Proceeding Paper

Minerals as Potential Catalysts in Heterogeneous Catalytic Ozonation: A Kinetic Study of p-CBA Degradation in Aqueous Solutions at pH 7 †

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Abstract: This study examines the removal of p-CBA via the application of heterogeneous catalytic ozonation in the presence of 13 minerals. The solids were used as raw materials or after hydrophilic/hydrophobic modification. The optimal minerals were zeolite, calcite, dolomite, and thermally treated talc. The kinetic study showed that the decomposition of ozone followed a first-order kinetic model for all ozonation systems, whereas the kinetic model of p-CBA removal depended on the materials that were applied. The catalytic degradation of p-CBA followed a second-order kinetic model, while in the presence of non-catalytic materials; the p-CBA abatement was in best agreement with the pseudo-second-order kinetic model, as single ozonation.

Keywords: catalytic ozonation; minerals; micropollutants; p-chlorobenzoic acid; reaction kinetics; water treatment

1. Introduction

Catalytic ozonation is an advanced oxidation process, effective in the degradation of organic pollutants existing in low concentrations (lower than mg/L)—i.e., considered to be micropollutants—by enhancing the decomposition of ozone towards the enhanced production of radicals [1,2]. Ozone is a powerful oxidant, and its oxidation potential is 2.07 V, but it presents quite high selectivity against several organic compounds [3]. The main product of ozone decomposition is hydroxyl radicals, which are even more powerful oxidative agents (i.e., 2.80 V) than molecular ozone, and react rather unselectively with all organic compounds [3,4]. The catalytic ozonation process can be carried out either by the addition of transitional dissolved metal ions acting as catalysts (homogeneous catalytic ozonation), or by the addition of appropriate solid materials (heterogeneous catalytic ozonation) [5]. The key issue in both processes is to use an efficient catalyst [6]. Minerals are among the main categories of solid materials used as catalysts in heterogeneous catalytic ozonation, due to their low cost, low toxicity, and common availability [7,8].

In this research, various minerals (as raw materials or after modification) were studied as potential catalysts in the heterogeneous catalytic ozonation process, under the same (comparable) experimental conditions. The catalytic activity of solid materials was evaluated via the comparison of kinetic constants, regarding the decomposition of ozone and the removal of p-chlorobenzoic acid (p-CBA). The extraction of the kinetics contributes to the elucidation of the micropollutant removal mechanism. p-CBA is an organic compound that is commonly used as a probe compound in the study of ozonation processes, due to its relatively slow (kinetically) reaction with ozone molecules ($k_{O_3} < 0.15\ M^{-1}s^{-1}$), while at the same time reacting much faster with hydroxyl radicals (reaction constant

$k_{\bullet OH} = 5.2 \times 10^9 \ M^{-1}s^{-1}$ [9,10]. As a result, the production of hydroxyl radicals can be indirectly evaluated.

2. Experimental Section

2.1. Materials and Analytical Techniques

All chemicals used in the experiments were of analytical grade. Acetonitrile and phosphoric acid used for the p-CBA determination were of HPLC grade. p-CBA was obtained from Sigma-Aldrich (St. Louis, MO, USA) and (as aforementioned) used as a model compound (initial concentration 4 μM). All aqueous solutions were prepared in distilled water with the pH adjusted to 7 (common pH for water treatment), and for this purpose K_2HPO_4 and KH_2PO_4 (Chem-Lab, Zedelgem, Belgium) were used as convenient buffer solutions. Eight commercially available solids were examined as potential catalysts, either as raw materials, or after proper modification, in powdered form (particle diameter < 63 μm), i.e., zeolite, talc, anatase, olivine, calcite, dolomite, kaolin, and Portafil®. Single and catalytic ozonation experiments were conducted in batch mode by following the procedure previously described by Psaltou et al. [11]. The concentration of O_3 was determined via the application of the indigo colorimetric method [12], while for the p-CBA determination high-performance liquid chromatography (HPLC), model of UV Spectrum UV 2000 (Thermo Fisher Scientific, Waltham, MA, USA) was used, according to the protocol also described by Psaltou et al. [11].

2.2. Modification of Examined Materials

The hydrophobic modification was conducted using the method proposed by Stylianou et al. [13] and Zapata et al. [14] to increase the hydrophobicity of a zeolite surface. According to this, 2 g of the respective material in powdered form (particles<63 μm) was dispersed in 10 mL of toluene using a sonicator (Nahita, model 610/6, Auxilab, Navarra, Spain) for 45 min. The suspension was then added to a solution of trichloro-methyl-silane (TriClMS, 10 mg/L, Sigma-Aldrich, USA) in toluene. The suspension was agitated for 24 h in an orbital shaker (model RS Lab 7-Pro) at ambient temperature. After that, the solids were separated using a PVDF filter (0.45 μm pore size), rinsed three times with ethanol to remove the excess TriClMS and, finally, dried at 80 °C overnight. The resulting hydrophobically modified sample is abbreviated hereafter as zeolite-H, and after calcination at 550 °C denoted as zeolite-TH. The calcination was used to remove crystalline water and hydroxyls from the surface/structure of the mineral, aiming to improve hydrophobicity. Furthermore, zeolite along with talc and kaolin were calcinated at 600 °C, and are abbreviated hereafter as zeolite-T, talc-T, and kaolin-T. The calcination was carried out by raising the temperature from room up to 600 °C within 2 h, and then the materials were left to cool at room temperature. The thermal treatment of solids improves the wettability of their surfaces.

3. Results and Discussion

In Table 1, the kinetic parameters of O_3 decomposition during the single and catalytic ozonation batch experiments are presented (with/without the presence of p-CBA), while the relevant kinetic parameters of p-CBA degradation/removal via the application of ozonation processes are presented in Tables 2 and 3. The decomposition of ozone in water can be characterized by two subsequent stages: during the first stage the reaction occurs quickly, while in the second the reaction rate is moderate or slowed down. During the first minute of the reaction, the oxidation occurs very rapidly, due to the instantaneous O_3 demand (IOD) [15] and the possible production of H_2O_2 in the ozonation system [9]. The two parameters—i.e., the IOD and the H_2O_2 production—are known to depend mainly on water quality and specific characteristics [9,15]. The experimental conditions were the same for all of the examined cases; hence, the first stage of the reaction was the same for all of the experiments. Therefore, in this study, the k-values represent the second (slower) kinetic stage of the reaction (1–30 min). The decomposition of O_3 in all examined ozonation systems fits well with the first-order kinetic model (Equation (1)), similar to the case of

p-CBA absence [16]; however, the respective experimental data for the p-CBA degradation present certain differences.

First-order kinetic model:

$$\ln(C_t/C_0) = k_1 * t \tag{1}$$

where C_0 is the initial O_3 concentration, C_t is the concentration of O_3 at time t, and k_1 (min^{-1}) is the rate constant of the first-order kinetic equation; k_1 was determined by the plot of curve $\ln(C_t/C_0)$ vs. time.

Second-order kinetic model:

$$(1/C_t) - (1/C_0) = k_2 * t \tag{2}$$

where C_0 is the initial O_3 concentration, C_t is the concentration of O_3 at time t, and k_2(L/μg·min) is the rate constant of the second-order kinetic equation; k_2 was determined by the plot of the curve $1/C_t$ vs. time.

Pseudo-second-order kinetic model:

$$t/C_t = 1/k_{2p}C_e{}^2 + t/C_e \tag{3}$$

where k_{2p} is the pseudo-second-order rate constant (L/μg·min), and C_t and C_e are the concentrations of p-CBA degraded at time t and at the equilibrium stage, respectively; k_2 can be calculated from the slop and intercept of the plot t/q vs. t.

Table 1. Values of first-order kinetic parameters for O_3 decomposition with and without the addition of p-CBA in the catalytic ozonation process. Experimental conditions: initial p-CBA concentration 4 μM (when added), O_3 concentration 2 mg/L, catalyst concentration 0.5 g/L, pH 7, temperature 23 ± 2 °C, reaction time 30 min.

Catalyst	Parameters of First-Order Kinetics			
	Absence of p-CBA		Presence of p-CBA	
	k_1 (min^{-1})	R^2	k_1 (min^{-1})	R^2
Materials not presenting catalytic activity				
No Catalyst (O_3)	0.037	0.995	0.072	0.999
Kaolin	0.094	0.997	0.095	0.995
Kaolin-T	0.060	0.991	0.062	0.993
Portafil®	0.097	0.995	0.121	0.996
Zeolite-H	0.107	0.995	0.204	0.999
Zeolite-TH	0.101	0.998	0.182	0.991
Materials presenting catalytic activity				
Zeolite	0.088	0.993	0.074	0.999
Zeolite-T	0.150	0.999	0.097	0.991
Talc	0.068	0.998	0.069	0.994
Talc-T	0.127	0.993	0.089	0.997
Anatase	0.119	0.992	0.084	0.999
Olivine	0.075	0.992	0.064	0.995
Calcite	0.064	0.991	0.059	0.991
Dolomite	0.076	0.995	0.072	0.992

Table 2. Values of pseudo-second-order kinetic parameters for p-CBA degradation in ozonation systems, when using inefficient catalytic materials. Experimental conditions: initial p-CBA concentration 4 μM, O_3 concentration 2 mg/L, catalyst concentration 0.5 g/L, pH 7, temperature 23 ± 2 °C, reaction time 30 min.

Catalyst	Parameters of Second-Order Kinetics		
	k_{2p} (L/μg·min)	C_{ep} * (μg/L)	R^2
No catalyst (O_3)	0.058	22.2	0.996
Kaolin	0.041	27.8	0.999
Kaolin-T	0.074	28.6	0.997
Portafil®	0.096	26.3	0.999
Zeolite-H	0.040	28.8	0.996
Zeolite-TH	0.049	26.3	0.997

* C_{ep}: residual p-CBA concentration.

Table 3. Values of second-order kinetic parameters for p-CBA degradation in ozonation systems, when using efficient materials as catalysts. Experimental conditions: initial p-CBA concentration 4 μM, O_3 concentration 2 mg/L, catalyst concentration 0.5 g/L, pH 7, temperature 23 ± 2 °C.

Catalyst	Parameters of Second-Order Kinetics		
	k_2 (L/μg·min)	R^2	Reaction Time (min)
Zeolite	0.030	0.993	5
Talc	0.008	0.999	30
Talc-T	0.025	0.999	5
Anatase	0.006	0.995	30
Olivine	0.006	0.998	30
Calcite	0.022	0.992	5
Dolomite	0.024	0.993	5

The Kinetic Parameters

For those materials presenting at least some catalytic activity, the k-values of O_3 decomposition in the presence of p-CBA were found to be generally lower than those without it, while in the presence of non-catalytic materials the corresponding k-values were higher (Table 1). When a catalytic material is added to the ozonation system, in most cases, it can accelerate the decomposition of O_3, and after the first minute of the oxidation reaction the O_3 concentration becomes quite small, resulting in lower slope of the curve. Moreover, from the data in Table 1 it becomes clear that an increase in the hydrophobicity of the solid surface improves the ozone's contact with it, and the kinetic constants of O_3 decomposition in the relevant systems are found to be very high. The highest O_3 decomposition constant in the presence of p-CBA belongs to the material zeolite-H (0.204 min^{-1}), which means that this is the most hydrophobic of all tested materials, while the respective constant of zeolite-TH was equal to 0.182 min^{-1}. Furthermore, the thermal treatment of zeolite and talc presented positive effects on ozone decomposition, while the kinetic constant of ozone decomposition in the presence of kaolin T was 34.7% lower than that in the presence of raw kaolin, as Table 1 shows.

The kinetic parameters of p-CBA degradation by ozonation are presented in Tables 2 and 3, noting also the duration of the catalytic reaction. The solid materials that cannot be characterized as catalysts—as they present similar or even lower efficiencies—regarding the p-CBA removal as compared to the application of a single ozonation process, showed the best agreement with the pseudo-second-order kinetic model (Table 2), while the solid materials presenting sufficient catalytic activity were found to fit better the second-order kinetic model (Table 3).

The second-order kinetic models refer to pollutant removal, based on physicochemical interactions between the existing phases that can share or exchange electrons, and the controlling step in this case is the velocity of the respective chemical/oxidation reaction [17,18].

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 efficiency. In these systems there is an equilibrium concentration, which is the removal limit [19], and depends on the examined material; for this research, that was ~0.18 μM (28 μg/L) for all of the examined non-catalytic materials, when applying a 30 min catalytic oxidation reaction. It is worth noting that although the hydrophobically modified zeolites presented the highest kinetic constants of ozone decomposition, they did not present catalytic activity. Their hydrophobic surface enhances the decomposition of ozone, but repels the organic molecule. This lack of contact diminishes the potential catalytic ability of these solid materials. On the other hand, the thermal treatment of minerals was found to enhance both ozone decomposition and p-CBA degradation, because it favored the contact of the reactants.

Nevertheless, for the most efficient catalysts of this study (i.e., zeolite-T), a kinetic model cannot be plotted, due to the rapid degradation of p-CBA, because the catalytic ozonation proceeds very rapidly, resulting in residual concentrations of the examined micropollutant below the respective analytical method detection limit (0.025 μM), i.e., even during the early stages of oxidation reaction. For the same reason, the second-order kinetic constants of zeolite, talc-T, calcite, and dolomite could be plotted, but only up to 5 min of oxidation time, because the concentration of p-CBA with the use of these catalysts was below the analytical limit of 0.025 μM when increasing the duration of oxidation. According to Table 3, the thermal treatment of the examined materials accelerated the oxidation activity of the raw materials, as the kinetic constants of p-CBA degradation for zeolite-T, talc-T, and kaolin-T were at least 44.6% higher than in the raw minerals. However, in the case of kaolin, its ability to degrade p-CBA was too weak for the thermally treated material to be considered a catalyst.

It is also important to note that in the literature there are some controversies regarding the application of kinetic models for the removal of micropollutants viathe implementation of heterogeneous catalytic ozonation. Yong et al. [20] considered that ozone can possibly oxidize the pollutant and simultaneously be involved in catalytic reactions with the catalyst surface, resulting in the pseudo-second-order kinetic model, which is in agreement with the findings of other researchers [21,22]. Furthermore, Sumegova et al. [16] found that the removal of methylene blue presents better agreement with the second-order kinetic model when zeolite is used as catalyst in the ozonation system, as was also observed by Shokrollahzadeh et al. [23], who examined the case of nano-ZnO application as a catalyst for the removal of azo dyes. Nevertheless, in other publications, the removal of micropollutants via the application of heterogeneous catalytic ozonation has shown best agreement with the pseudo-first-order kinetic model [24]. Regardless of these contradictions, with the obtained results in this research, it becomes apparent that the kinetic order of a micropollutant removal is not random but, when applying the same experimental conditions, depends on the solid material used as a catalyst—and specifically on the "intensity" of its catalytic activity (i.e., the production of $^\bullet$OH).

4. Conclusions

In this study, 13 different solid materials (raw or after modification, thermal or chemical) were examined as potential catalysts for the heterogeneous catalytic ozonation process of p-CBA removal, used here as a typical "model" micropollutant of polluted waters. The extraction of the kinetic constants facilitates the ranking of the examined materials according to their ability to enhance ozone decomposition and micropollutant removal. Ozone decomposition generally follows the first-order kinetic model in all cases, while the kinetic model for p-CBA removal presented certain differences. In the presence of materials with catalytic activity, the p-CBA degradation is in best agreement with the second-order kinetic model, while in the case of non-catalytic materials it follows a pseudo-second-order kinetic model. The most efficient catalysts were found to be zeolite, calcite, and dolomite, along with the thermally treated talc, which were in best agreement with the second-order

kinetic model. From the combined study of the kinetic constants of ozone decomposition and p-CBA removal, it becomes clear that the thermal treatment was beneficial for the catalytic ability of examined materials, while the chemically modified hydrophobic materials inhibited the effectiveness of catalytic ozonation, as the surface coating with silane eventually prevented its efficient contact with p-CBA, and these oxidation systems followed the pseudo-second-order kinetic model.

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