both the neutral and the positive state of the material, i.e., at neutral and acidic pHs, respectively ($PZC = 7.2$). Similar results were published by Kermani et al. [14] and Liu et al. [15]; in both cases, positively charged materials showed the highest catalytic activity. Huang et al. [16] claimed that the oxygen groups on the catalyst surface were coupled with bisphenol A via hydrogen bonds, and thus the degradation of ozone was promoted, resulting in increased system efficiency. Through this mechanism, the removal of this micropollutant was increased by increasing the pH value.

Furthermore, the hydrophobic molecules of ozone can be attracted by non-polar surfaces, and thus the contact between them is favored [17]. By enhancing the hydrophobic degree of a material, the respective contact can be improved, and the production of hydroxyl radicals can be accelerated. A possible way in which both hydrophobic behavior and point-of-zero-charge (PZC) can be simultaneously increased is the thermal treatment of a material. During thermal treatment, hydrophilic groups, such as hydroxyls, are gradually removed. However, at elevated temperatures (i.e., >900 °C), the surface becomes more hydrophilic due to the decrease in other hydrophobic components, such as in the case of talc siloxanes [18].

The objectives of this work were to study the effects of thermal treatment on the major physicochemical properties of selected natural minerals, acting as potential catalysts in the ozonation process. Subsequently, these properties were correlated with the respective catalytic activity regarding the oxidation of p-CBA by the application of heterogeneous catalytic ozonation. The effect of applied common experimental conditions on their catalytic activity was also investigated. p-CBA was selected as a typical model organic compound because it cannot practically react with ozone molecules ($k_{O_3} < 0.15 \text{ M}^{-1}\text{s}^{-1}$), and it can only be degraded by the presence of hydroxyl radicals ($k_{\bullet OH} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) [19]. Therefore, acceleration of their production can be indirectly estimated by the enhancement of p-CBA removal.

2. Materials and Methods

2.1. Materials

All the chemicals used in the experiments were of analytical grade. The acetonitrile and phosphoric acid used for p-CBA determination were HPLC-grade and purchased from Sigma-Aldrich (St. Louis, MO, USA). p-CBA was obtained from the same company, and it was used as a model compound at an initial concentration of 4 μM . All aqueous solutions were prepared in deionized water. For pH adjustment, K_2HPO_4 and KH_2PO_4 (Chem-Lab, Zedelgem, Belgium) were used for the preparation of a convenient buffer solution. All the examined solid materials/catalysts were commercially available, and they were pre-treated with ozone before the experiments. Zeolite (Clinoptilolite) from the Metaxades area (Alexandroupoli, Thrace region, Greece) and talc from the Arnissa area (Edessa, Macedonia region, Greece) were calcined at the temperatures 100 °C (zeolite-1, talc-1), 300 °C (zeolite-3, talc-3), 600 °C (zeolite-6, talc-6) and 800 °C (zeolite-8, talc-8), while kaolin (clay) from the Leukogia area (Drama, Macedonia region, Greece), which was used as a comparison measure, was only calcined at 600 °C and abbreviated as kaolin-6. Calcination was carried out by raising the temperature from room temperature up to 800 °C in 2 h, and then the materials were left to cool at room temperature.

2.2. Experimental Procedures

The ozonation experiments were performed in batch mode. O_3 was generated using a corona discharged O_3 generator (Ozonon-Triogen Model TOGC2A) with pure oxygen as the feed gas. The initial p-CBA concentration was 4 μM , and the pH values were adjusted between 6 and 8 with the addition of an appropriate amount of 0.005 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ buffer solution. The initial concentration of O_3 was 2 mg/L, based on preliminary experiments. Solid materials/potential catalysts (0.5 g/L) were introduced to the dark reaction vessel just before the addition of O_3 solution. The catalytic ozonation reaction time was 30 min for all the experiments, and appropriate samples were received during convenient reaction time intervals, i.e., 1, 3, 15 and 30 min; filtered through 0.45 μm membrane filters; and the residual concentrations of O_3 and p-CBA were determined. The oxidation reaction was stopped by the addition of an appropriate amount of indigo solution. Single ozonation experiments were conducted in the same way but without the addition of a solid/catalyst, while adsorption experiments were performed without the addition of O_3 . TBA was used as a scavenger to capture the $\bullet\text{OH}$ radicals. The dosage of tert-butyl alcohol (TBA) purchased from Sigma-Aldrich was 0.3 mM, calculated based on the equation proposed by Wang et al. [20].

2.3. Analytical Techniques

Ozone concentrations were determined by the Indigo method [21]. The color change of indigo solution was measured at 600 nm by a spectrometer (Lange, DR3900). The specific surface area of catalysts was calculated by nitrogen gas adsorption at liquid N₂ temperature (77 K) by using an ASAP2020 analyzer, according to the Brunauer–Emmet–Teller (BET) method. Point-of-zero-charge (PZC) values were determined by the immersion technique [22]. Aqueous solutions of NaNO₃ (0.1 M) with pH values ranging from 3 to 11 were prepared, and 0.25 g of the mineral was added to each solution. Suspensions were equilibrated for 24 h. The PZC value was identified as the pH value, where the pH of blank solution is equal to the pH of mineral suspension. A High-Performance Liquid Chromatography system (Thermo Fisher Scientific, Waltham, MA, USA, HPLC model of UV Spectrum UV2000) was used to determine the residual p-CBA concentration. An Agilent 4.6 × 250 mm reversed phase column (model Eclipse Plus C18) was used, and the compound was measured at 254 nm. The mobile phase consisted of acetonitrile and phosphoric acid (10 mM) in the ratio 40:60 v/v. The pH of solutions was measured by a pH meter (Jenway, Cole Palmer, UK, model 3540). The mineralogical transformations of thermally treated materials were determined by X-ray diffraction (XRD), using a D8 Advanced instrument (Bruker, Karlsruhe, Germany) operating at 40 mA and 40 kV with Cu radiation ($\lambda = 1.54$ nm), the detector LYNXEYE (1D mode) (Bruker Karlsruhe, Germany) were used. The data were collected in the 2θ range of 5–60°, with increments of 0.010° and a counting time of 0.1 s per step for talc and 0.2 s for zeolite materials. The rotation time was 15 per min for both materials. Thermogravimetric analysis and Differential Thermal Analysis (TG-DTA) were obtained simultaneously by using a Perkin Elmer (Waltham, MA, USA) STA 6000 Thermal Analyzer instrument. The samples were heated from 20 to 900 °C at a constant rate of 20 °C/min in a nitrogen atmosphere (flow 20 cm³/min). Regarding the chemical characterization of minerals, the total content of chemical components was determined by the application of flame atomic adsorption spectroscopy (Perkin Elmer, Waltham, MA, USA, model AAnalyst 800).

3. Results and Discussion

3.1. Catalysts Characterization

The first part of this study focuses on the effect of thermal treatment on the structure and major physicochemical characteristics of the examined minerals/potential catalysts for the heterogeneous catalytic oxidation process. Zeolite and talc were thermally treated at various temperatures up to 800 °C, while kaolin was only calcined at 600 °C. The respective specific surface area (S_{BET}) of the materials was rather low, e.g., 21 m²/g, 10.5 m²/g and 13 m²/g for zeolite, talc and kaolin, respectively, and their chemical compositions are shown in Table 1.

Table 1. Chemical composition of examined raw minerals.

Minerals	Chemical Composition (%)								mg/Kg	
	SiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	Fe ₂ O ₃	LOI	NiO	Cr ₂ O ₃
Zeolite	70.5	12.1	0.58	2.91	1.45	2.82	0.67	8.9 ^a	ND	ND
Talc	65.8	ND	28.6	0.01	0.01	0.04	0.73	4.6 ^b	1500	20
Kaolin	50.9	33.1	0.71	0.10	0.28	1.19	0.70	12.9 ^a	120	ND
Detection Limit	0.1	0.05	0.0005	0.004	0.001	0.002	0.01	0.1	100	50

^a: Determination at 900 °C as clarified by TG-DTA. ^b: Determination at 1200 °C, since the loss on ignition of talk is partial at 900 °C as verified by TG-DTA.

Generally, the mineral structure contains adsorbed and structural water molecules. Under the effect of thermal treatment, the water molecules are removed at different stages. Thermogravimetric Analysis (TGA) was used to monitor the respective weight loss of minerals with the increase in

temperature. The TGA diagram of zeolite (Figure 1a) shows continuous mass loss during heating up to 700 °C, due to the initial loss of hygroscopic water and the subsequent de-hydroxylation of the crystal lattice. These TGA results suggest that the surface chemistry of zeolite changes with thermal treatment. On the other hand, the diagram of talc (Figure 1b) shows that there was only a small weight loss due to the removal of adsorbed water molecules, even at the higher temperatures. According to Yi et al. [18], the de-hydroxylation of talc only occurs at temperatures higher than 900 °C, which were not part of the present study. The weight loss for talc up to 900 °C was only 1.3%, while in the same temperature range; zeolite lost 8.9% of its weight. This is evidence that in talc, no major structural modifications are occurring. During thermal treatment, both minerals only displayed an endothermic effect.

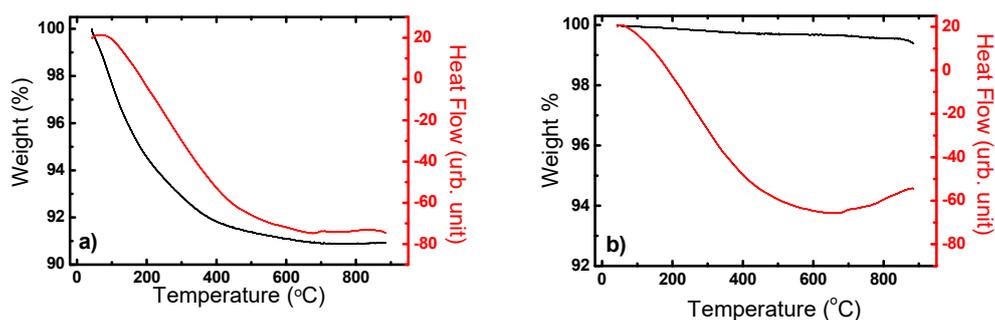


Figure 1. Analysis and Differential Thermal Analysis (TG-DTA) diagrams of (a) zeolite and (b) talc.

The XRD diagrams of raw materials, as well as of the thermally treated samples, are shown in Figure 2. Heating at 900 °C did not significantly affect talc's mineral structure. On the contrary, the zeolite material collapsed when heated at 600 °C, while at even higher temperatures it was transformed to poorly crystallized phases. Upon heating, zeolites undergo a series of chemical and structural changes until they are eventually largely converted to an amorphous material [23]. Similar observations have been reported by Christidis et al. [24], where a Greek zeolite collapses after heating at 450 °C. Clinoptilolite dehydrates at temperatures up to 300 °C and dehydroxylates at temperatures up to 800 °C, while at even higher temperatures, it decomposes and transforms into amorphous Al-Si and Si glasses [25]. Figure 2a shows the initial raw zeolite containing clinoptilolite (card PDF 01-089-7539) as its major crystalline phase, accompanied by orthoclase (card PDF 01-086-0437), anorthoclase (card PDF 01-075-1634) and quartz (card PDF 01-079-1910). The same structure was presented by the respective calcined material at 300 °C. When zeolite was thermally treated above 500 °C, the characteristic reflections/peaks of clinoptilolite disappeared entirely, and only those of orthoclase, anorthoclase and quartz remained. Figure 2b shows the XRD spectra of talc before and after thermal treatment at temperatures of 300 °C, 600 °C and 800 °C. The diffraction peaks, appearing at 9.44°, 18.97°, 28.60° and 48.79°, agree well with the crystal structure of talc, indicating that both the raw material and the thermally treated material used in this work were talc.

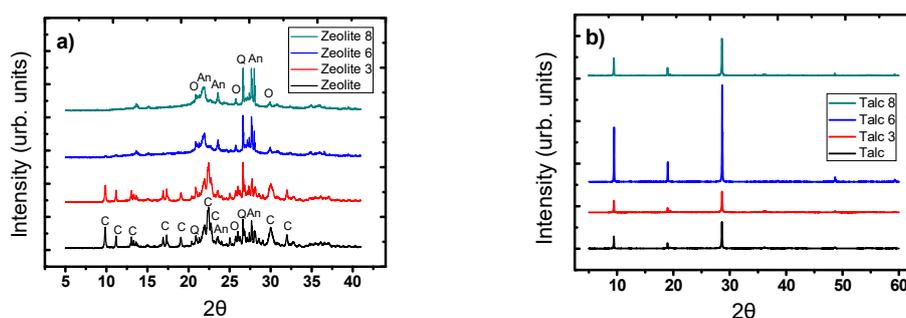


Figure 2. X-ray diffraction (XRD) patterns of raw materials and of thermally treated samples: (a) zeolite and (b) talc. Peaks for (a): C-clinoptilolite, O-orthoclase, An-anorthoclase, Q-quartz.

The surface charge of any solid material in a solution is based mainly on its PZC value. The PZC of raw kaolin was 3.1, and this value was unchanged up to the temperature of 100 °C. After that, there was an increase in the PZC value, probably due to dehydroxylation. At 800 °C, the PZC increased to 4.4, probably due to the formation of meta-kaolin, as Torres Sánchez and Tavani observed [6]. Its structural water began to be removed at 500 °C and completed at 600 °C, as verified by the weight loss in Supplementary Materials Figure S1. In the same temperature range, the PZC of kaolin increased sharply. The PZC of zeolite and of talc were also found to increase but to a lower extent. The PZC of raw zeolite and of talc were 6.8 and 5.9, and after calcination at 800 °C, they increased by 0.4 and 0.8 units, respectively. Changes to the values of PZC depend on the heating temperature of each material and are shown in Figure 3.

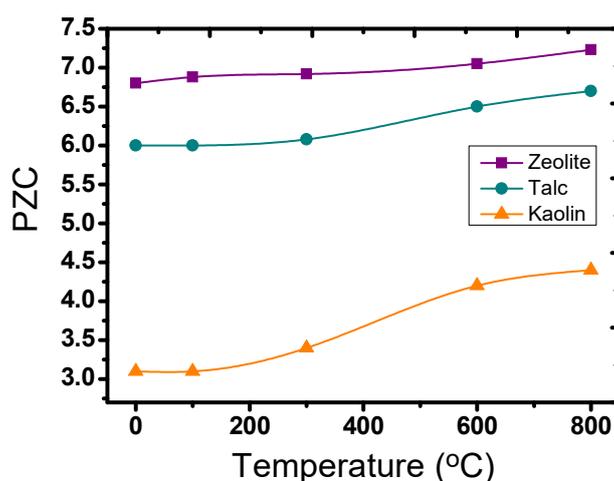


Figure 3. Point-of-zero-charge (PZC) of zeolite, talc and kaolin after calcination treatment in the temperature range 100–800 °C.

One of the main mechanisms regarding the formation of charges on the surface of an oxide in aqueous media is the sorption of metal hydrolytic complexes derived from the hydrolysis of solid material [26]. Therefore, the differences in PZC values in the experiments were provoked by the formation of these hydro-complexes on the surface of minerals. This is in accordance with the results of other relevant studies on several oxides [6,27]. Furthermore, Stanković et al. [28] have observed that the PZC of a hydrous oxide was found to depend more on the hydration degree than on the crystal structure of the oxide, and generally the PZC value shifts towards the alkaline pH region during the dehydration process.

3.2. Catalytic Activity of the Examined Natural Minerals

In this study, the catalytic activity of three natural minerals was investigated before and after their thermal treatment, regarding the application of heterogeneous catalytic ozonation for the destruction by oxidation of p-CBA. All these materials showed rather low uptake (adsorption) capacities independently of calcination temperature (Table S1). Therefore, none of them can be characterized as an efficient adsorbent material, at least for the examined micropollutant. The absorption capacity is illustrated in Figure 1 for the negative values of time.

The catalytic activity of these solids was evaluated through p-CBA removal efficiency in the ozonation process, and the obtained results of heterogeneous catalytic ozonation were compared with those of single ozonation application. The red, dashed line in Figure 4 and Figures 6–8 represents the p-CBA analytical detection limit. All these materials were found to enhance the decomposition of ozone when compared with single ozonation (Figure S2), but not all of them were found to present catalytic activity. Catalytic activity means the acceleration of p-CBA removal due to the enhancement of hydroxyl radical production. Raw zeolite and talc can be considered as catalysts, while kaolin,

neither before or after its calcination, was found to present any catalytic activity (Figure 4). Kaolin is a material with PZC 3.1. After thermal treatment, the PZC of kaolin increased to 4.7. Therefore, in both forms, it is a strongly negatively charged solid in the neutral pH range, where most of the experiments were performed. Ozone molecules tend to approach neutrally charged and non-polar surfaces more effectively, enhancing their decomposition into hydroxyl radicals when coming into contact [5,7–9,29]. Raw talc (with PZC 5.9) presents lower catalytic activity than talc-8, which has PZC equal to 6.5 and a more hydrophobic surface. The catalytic activity of neutrally charged raw zeolite was enhanced through the application of thermal treatment, because the PZC and the hydrophobicity of the material increased. The best relevant performance was presented by the zeolite-8, where the efficiency of treatment process was 98.5% even from the first min of reaction/oxidation time. All zeolites showed higher catalytic activity even than talc-8 because they were neutrally charged, while talc-8 with PZC 6.5 was slightly negatively charged throughout the oxidation process. However, among the talc materials, talc-8 was optimum and removed 95.5% of p-CBA, even from the first min of oxidation.

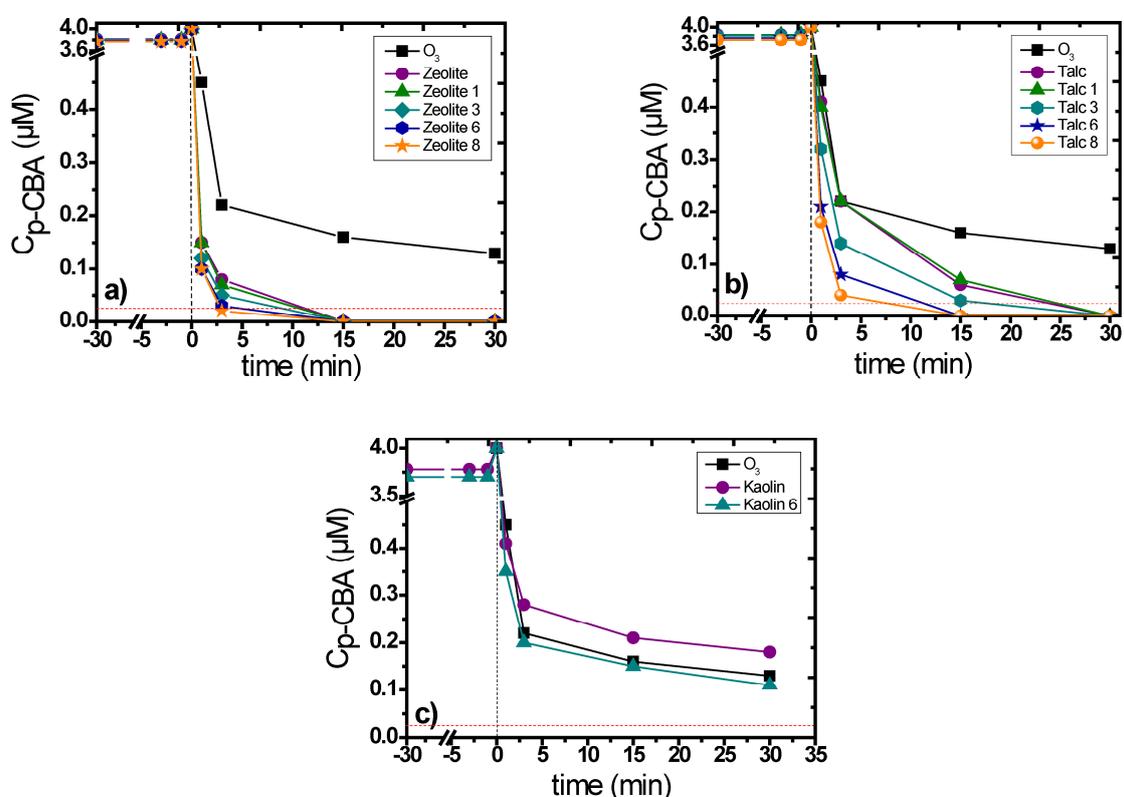


Figure 4. Effect of calcination temperature on the catalytic activity of examined natural minerals: (a) zeolite, (b) talc, and (c) kaolin; experimental conditions: C_{p-CBA} 4 μM , C_{O_3} 2 mg/L, C_{cat} 0.5 g/L, pH 7, temperature 23 ± 2 °C.

The high correlation between PZC values and the efficiency of the heterogeneous catalytic ozonation process is shown in Figure 5 for the cases of thermally treated zeolite and talc. An almost linear response was observed between PZC values and their respective catalytic ozonation efficiency. Correlation was performed considering the values from the first min of reaction/oxidation time because differences in respective performances at that early oxidation time were more pronounced. The difference in the efficiency between talc and talc-8 was higher when compared with relevant observations in the case of zeolite, because the increase of the PZC value was greater for talc (Figure 3).

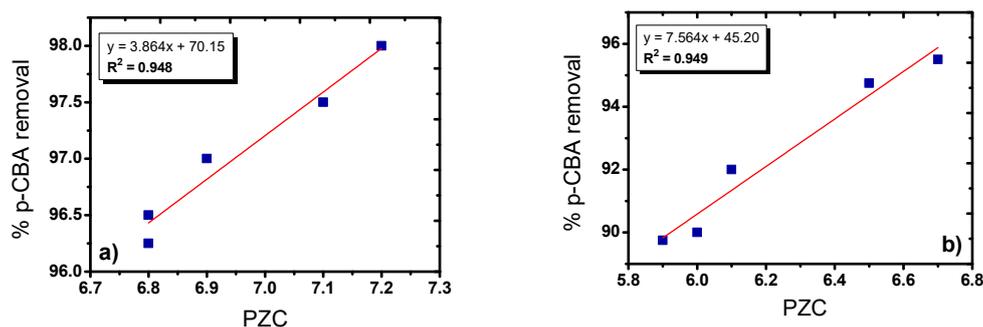


Figure 5. Correlation between PZC values (as obtained from raw and thermally treated mineral samples) and the respective catalytic efficiency calcinated materials, considering the first min of reaction/oxidation: (a) zeolite and (b) talc; experimental conditions: C_{p-CBA} 4 μM , C_{O_3} 2 mg/L, C_{cat} 0.5 g/L, pH 7, temperature 23 ± 2 °C.

In addition to removing/oxidizing p-CBA, other evidence that the catalytic ozonation process was based on the formation of the radicals' mechanism was the efficiency of the system in the presence of TBA. TBA is a known hydroxyl radical scavenger with a high reaction rate constant with hydroxyl radicals equal to $5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ [20]. Figure 6 shows the efficiency of single and catalytic ozonation in the absence and presence of TBA, when zeolite-6 and talc-6 were used as catalysts. When TBA was added to the treatment system, the removal of p-CBA was 6.3%, 12.5% and 9.5% with the application of single ozonation or by the addition of zeolite and talc, respectively, after 30 min of oxidation time. The inhibition effect within the first 3 min of the relevant scavenging reaction was estimated at 94.5%, 99.3% and 99.5%, respectively. The presence of TBA also reduced the decomposition of ozone in all oxidation reactions (Figure S3). It is also worth noting that the application of higher ozone concentrations could not be beneficial in the relevant systems because ozone does not practically react with p-CBA ($k_{O_3} < 0.15 \text{ M}^{-1}\text{s}^{-1}$) [19].

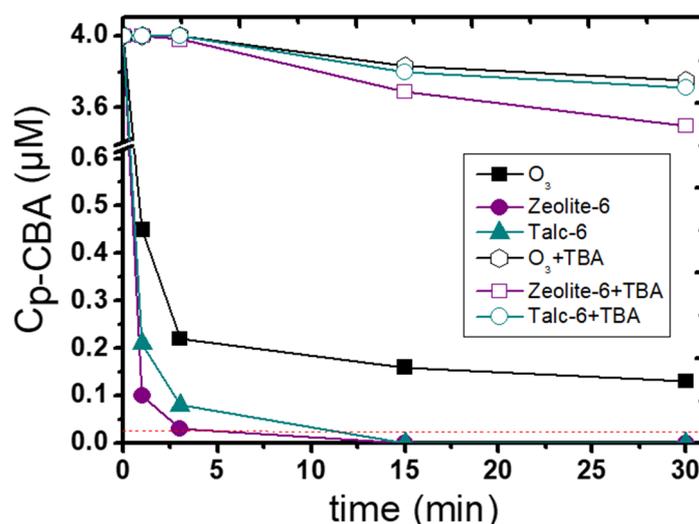


Figure 6. Effect of tert-butyl alcohol (TBA) in the removal of p-CBA during the application of single and catalytic ozonation processes; experimental conditions: C_{p-CBA} 4 μM , C_{TBA} 0.4 mM, C_{O_3} 2 mg/L, C_{cat} 0.5 g/L, pH 7, temperature 23 ± 2 °C.

3.3. Influence of the Main Experimental Parameters on the Removal of p-CBA

There are several factors that can affect the efficiency of the heterogeneous catalytic ozonation process. The most important among them are pH and temperature, which influence the stability of ozone in water [4]. The influence of experimental conditions was studied for the examined materials,

especially in the cases of zeolite-6 and talc-6, calcined at 600 °C. The difference in the respective efficiencies between materials calcined at temperatures 600 °C and 800 °C was rather negligible. Also, the moderate calcination temperature of 600 °C is more practically feasible and less costly.

pH value is a very important aspect of the ozonation process because it highly influences the ozone decomposition and the subsequent production of hydroxyl radicals. As the pH raises, the decomposition of ozone accelerates (Figure S4). Figure 7 shows p-CBA removal when zeolite-6 and talc-6 were added to the system as catalysts for pH values 6, 7 and 8. As expected, higher pollutant degradation was observed at pH 8, independently of the catalyst that was added to the oxidation system. At pH 8, p-CBA was almost totally removed, already within the third min of oxidation time. In contrast, at pH 6 and for the same time (third min) the p-CBA removal was 91.7% and 93% for zeolite-6 and talc-6, respectively. Less efficiency at this (slightly acidic) pH value could be attributed to the lower production of hydroxyl radicals, since p-CBA cannot practically react with ozone molecules, only hydroxyl radicals. Neutrally charged talc and slightly negatively charged zeolite were found to degrade p-CBA almost entirely after 15 min of reaction/oxidation time in pH range 6–8.

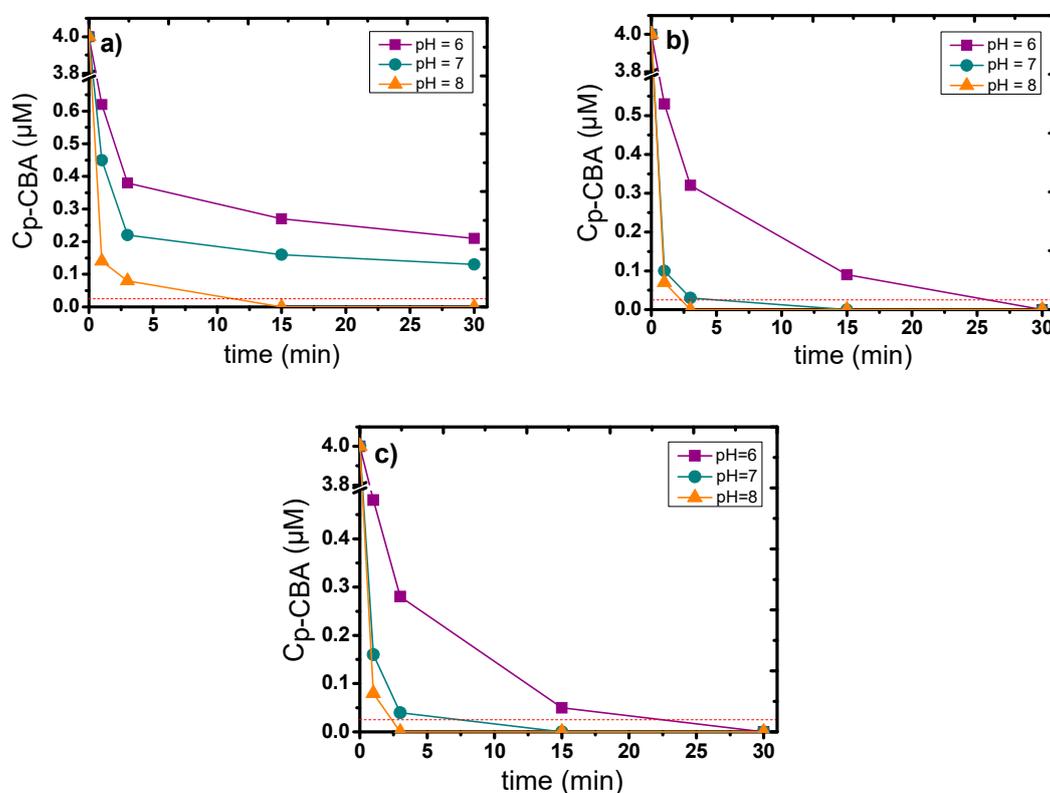


Figure 7. Influence of pH values on p-CBA removal by the application of (a) single ozonation and heterogeneous catalytic ozonation, using qualified catalysts: (b) Zeolite-6 and (c) Talc-6; experimental conditions: C_{p-CBA} 4 μ M, C_{O_3} 2 mg/L, C_{cat} 0.5 g/L, temperature 23 ± 2 °C.

Furthermore, ozone molecules are more stable in an aqueous solution at lower temperatures; therefore, ozone decomposition reactions and the respective production of radicals are slower. For this reason, the removal efficiency of micropollutants was decreased by decreasing the solution temperature (Figure 8). At 15 °C, the production of hydroxyl radicals was limited, and the p-CBA was removed by 93.2% and 82% with the addition of zeolite-6 and talc-6, respectively, after 30 min of reaction/oxidation time. According to the van't Hoff rule, an increase in temperature of 10 °C will double the reaction kinetics rate. Although a rise in temperature can increase ozone decomposition and chemical reaction rates, it simultaneously decreases the dissolved ozone concentration in water [30]. Table 2 shows the escape of ozone in the gas phase at various temperatures under the assumption that the equilibrium of

ozone in the gas/aqueous phase would be achieved quickly, resulting in lower ozone participation at the oxidation/reaction stage. These calculations are based on Wang et al.'s study [31] and are presented in the supplementary text S1. However, even in such an extreme theoretical hypothesis, ozone behavior depends on the temperature of the reaction. An increase in the temperature of an aqueous solution accelerates the escape of ozone in the gaseous phase (Table 2). Thus, increasing the reaction kinetic for p-CBA degradation by increasing the temperature from 15 °C to 25 °C exceeds the corresponding increase of ozone escape in the gaseous phase, while at 35 °C the higher escape of ozone in the gaseous phase results in lower degradation of p-CBA. Furthermore, increasing the temperature generally decreases the adsorption of micropollutants (Table S2) on the surface of catalysts, reducing the efficiency of heterogeneous catalytic ozonation reactions [30]. The actual ozone concentration during the experiments as a function of temperature is shown in supplementary Figure S5.

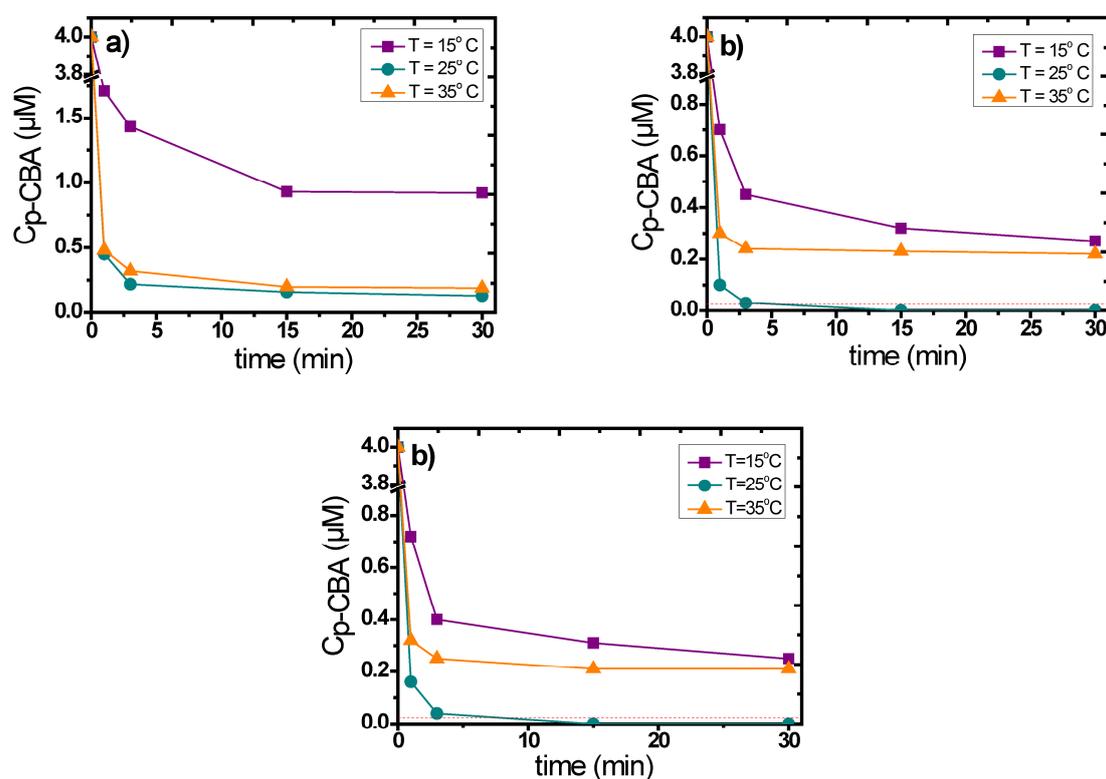


Figure 8. Influence of temperature on the removal of p-CBA by the application of (a) single ozonation and heterogeneous catalytic ozonation using optimum defined catalysts: (b) zeolite-6 and (c) Talc-6; experimental conditions: C_{p-CBA} 4 μM , C_{O_3} 2 mg/L, C_{cat} 0.5 g/L, pH 7.

Table 2. Theoretically calculated ozone escape from aqueous solution into air for various temperatures during the reaction/oxidation stage.

Reaction Time (Min)	Ozone Escape		
	15 °C	25 °C	35 °C
0.1	3.8%	4.7%	5.6%
1	5.8%	7%	8.3%
3	7.7%	9.4%	11.1%
15	9.6%	11.7%	13.9%
30	11.5%	14.1%	16.7%

In this study, the optimum temperature for the removal of pollutants by the application of heterogeneous catalytic ozonation was 25 °C. After 3 min of reaction time, the concentration of p-CBA was 34.4 $\mu\text{g/L}$, 4.7 $\mu\text{g/L}$ and 6.3 $\mu\text{g/L}$ in the O_3 , zeolite-6/ O_3 and talc-6/ O_3 oxidation processes. When

the temperature was raised to 35 °C, the removal efficiency for the same duration/oxidation time decreased by 31.3%, 87.5% and 68%, respectively. This reduction was mainly attributed to lower adsorption capacity (Table S2), as well as the increase of ozone escape towards the gas/air phase. Similar observations were also reported by Luo et al., 2018 [32].

4. Conclusions

In this study, the catalytic activity of three natural minerals, selected after preliminary screening experiments, was examined after thermal pre-treatment in the temperature range between 100° and 800 °C, during the application of heterogeneous catalytic ozonation process for the removal of p-CBA. The PZC of these solid materials was increased by thermal treatment. A PZC value around the pH value of the solution favors the efficient contact of ozone molecules with the catalyst surface and therefore can accelerate its decomposition, leading to the production of •OH radicals.

For the PZC values of the examined minerals approaching the circa-neutral solution pH (i.e., for the neutrally charged solids), the efficiency of the oxidation process increased. At pH 7 and 25 °C, the negatively charged kaolin surface showed no catalytic activity. Under the same conditions, talc (as a raw material with PZC 5.9) was found to present moderate catalytic activity, but after its calcination at 800 °C, performance increased by 56% even after the first min of oxidation time because the respective PZC value increased to 6.5. Furthermore, neutrally charged raw zeolite was found to efficiently remove p-CBA and increase the PZC value (to 7.2) after calcination further improved its performance.

The higher production of •OH and the subsequent higher efficiency of the oxidation process were found to be closely related to the neutrally charged surfaces of solid materials, acting as catalysts that can more effectively attract ozone molecules. The optimum conditions for all the examined parameters were a pH value of 8 and a temperature of 25 °C. Where the dissolution of ozone in the aqueous phase was satisfactory, the decomposition of ozone was fast and the production of •OH radicals was high. The removal of p-CBA was based on the mechanism of radical production and was verified by the addition of TBA, which substantially reduced the efficiency of the treatment system (in the range of 94.5% in the case of single ozonation).

Supplementary Materials: The following are available online at <http://www.mdpi.com/2071-1050/12/24/10503/s1>, Figure S1: (a) TG-DTA and (b) XRD diagram of kaolin; Peaks for K: Kaolin, I: Illite. Figure S2: Influence of the thermal pre-treatment on ozone decomposition in comparison to single ozonation: (a) zeolite, (b) talc, and (c) kaolin. Experimental conditions: ozone concentration 2 mg/L, catalyst concentration 0.5 g/L, p-CBA concentration 4 µM, pH 7 and temperature 23 ± 2 °C. Figure S3: Effect of TBA on ozone decomposition in the catalytic ozonation systems, as compared to single ozonation. Experimental conditions: ozone concentration 2 mg/L, catalyst concentration 0.5 g/L, p-CBA concentration 4 µM, TBA concentration 0.4 mM, pH 7 and temperature 23 ± 2 °C. Figure S4: Effect of pH value on the decomposition of ozone; (a) Single ozonation, (b) zeolite-6, and (c) talc-6. Experimental conditions: ozone concentration 2 mg/L, catalyst concentration 0.5 g/L, p-CBA concentration 4 µM and temperature 23 ± 2 °C. Figure S5: Effect of temperature on ozone decomposition; (a) Single ozonation, (b) zeolite-6, and (c) talc-6. Experimental conditions: ozone concentration 2 mg/L, catalyst concentration 0.5 g/L, p-CBA concentration 4 µM and pH 7. Table S1: Adsorption capacity of natural minerals thermally pre-treated at various temperatures for the case of p-CBA removal. Experimental conditions: catalyst concentration 0.5 g/L, p-CBA concentration 4 µM, pH 7, temperature 23 ± 2 °C and adsorption time 30 min. Table S2: Adsorption capacity of zeolite-6, and talc-6 for the case of p-CBA removal at various temperatures. Experimental conditions: catalyst concentration: 0.5 g/L, p-CBA concentration: 4 µM, pH: 7 and adsorption time 30 min. Text S1: Example of calculation, regarding the theoretical escape of ozone from the water during the experiment.

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., E.K. and K.K.; investigation, S.P. and K.K.; 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 RESEACH-CREATE-INNOVATE (project code: T1EDK-02397).



Co-financed by Greece and the European Union

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

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