

# Performance of Heterogeneous Catalytic Ozonation with Minerals in Degradation of p-Chlorobenzoic Acid (p-CBA) from Aqueous Solutions <sup>†</sup>

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**Abstract:** Water pollution is a critical environmental issue nowadays. One major problem is the pollution of freshwaters by pollutants of low concentrations (ng/L–μg/L), known as micropollutants. The most promising techniques for micropollutants degradation are Advanced Oxidation Processes (AOPs). Heterogeneous catalytic ozonation is among them, and recent studies have shown that it can be an efficient water treatment technique. The aim of this study is to evaluate the catalytic activity of five minerals (anatase, dolomite, kaolin, talc and zeolite) on the ozonation of small concentrations of p-CBA at pH 7 by batch mode experiments. p-CBA was employed as a model compound for evaluation of single and catalytic ozonation performance, because it cannot be efficiently removed by direct ozonation ( $k_{O_3} < 0.15 \text{ M}^{-1}\text{s}^{-1}$ ), while it has high reactivity with hydroxyl radicals ( $k_{OH} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ). It was found that all applied solid materials can be characterized as catalysts, except kaolin, the use of which presented almost the same performance with single ozonation. The best results were obtained by zeolite and dolomite (>99.4%) within 15 min reaction/oxidation time. These materials were neutrally (PZC = 6.8) and positively (PZC = 8.9) charged, respectively, during the oxidation process (pH 7), favoring the contact of micropollutant and ozone with the catalysts' surface. On the other hand, the addition of anatase and talc in the ozonation system resulted in 97.5% and 98.5% p-CBA degradation, respectively, due to their slightly negative surface charge throughout the reaction. Conclusively, the experimental results indicated that the performance of heterogeneous catalytic ozonation is strongly depending on the surface charge of the solid materials (catalysts).

**Keywords:** heterogeneous catalytic ozonation; adsorption; minerals; p-chlorobenzoic acid; water treatment

## 1. Introduction

The presence of micropollutants (μg/L–ng/L) in water significantly affects its quality. Ozonation is a long-studied method for water and wastewater treatment [1]. Ozone is an efficient oxidant, but it does not react with aldehydes and carboxylic acids, so it cannot achieve total mineralization. Furthermore, the oxidative reactions of ozone are slow and selective. For the obviation of these restrictions, Advanced Oxidation Processes (AOPs) are applied. One of them is heterogeneous catalytic ozonation [2]. This process is based on ozone decomposition and the consequent production of hydroxyl radicals ( $\cdot\text{OH}$ ), which are more powerful oxidizing agents and react

non-selectively [3]. In many studies, minerals have been used as potential catalysts in heterogeneous catalytic ozonation, due to their low cost, low toxicity and common availability [4,5].

The aim of this study is to evaluate the catalytic activity of some minerals and to correlate their physicochemical characteristics with their efficiency in the heterogeneous catalytic ozonation process. For that purpose, five different minerals were used as catalysts: anatase, dolomite, kaolin, talc and zeolite in catalytic ozonation of p-CBA. The most widely used catalyst among them is zeolite [6–8], but there are also some researches about anatase [5,9] and kaolin [4,10]. p-CBA was employed as a model compound, because it cannot be efficiently removed by direct ozonation ( $k_{o_3} < 0.15 \text{ M}^{-1}\text{s}^{-1}$ ), while it has high reactivity with hydroxyl radicals ( $k^{\bullet\text{OH}} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ) [11,12]. As a result, the production of hydroxyl radicals can be indirectly evaluated.

## 2. Materials and Methods

All the chemicals were of analytical grade, except from HPLC-grade acetonitrile (Chem-lab, Zedelgem, Belgium) and phosphoric acid (Sigma-Aldrich, St. Louis-MO-USA). p-CBA (Sigma-Aldrich, St. Louis-MO-USA) was used as the model organic compound at initial concentration of 4  $\mu\text{M}$ . All the solutions were prepared by distilled water. Anatase, dolomite, kaolin, talc and zeolite were used as catalysts.  $\text{K}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$  (Chem-lab, Zedelgem, Belgium) were used for pH adjustment. Adsorption, ozonation and catalytic ozonation experiments were performed in batch mode following the procedure described by Psaltou et. al., 2018 [13]. The residual concentration of p-CBA was determined by HPLC (Thermo, Massachusetts-MA-USA) with UV detector at 254 nm (Thermo, UV2000). The mobile phase was consisted from 60% v/v of 10 mM phosphoric acid and 40% v/v of acetonitrile. The detection limit of p-CBA was 0.025  $\mu\text{M}$ . The concentration of ozone in aqueous solutions was determined by common indigo method [14]. The surface area and the pore size distribution of the minerals were calculated, according to the Brunauer–Emmet–Teller (BET) method. The Point of Zero Charge (PZC) was determined by the potentiometric mass titration method [15].

## 3. Results

In adsorption, the ozonation and catalytic ozonation experiments' pH was stable at 7, where the p-CBA is negative charged ( $\text{pK}_a = 4.1$ ) and the potential catalysts were of different charge: negative (anatase, kaolin, talc), almost neutral (zeolite) and positive (dolomite). The physicochemical characteristics of these catalysts are presented in Table 1.

**Table 1.** physicochemical characteristics of minerals.

| Materials | Physicochemical Characteristics |     |                                            |                               |
|-----------|---------------------------------|-----|--------------------------------------------|-------------------------------|
|           | PZC                             | IEP | $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) | Pore Volume ( $\text{mL/g}$ ) |
| Anatase   | 6.2                             | 6.5 | 9.9                                        | 0.089                         |
| Dolomite  | 8.9                             | 9.3 | 5.1                                        | 0.030                         |
| Kaolin    | 3.3                             | 4.1 | 13                                         | 0.042                         |
| Talc      | 5.9                             | 2.5 | 10.5                                       | 0.065                         |
| Zeolite   | 6.8                             | 2.2 | 21                                         | 0.164                         |

### 3.1. Adsorption of p-CBA by Minerals

The adsorption of p-CBA from aqueous solutions by the examined catalysts showed rather low uptake capacity at pH 7 (Table 2). Isoelectric point (IEP) is the main physicochemical characteristic that determines the affinity between the organic molecule and the solid material in adsorption process. Although dolomite was the only mineral that was positively charged throughout adsorption process, its adsorption capacity was very low (12.5  $\mu\text{g}$  p-CBA/g), due to its low specific surface area (Table 1). Talc showed significantly higher uptake capacity than the other catalysts,

which was 200.4  $\mu\text{g p-CBA/g}$ . A lower adsorption capacity (9.4  $\mu\text{g p-CBA/g}$ ) was determined by kaolin, probably because it has the same IEP value with the  $\text{pK}_a$  of p-CBA.

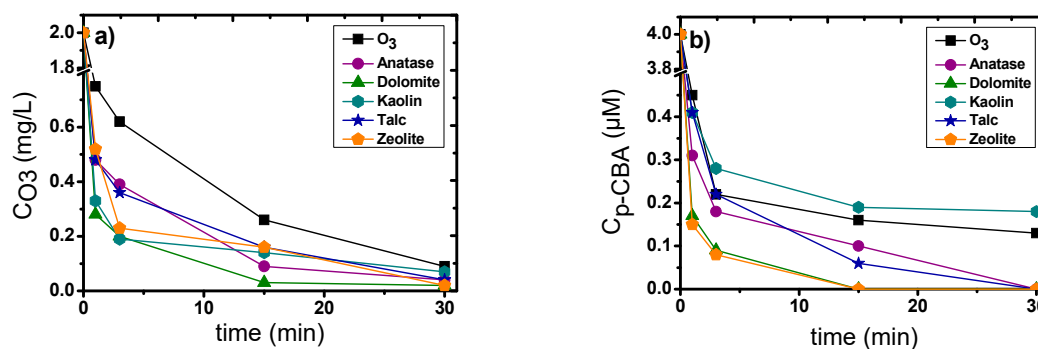
**Table 2.** Adsorption loading of p-CBA ( $C_0 = 4 \mu\text{M}$ ) onto the minerals ( $C_{\text{cat}} = 0.5 \text{ g/L}$ ).

| Parameter                               | Anatase | Dolomite | Kaolin | Talc  | Zeolite |
|-----------------------------------------|---------|----------|--------|-------|---------|
| $q$ ( $\mu\text{g p-CBA/gr catalyst}$ ) | 56.4    | 12.5     | 9.4    | 200.4 | 97.1    |

### 3.2. Heterogeneous Catalytic Ozonation with the Examined Catalysts

The objective of this study was to evaluate the catalytic activity of the examined minerals. Figure 1a shows the results of ozone decomposition in single and catalytic ozonation of p-CBA at pH 7 using the five minerals as catalysts. All the catalysts increased ozone decomposition compared to single ozonation. Higher ozone degradation was presented by dolomite, which consumed 98.5% at 15 min reaction time. Kaolin and zeolite presented a fast consumption at the first 3 min, which reached 89%, and then the ozone consumption slowed down. However, the micropollutant removal did not present the same behavior.

From the results presented in Figure 1b, it is obvious that the highest degradation occurred when dolomite and zeolite were used as catalysts, which can achieve up to 97.8% p-CBA removal already after the 3<sup>rd</sup> min of reaction/oxidation time. Although these two catalysts did not consume ozone the same way, they presented similar results in p-CBA degradation. However, for almost all examined catalysts, complete degradation of p-CBA (i.e., close to the respective analytical detection limit) was achieved after 30 min of reaction time except from kaolin. As aforementioned, p-CBA is considered an  $\cdot\text{OH}$  probe compound because it reacts quickly with hydroxyl radicals and, at the same time, presents very low reactivity against ozone molecules. This indicates that the acceleration of micropollutant degradation was mainly due to the increased production of hydroxyl radicals.



**Figure 1.** degradation by heterogeneous catalytic ozonation, (a) Ozone decomposition, (b) p-CBA degradation; experimental conditions:  $C_{\text{O}_3} = 2 \text{ mg/L}$ ,  $C_{\text{p-CBA}} = 4 \mu\text{M}$ ,  $C_{\text{cat.}} = 0.5 \text{ g/L}$ ,  $\text{pH} = 7$ ,  $T = 23 \pm 2^\circ\text{C}$ .

Three of the examined materials (dolomite, talc, zeolite) promoted ozone degradation slowly, as their constants are  $0.079 \text{ min}^{-1}$ ,  $0.070 \text{ min}^{-1}$  and  $0.074 \text{ min}^{-1}$ , respectively (Table 3). Anatase has the highest kinetic constant for ozone decomposition,  $0.121 \text{ min}^{-1}$ . However, regardless of their differences, all the examined catalysts enhanced ozone decomposition compared with single ozonation ( $0.037 \text{ min}^{-1}$ ).

**Table 3.** Values of first order kinetic constant ( $k$ ,  $\text{min}^{-1}$ ) for ozone decomposition without p-CBA in catalytic ozonation systems; Experimental conditions:  $\text{Co}_3 = 2 \text{ mg/L}$ ,  $C_{\text{cat}} = 0.5 \text{ g/L}$ ,  $\text{pH} = 7$ ,  $T = 23 \pm 2 \text{ }^\circ\text{C}$ .

| $k$ ( $\text{min}^{-1}$ ) | $\text{O}_3$ | Anatase | Dolomite | Kaolin | Talc  | Zeolite |
|---------------------------|--------------|---------|----------|--------|-------|---------|
|                           | 0.037        | 0.121   | 0.079    | 0.101  | 0.070 | 0.074   |

#### 4. Discussion

The heterogeneous catalytic ozonation of p-CBA by using minerals as catalysts (anatase, dolomite, kaolin, talc, zeolite) in aqueous solutions was found to be capable of increasing the removal/degradation of initial p-CBA concentration compared to a single ozonation process except in the case of kaolin. Since p-CBA degradation is particularly favored by the presence of hydroxyl radicals (and not by single ozonation), it is concluded that four of the examined catalysts can enhance the decomposition of ozone on their reactive sites. The best results were obtained with the presence of dolomite and zeolite at 3 min reaction time, with p-CBA removal up to 97.8%, which increased to 99.4% at 15 min reaction time. The catalytic performance of zeolite was probably due to the neutral charging of its surface ( $\text{PZC} = 6.8$ ) in combination with its adsorption capacity ( $97.1 \mu\text{g/g}$  catalyst), which favored the affinity between ozone/hydroxyl radicals and p-CBA. Dolomite has a high point of zero charge at 8.9, and it was positive charged throughout the reaction. On the other hand, p-CBA has  $\text{pK}_a$  4.1, i.e., it is negative charged at pH 7. The opposite charge creates an affinity between the catalyst and the organic molecule, and as a result, heterogeneous catalytic ozonation is favored. This affinity did not favor the adsorption process, because the specific surface area and the pore volume of dolomite are small (Table 1). Although they present high ozone decomposition constants, anatase and kaolin did not remove p-CBA satisfactorily, because they have low adsorption capacity and the production of hydroxyl radicals are so quick that the produced oxidative species cannot react with the pollutant. Talc with high adsorption capacity and low kinetic constant removed p-CBA by 94.5% at 3 min of reaction due to its negative charge that does not favor the production of hydroxyl radicals. From the results of this study, it is obvious that the catalytic activity and the adsorption capacity of a catalyst are affected by its physicochemical characteristics. Surface charge has the greater effect ( $\text{PZC}$  and  $\text{IEP}$ ) on which the decomposition of ozone and the adsorption capacity depends.

**Author Contributions:** S.P. and M.M. conceived and designed the experiments; S.P. performed the experiments; S.P. and E.K. analyzed the data; A.Z. and M.M. contributed reagents/materials/analysis tools; S.P. wrote the paper.

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