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APPLICATION OF HETEROGENEOUS CATALYSTS IN OZONATION OF MODEL COMPOUNDS IN WATER

A Thesis Submitted to the College of Graduate Studies and Research in
Partial Fulfillment of the Requirements for the Degree of

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In the Department of Chemical Engineering
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Canada

By

Carlos Alberto Guzman Perez

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ABSTRACT

The presence of micropollutants, particularly pesticides, in surface waters across Canada has been of concern not only for their environmental impact, but also for their potential effects on human health and recalcitrant nature to conventional water treatment methods. Although ozone has been mainly applied for disinfection of drinking water, oxidation of trace organics by ozonation has been considered potentially effective. In an effort to meet increasingly stringent drinking water regulations, different solid catalysts have been used to enhance the removal of water contaminants by ozonation. In spite of the increasing number of data demonstrating the effectiveness of heterogeneous catalytic ozonation, the influence of different factors on the efficiency of micropollutants oxidation is still unclear.

In the present work, application of three solid catalysts in ozonation of two model micropollutants in pure water was examined using a laboratory-scale reaction system over a range of operating conditions. The three catalysts investigated were activated carbon, alumina, and perfluorooctyl alumina, and the two model micropollutants were the pesticides atrazine and 2,4-dichlorophenoxyactic acid. The effects of solution pH, presence of a radical scavenger, pesticide adsorption on catalyst, and catalyst dose on micropollutant removal were investigated. Solution pH was found to significantly influence the catalyst ability to decompose ozone into free hydroxyl radicals. The effect of these free radicals was markedly inhibited by the radical scavenger resulting in a negative impact on pesticides degradation. In general, the removal rate of pesticides was found to increase with increasing doses of catalyst.

In the ozonation process in the presence of activated carbon, atrazine removal rates increased four and two times when using a catalyst dose of 0.5 g L^{-1} at pH 3 and 7, respectively, whereas observed reaction rates for 2,4-D increased over 5 times in the presence of 1×10^{-4} M tert-butyl alcohol at pH 3. In the ozonation system catalyzed by 8 g L^{-1} alumina, the observed reaction rate constant of atrazine removal notably improved at neutral pH by doubling the micropollutant removal rate. For the pesticide 2,4-D in the presence of 1×10^{-4} M tert-butyl alcohol at pH 5, the observed removal rate was over ten times higher than that for the non-catalytic ozonation process using also using a catalyst dose of 8 g L^{-1}. Modification of alumina to produce perfluorooctyl alumina resulted in a material able to significantly adsorb atrazine, while not exhibiting affinity for adsorption of 2,4-D. In spite of its adsorptive properties, perfluorooctyl alumina was found to enhance neither molecular ozone reactions nor ozone decomposition into hydroxyl radicals. Thus, the observed removal rates for atrazine and 2,4-D by ozonation in the presence of perfluorooctyl alumina did not increase significantly.

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DEDICATION

This work is dedicated to my mother, Yolanda Pérez Centeno, and the loving memory of my late sister, Luz Angelica Guzmán Pérez (1980-2010). I wish you were here to see me completing my M.Sc. thesis.

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NOMENCLATURE

2,4-D	2,4-Dichlorophenoxyacetic acid ($C_8H_6Cl_2O_3$)
2,4-DCP	2,4-Dichlorophenol
α	Surface coverage of perfluorooctyl groups (μmol m^{-2})
AC	Activated carbon
Al_2O_3	Aluminum oxide (Alumina)
AOP	Advanced oxidation process
ATZ	Atrazine ($C_8H_{14}ClN_5$)
C_{As}	Concentration of species A in the bulk solution
D_A	Fick's diffusivity of species A (cm^2 s^{-1})
D_{eA}	Effective diffusivity of species A (cm^2 s^{-1})
E	Weisz-Prater parameter
EDC	Endocrine disrupting chemical
f_{OH}	Fraction of micropollutant degraded by hydroxyl radicals
H_2O_2	Hydrogen peroxide
HO_2^-	Hydroperoxide ion
$HO_2^\bullet$	Hydroperoxyl radical
HPLC	High performance liquid chromatography
k_a	Apparent first-order adsorption rate constant (L g^{-1} s^{-1})
k_D	Pseudo first-order ozone decomposition rate constant (s^{-1})
k_{O3}	Reaction rate constant of micropollutant with molecular ozone (M^{-1} s^{-1})
k_{OH}	Reaction rate constant of micropollutant with hydroxyl radicals (M^{-1} s^{-1})
k_{obs}	Observed reaction rate constant (M^{-1} s^{-1})

L_p	Dimensional parameter of catalyst particle (cm)
M	Micropollutant
m	Mass of catalyst (g)
n	Number of moles (mol)
NOM	Natural organic matter
$O_2^{\bullet -}$	Superoxide ion radical
O_3	Ozone or non-catalytic ozonation process
$O_3^{\bullet -}$	Ozonide ion radical
O_3/AC	Ozonation process catalyzed by activated carbon
O_3/Al_2O_3	Ozonation process catalyzed by alumina
O_3/Fe^{2+}	Ozonation process catalyzed by iron (II)
O_3/PFOA	Ozonation process catalyzed by perfluorooctyl alumina
O_3/Mn^{2+}	Ozonation process catalyzed by manganese (II)
O_3/H_2O_2	Ozonation process in the presence of hydrogen peroxide
OH	Alumina hydroxyl groups
•OH	Hydroxyl radicals
OH^-	Hydroxide ion
PFOA	Perfluorooctyl Alumina
pH_{PZC}	pH of point of zero charge
pK_a	Acid dissociation constant
$\left(-r_A\right)_{obs}$	Observed catalytic reaction rate of species A (M s^{-1})
R	Catalyst particle radius (cm)
R_{ct}	Ratio of hydroxyl radical concentration to ozone concentration

S	Catalyst surface area (m^2)
S_{BET}	Catalyst specific surface area (m^2 g^{-1})
SHB	Staehelin, Hoigné, and Buhler
TBA	Tert-butyl alcohol ($C_4H_{10}O$)
UV	Ultraviolet light
W	Catalyst dose (g L^{-1})

1. INTRODUCTION

With the development of modern analytical techniques and detection of a large number of micropollutants in sources of potable water, public awareness of their potentially negative health and environmental effects has increased. Similarly, interest in developing effective treatment methods for the removal of organic oxidation has been growing over the past three decades. Although the combined use of ozone and catalysts to improve the performance of oxidation of these water contaminants with ozone dates back to the 1970s, it took until the mid-1990s that the first research works focusing on the application of ozone and solid catalysts were reported. Thus, this research project stems from potential hazards of water micropollutants, and aims to provide a better understanding for the development of efficient ozonation processes in the presence of solid catalysts.

1.1. Research Motivation

The widespread presence of pesticide mixtures in surface waters has become a major issue because of their serious health hazards and the inefficiency of conventional water treatment processes in removing these contaminants. Among the most widely used pesticides, the herbicides atrazine (ATZ) and 2,4-dichlorophenoxyacetic acid (2,4-D) have been frequently detected in sources of potable water. Although the positive effect of micropollutant oxidation in ozone-disinfection applications has already been recognized, conventional ozonation has recently been considered as a potential technology for micropollutant degradation [1]. It should be noticed however that a large number of contaminants, including atrazine and 2,4-D, exhibit low rates of reaction with ozone [2].

To improve the removal of water contaminants by ozonation processes, combination of ozone with the adsorptive and catalytic properties of solid catalysts has been investigated [3-5]. However, the influence of the major operating variables on this catalytic process is still unclear [5, 6]. Therefore, to consider the potential application of combined ozone and heterogeneous catalysts in water and wastewater treatment, it is essential to assess the effectiveness of ozonation of recalcitrant contaminants in the presence of solid catalysts under various operating conditions.

The feasibility of heterogeneous catalytic ozonation for water treatment has already been reported in the 1970s. However, it was in the 1990s that different research groups started documenting their findings in this field of ozone application [7]. Heterogeneous catalytic ozonation, though less studied than the homogeneous process, is more attractive as it provides greater oxidation efficiency, costs less and is more feasible for practical applications when compared to other processes such as O_3/Mn^{2+} and O_3/H_2O_2 systems [8, 9]. Studies with materials such as activated carbon (AC) and alumina (Al_2O_3) represent potential applications because these adsorbents can enhance reaction of ozone in water treatment facilities. While activated carbon has excellent adsorbing properties for organic micropollutants, alumina exhibits a great affinity towards ionisable compounds [3]. On the other hand, adsorptive properties of alumina can be modified by addition of hydrophobic groups such as perfluorooctlyl alumina (PFOA) on catalyst surface so that adsorption of non-polar micropollutants and stability of molecular ozone can be enhanced [10].

Considering that heterogeneous catalytic ozonation is a highly promising method for increasing the efficiency of the ozonation process, it is necessary to conduct comparative studies that allow us to develop efficient and feasible catalytic systems. By examining the efficiency of O_3/AC, O_3/Al_2O_3, and O_3/PFOA systems in degrading pollutants with differing properties, a better understanding of fundamentals of the oxidation process, such as mechanism of ozone reaction and contribution of compound adsorption, can be achieved. Their high potential risk for human health, frequent detection in surface and ground waters, contrasting solubilities in water, and different reactivity towards ozone make atrazine and 2,4-D two suitable model pollutants for the proposed study on heterogeneous catalytic ozonation.

1.2. Research Objectives

The main objective of this work was to investigate the catalytic activity of alumina, activated carbon, and perfluorooctyl alumina in the removal of two model pollutants (ATZ and 2,4-D) under various operating conditions. This was achieved by pursuing the following specific objectives:

- Determine catalyst activity by characterizing their most relevant physicochemical properties.
- Establish the effects of compound adsorption on catalyst by examining adsorption as blank tests.
- Quantify and compare the ability of different catalysts to enhance ozone decomposition into hydroxyl radicals.
- Compare the rates of ozone consumption and pesticide removal in concentration during non-catalytic ozonation and ozonation in the presence of alumina, activated carbon, and perfluorooctyl alumina catalysts.

- Estimate the contributions of molecular ozone and free radical reactions for pollutant degradation and assess the inhibitory effects of a radical scavenger.
- Provide kinetic parameters for the different catalytic ozonation systems to compare their efficiency in degrading the model pollutants.

1.3. Scope of the Research

This thesis consists of six additional chapters, with their contents described as follows:

- Background: briefly provides an introduction to the environmental and human health effects of model micropollutants and application of ozone-based oxidation processes in water treatment. This chapter also examines the most important factors affecting ozone reactivity and models, as well as parameters, commonly used to represent the kinetics of ozonation processes.
- Experimental: describes the materials, experimental procedures, and analytical methods performed by the author for the present research.
- Catalyst Characterization and Adsorption of Model Micropollutants: summarizes the most relevant physicochemical properties of the catalysts under investigation. It also presents and discusses the results of atrazine and 2,4-D adsorption on each catalyst.
- Ozone Decomposition: examines the ability of each catalyst to accelerate ozone transformation into hydroxyl radicals under various operating conditions, and provides a general insight into catalyst performance in ozonation systems.

- Ozonation of Atrazine: presents the results of the combined action of ozone and each catalyst for removal of atrazine, and discusses the effects of various operating conditions and possible reaction pathways based on the R_{ct} concept.
- Ozonation of 2,4-Dichlorophenoxyacetic Acid: compares the efficiency of non-catalytic ozonation process and catalytic ozonation processes in removing 2,4-D based on the observed reaction rate constant (k_{obs}), and discusses the influence of the experimental conditions, as well as possible reaction pathways.
- General Conclusions and Recommendations: summarizes the most important findings from the research and presents recommendation for future work.

1.4. Contribution of This Work

In this work, ozonation of two micropollutants in the presence of three different solid catalysts was examined. These two water contaminants exhibit contrasting affinities for adsorption on each of the catalysts, and their degradation reactions develop through different pathways. Thus, this study contributes to providing a better understanding of the fundamentals of heterogeneous catalytic ozonation processes under various operating conditions.

Another significant contribution is that the experimental results obtained and kinetic approaches used may be applied to predict the catalytic activity of the solid materials examined on the removal of other micropollutants. Similarly, kinetic parameters for ozonation processes may be used for the degradation of the two micropollutants in bench-scale applications.

Experimental results from this work also indicated that some of the catalysts studied have potential applications to improve the efficiency, in removing water micropollutants, in existing wastewater treatment plants that include ozonation systems as their last purification stage.

2. BACKGROUND

Detection of a large number of micropollutants, such as pesticides commonly found in surface waters, has raised public awareness of their detrimental environmental and health impacts. As a result, several research groups have been encouraged to study the application of the combined used of ozone and solid catalysts for the removal of water micropollutants. To be able to understand the various aspects of heterogeneous catalytic ozonation, an insight of the fundamentals of ozonation is required, including: ozone-based oxidation processes in water treatment, kinetics of ozonation processes, and reactivity of model compounds towards ozone and hydroxyl radicals. Each of these topics is addressed in the present section.

2.1. Micropollutants in Surface Waters and Conventional Treatment

In Canada, more than 80% of all pesticides used correspond to the broad category of herbicides. Among these agricultural chemicals, the herbicide 2,4-dichlorophenoxyacetic acid, a well known phenoxy herbicide, and atrazine, belonging to the triazine family, have been extensively monitored in the past three decades [11]. These chemicals typically occur in trace levels, and the concern is primarily for their potential to cause chronic health problems. They are hormone-mimicking toxins, also known as endocrine disrupting chemicals (EDCs), and thus can disrupt delicate hormonal processes in humans and animals. Epidemiological and laboratory animal studies suggest that prenatal and nursing exposure to atrazine can cause abnormalities in the developing fetus and newborn babies. These abnormalities include intrauterine growth retardation, low birth weights, and higher rates of prostate inflammation in males. 2,4-D, claimed to be one of the safest pesticides in the market because of its selectivity, has been reported to cause lymphomas and various cancers [12]. In addition, long-term exposure of 2,4-D has been linked to damage to the liver, kidneys, and the digestive, muscular, and nervous systems.

The half-life of these pesticides is longer, by several orders of magnitude, than the half-lives of other known environmental pollutants in water, and thus they pose a serious threat to contaminate different water sources, if left untreated [12]. Several studies have shown that various pesticides, including atrazine and 2,4-D, are relatively stable and cannot be degraded by conventional water purification process, such as coagulation and chlorination [13-16]. Therefore, new technologies need to be developed to ensure that drinking water is safe by reducing health risks resulting from the consumption of trace amounts of EDCs present in sources of drinking water.

2.2. Ozone-based Oxidation Processes in Water Treatment

In the late 1970s, the discovery of trihalomethanes (THM) in drinking water, due to the formation of organic disinfection-by-products during chlorination of natural organic matter (NOM) present in the raw water, gave rise to the search for alternative oxidant-disinfectants that could play the role of chlorine without generating the problem of trihalomethane formation. In recent years, the application of ozone as a disinfectant has become increasingly common because of its effectiveness in treating pathogens. Due to its strong oxidizing properties, ozone is also applied in a wide range of processes including bleaching in the pulp and paper industry and metal oxidation in the semiconductor industry [1]. However, its main application is in the treatment and purification of many types of water. In ground and surface waters for drinking water use, ozonation processes have recently aroused special interest because of the positive side effect of micropollutant oxidation in ozone-disinfection applications.

Ozone can degrade water impurities via direct reaction or undergo decomposition through a chain reaction mechanism resulting in the production of free hydroxyl radicals (•OH) [1]. Free hydroxyl radical is the major secondary oxidant formed from ozone decomposition in water, which is fast-reacting and thus involves non-selective reactions. When these •OH are the dominant oxidants in the solution, the process is called an advanced oxidation process (AOP). This process causes micropollutants to be oxidized by both ozone (directly) and •OH (indirectly). Ozone-based AOPs include processes that involve ozone with ultraviolet radiation, ozone with hydrogen peroxide (H_2O_2), hydrogen peroxide with ultraviolet radiation, and ozone at high pH values. The hydroxyl radical is an extremely powerful oxidant whose reaction rate constants with organic molecules are generally in the range 10^8 to 10^{10} M^{-1} s^{-1} [17]. This means that AOP treatment of typical organic substrates will be practical, even if the steady-state concentration of •OH is only between 10^{-10} to 10^{-12} M.

On the other hand, molecular ozone is a highly selective oxidant. Unfortunately, molecular ozone has a relatively low solubility in water, and is quickly decomposed by the various solutes present in surface waters, which significantly affects its reactivity in water [10]. In this regard, two-phase ozonation improves the stability and solubility of ozone. This new system of chemical oxidation is based on liquid-liquid extraction of organic substances from the aqueous phase into a hydrophobic phase (e.g., non-polar fluorinated hydrocarbon solvent saturated with ozone) and subsequent oxidation by molecular ozone dissolved in the same phase. Thus, enhancement of ozone stability and solubility and adsorption of micropollutants result in high degradation rates of water contaminants by direct reactions with molecular ozone [3].

Heterogeneous catalytic ozonation aims to enhance removal of more refractory compounds through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst. The main advantages of the catalytic ozonation processes with respect to traditional non-catalytic ozonation are better ozone utilization, increased contaminant removal efficiency, and, in some cases, greater degree of organic matter mineralization [4, 18]. It should be noticed that a large fraction of •OH, being generated from ozone, may be trapped by impurities (radical scavengers) present in the water matrix, and thus they may not be available for micropollutant elimination [19]. To overcome this hindrance, the performance of different solid catalysts has been examined. Studies with materials such as activated carbon and alumina, and modified alumina suggest that these catalysts present potential applications [3]. These catalysts can improve the efficiency of ozonation processes either by increasing the conversion of the ozone into hydroxyl radicals or enhancing reactions between molecular ozone and micropollutants. However, the influence of the major operating variables (e.g., solution pH and catalyst dose) on ozonation processes in the presence of these catalysts is still unclear [3, 5, 6].

2.3. Kinetics of Ozonation Processes

This section provides various methods and the basic chemical models that have been developed in previous works, and commonly used, to determine ozone decomposition rates, contribution of •OH for micropollutant removal, and overall micropollutant removal rate. In addition, intrinsic kinetic parameters, as well as previous studies, of ozonation of the two model micropollutants are presented.

2.3.1. Ozone Decomposition into Hydroxyl Radicals

Ozone is an unstable compound with a relatively short half-life, being even markedly shorter in water than in air. Factors affecting the decomposition of ozone in water are temperature, pH, ultraviolet light, and type and content of organic matter. Depending on the water quality, the half-life of ozone is in the range of seconds to hours [19]. Ozone decays through a chain reaction partly to form hydroxyl radicals (•OH). This species is the major secondary oxidant formed from ozone decomposition in water, which is fast-reacting and thus involves non-selective reactions. Due to their high reactivity, •OH have a very short half-life (e.g. less than 10 ms at an initial concentration of 10^{-4} M) [1].

Radical-Type Chain Reaction Mechanism

The mechanism and the kinetics of the elementary reactions involved in ozone decomposition have been investigated in several studies [20-22]. At low to moderate pH levels, the mechanism of Staehelin, Hoigné, and Buhler (SHB) [23] is generally accepted as the mechanism of ozone decay in aqueous solutions [24]. According to SHB mechanism, ozone transformation into •OH occurs in a radical-type chain reaction which involves the sequence of reactions shown below.

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad (2.1)$$

$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \qquad (2.2)$$

$$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -} \qquad (2.3)$$

$$HO_2^{\bullet} \rightleftharpoons H^+ + O_2^{\bullet-} \quad (2.4)$$

$$O_2^{\bullet-} + O_3 \rightarrow O_2 + O_3^{\bullet-} \quad (2.5)$$

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^{\bullet} \quad (2.6)$$

$$HO_3^{\bullet} \rightarrow \bullet OH + O_2 \quad (2.7)$$

$$\bullet OH + O_3 \rightarrow HO_2^{\bullet} + O_2 \quad (2.8)$$

From Eq. (2.1) and Eq. (2.2), it is evident that hydroxide (OH^-) and hydroperoxide (HO_2^-) ions act as initiators of the chain decomposition of ozone. It is clear that solution pH is a major factor in ozone decomposition through formation of •OH. It should be noticed that pH does not only directly affect the concentration of OH^- in solution, but it also influences acid/base equilibrium of H_2O_2 (pK_a = 11.2) and $HO_2^{\bullet}$ (pK_a = 4.7), and hence the overall reaction rate of ozone decay. According to Eq. (2.2), HO_2^-, formed during ozone decay in aqueous solution, will produce H_2O_2 under acidic pH conditions, which is only reactive in its dissociated form. Whereas OH^- exhibits a small reaction rate constant with ozone (70 $M^{-1}s^{-1}$), HO_2^- (deprotonated form of H_2O_2) shows a high reactivity towards ozone ($k_{O3} = 2.8 \times 10^6$ $M^{-1}s^{-1}$) [19]. Thus, an increase in the solution pH (>6) will result in the significant concentrations of HO_2^- (and OH^-) and therefore higher rates of •OH production. It should be noticed that H_2O_2, even when formed as a kinetically important intermediate, will only accumulate during the ozonation process if low pH levels (pH <6) are maintained [22]. As a consequence, at neutral pH values H_2O_2 can become an important initiator for the radical-type chain reaction [25]. Similarly, the perhydroxyl (or hydroperoxyl) radical ($HO_2^{\bullet}$) reacts predominantly when dissociated to the superoxide ion radical ($O_2^{\bullet-}$). These species also play an important role, since superoxide radical produced in Eq. (2.4) can lead to other reactions with ozone, propagating the ozone the reaction chain and causing more •OH to be formed.

Effect of Impurities and Catalysts

In non-pure water, the SHB radical-type chain reaction can be initiated, promoted, or inhibited by various solutes. Initiators are those species that directly react with ozone to produce $O_2^{\bullet-}$, which is key to propagating free radical species. This species reacts much more rapidly with molecular ozone than with most other solutes to yield other free radicals, such as the ozonide ion radical $O_3^{\bullet-}$, which eventually leads to the hydroxyl radical. Solutes that convert •OH into $O_2^{\bullet-}$ are known as promoters. On the other hand, inhibitors of the ozone decomposition are those species that while reacting with the hydroxyl radical do not primarily form $O_2^{\bullet-}$, thus terminating the radical chain reaction [23]. The inhibitors are also called hydroxyl radical scavengers because their presence limits or inhibits the action of these radicals on target contaminants [23, 24]. Examples of initiators found in ozone reacting systems are hydroxide ions, hydroperoxide ions, and glyoxylic acid. In the group of promoters, one can cite methanol, glyoxylic acid, and formic acid. Typical scavengers include bicarbonates and carbonates and tert-butyl alcohol (TBA). Of great interest is to notice that some solid catalysts, such as activated carbon, have been reported to act as initiators of ozone decomposition [26].

Rate of Reaction

Application of SHB mechanistic approach to determine ozone decomposition kinetics requires the knowledge of the interaction of multiple pathways as well as the concentrations of well-defined species that act as initiators, promoters, or inhibitors. As an alternative to this approach, empirical kinetic laws of different complexity describing the rate of ozone depletion have been developed [23, 24]. By this approach, the suggested rate equations are fitted to the experimental data of ozone concentration versus time obtained from a particular ozonation process. In this regard, Sotelo and coworkers [21] demonstrated that ozone self-decomposition, at different pH levels and temperatures, follows a two-term rate supported by a reaction mechanism. However, they also found that at constant pH and temperature ozone decomposition follows simple first-order kinetics with respect to ozone concentration. Thus, ozone decay rate in pure water can be expressed by:

$$-r_{\mathrm{O_3}} = -\frac{d[\mathrm{O_3}]}{dt} = k_D[\mathrm{O_3}] \tag{2.9}$$

where k_D (s^{-1}) is the pseudo first-order ozone decomposition rate constant. According to Eq. (2.9), rate constants for ozone self-decomposition could be determined from the slope of the relationship between $\ln([O_3]/[O_3]_0)$ and reaction time. After integrating, rearranging, and using the initial ozone concentration of ozone $[O_3]_0$, ozone concentration can be readily predicted by:

$$[\mathrm{O_3}] = [\mathrm{O_3}]_0 \exp(-k_D t) \tag{2.10}$$

Pseudo first-order kinetics, Eq. (2.9), has not only been used to describe ozone decomposition in pure water, but also it has been applied to predict ozone concentration in natural waters [27] as well as characterize catalytic ozonation processes involving solid catalysts [9, 28, 29]. In catalytic systems, the observed first-order rate constant with respect to ozone concentration for the overall reaction takes into consideration both the heterogeneous reaction taking place on the catalyst surface and the homogeneous reactions occurring in the aqueous phase. The following rate equation has been proposed to describe the process [7, 29]:

$$-\frac{d[\mathrm{O_3}]}{dt} = k_{D,Ho}[\mathrm{O_3}] + k_{D,He}W[\mathrm{O_3}] = \left(k_{D,Ho} + k_{D,He}W\right)[\mathrm{O_3}] = k_D[\mathrm{O_3}] \qquad (2.11)$$

where W (g $\mathrm{L^{-1}}$) represents the dose of the catalyst. Thus, a plot of k_D against W should yield a straight line of slope $k_{D},_{He}$ ($\mathrm{s^{-1}}$ $\mathrm{g^{-1}}$ L) and intercept $k_{D,Ho}$ ($\mathrm{s^{-1}}$), corresponding to the catalyst contribution and non-catalytic ozone decay rate constant, respectively.

2.3.2. Non-catalytic and Heterogeneous Catalytic Ozonation

Conventional or non-catalytic ozonation refers to typical application of ozone in water treatment processes without the addition of other chemical species. As explained above, its efficiency in removing water micropollutants is influenced by several factors such as pH and presence of radical scavengers. Depending on the mechanism, kinetics of heterogeneous catalytic ozonation systems may account for reactions of micropollutants taking place on the catalyst surface, whereas kinetics of non-catalytic ozonation process are limited to reactions in the aqueous solution. Mechanisms of reaction and kinetic formulations widely used to quantify and compare different ozonation processes are presented below.

Mechanisms of Reaction and Kinetic Formulation

An ozonation process is always based on the effect of direct and indirect reaction mechanisms as a consequence of the decomposition of ozone into •OH in water. Since these radicals have an even stronger oxidation mechanism than that of ozone, their effect on micropollutants removal must be considered. In practice, both direct and indirect oxidation reactions take place. In most cases, one reaction pathway will dominate depending on various factors, such as pH and chemical composition of the water. These reactions are generally assumed to be of second order (first order with respect to the pollutant and first order with respect to the oxidant) [24]. Thus, for an ozone-reacting micropollutant M, the chemical reaction and its rate can be represented by

$$\mathrm{O_3} + \mathrm{M} \xrightarrow{k_{\mathrm{O_3}}} \mathrm{P} \tag{2.12}$$

$$\bullet\mathrm{OH} + \mathrm{M} \xrightarrow{k_{\mathrm{OH}}} \mathrm{P} \; \mathrm{OH} \xrightarrow{\mathrm{kOH}} \tag{2.13}$$

Therefore, in a batch reactor the overall removal of M can be described by a set of two second-order rate equations [2]:

$$-\frac{d[\mathrm{M}]}{dt} = k_{O_3}[\mathrm{O_3}][\mathrm{M}] + k_{OH}[\bullet\mathrm{OH}][\mathrm{M}] \tag{2.14}$$

where k_{O3} ($\mathrm{M^{-1}s^{-1}}$) and k_{OH} ($\mathrm{M^{-1}s^{-1}}$) are reaction rate constants of the micropollutant with molecular ozone and hydroxyl radicals, respectively.

In contrast to non-catalytic and homogeneous ozonation systems, catalytic ozonation processes generally involve reactions of the micropollutants taking place on the surface of the catalyst. Thus, to determine kinetics of an ozonation process requires the elucidation of the mechanism. There are usually three possible mechanisms of catalytic ozonation in heterogeneous systems [3]. The first approach involves the adsorption of ozone on the catalyst surface leading to the formation of free radicals which react with non-adsorbed pollutant in the bulk liquid. The second reaction pathway involves adsorption of pollutant and its further reaction with non-adsorbed ozone. In the third reaction mechanism, adsorption of both ozone and pollutant and subsequent reaction between adsorbed species take place. Depending on the micropollutant, catalysts may exhibit a combination of the mentioned mechanisms, and homogeneous reactions may also play an important role in micropollutant degradation.

With regard to activated carbon, it has been observed that activated carbon acts both as an adsorbent of the organic pollutants and as a catalyst in the ozonation reaction [5, 30]. As a result of ozone interaction with AC active centers, the reduction of ozone on the activated carbon surface generates OH^- ions and H_2O_2 that enhance the ozone decomposition into •OH. Thus, the hydroxyl radicals formed are not bound to the surface of activated carbon, but they are free to react in the aqueous phase. Therefore, activated carbon is considered an initiator of the radical-type chain reaction [30-32]. Due to the nature of AC active sites, the catalytic activity of activated carbon to transform ozone into hydroxyl radicals is greatly influenced by the solution pH [6, 7]. According to Beltran and coworkers at acidic pH levels ($2<pH<6$), ozone decay rates are practically independent of the pH value without production of •OH, whereas at $pH > 6$ it increases significantly with the increase of pH that leads to the formation of •OH. However, experimental results of ozonation in the presence of AC at low pH levels have shown significant increase of micropollutant removal when compared with non-catalytic ozonation and adsorption, indicating the existence of a catalytic reaction mechanism under these conditions [30, 33]. Except for the work reported by Faria et al. [5], several studies have shown that the presence of a radical scavenger significantly reduces the rate of micropollutant removal by activated carbon catalytic ozonation. Thus, the inhibition of the process observed in the presence of bicarbonates or tert-butyl alcohol radical scavengers clearly suggests the presence and participation of •OH in the bulk liquid [33, 34].

Previous studies suggest that enhancement of ozone conversion into more reactive species is a result of the interaction between ozone and alumina active sites [3, 35]. In this case, negligible adsorption of water micropollutant on aluminum surface cannot influence the catalytic ozonation of the target compound. Recently, Qi et al [4] observed that 2,4,6-trichloroanisole, a non-dissociating compound scarcely adsorbed on alumina, was efficiently degraded by ozonation catalyzed by alumina. However, since its degradation pathway involved reactions of hydroxyl radicals mainly taking place in the bulk liquid, the presence of a radical scavenger significantly inhibited •OH and thus notably decreased the micropollutant removal rate [4]. According to this mechanism, the adsorption of organics on the catalyst's surface would not be necessary to provide the catalytic effect. Conversely, micropollutant adsorption would probably inhibit the interaction between ozone and alumina active sites due to an overlaying of hydroxyl groups. It should be noticed however that the surface of alumina can strongly coordinate with water molecules on the surface. Thus, effective adsorption of organic molecules will be limited to ionisable compounds and therefore the adsorption will be governed by the pH of point of zero charge (pH_{pzc}) of alumina, pH of the solution, and acid dissociation constants (pK_a) values of the compound [4, 36, 37]. In contrast with the results obtained with 2,4,6-trichloroanisole, experimental observations using natural organic matter [37] and fulvic acids [38], where an extensive uptake of organics on alumina surface was observed, suggest that that hydroxyl radical transformation from ozone does not occur or represent a negligible contribution to the oxidation pathway of organic species.

Although free radicals, such as hydroxyl radicals, are strong oxidative species, their reactions are not selective. Conversely, molecular ozone, also a powerful oxidant, exhibits high selectivity in reactions with water pollutants. However, its low solubility in water limits its oxidative effect. To enhance molecular ozone reactions through ozone stabilization, perfluorooctanoic acid groups immobilized on the surface of alumina (perfluorooctyl alumina) have shown to have high ozone adsorption capacity and, thus, providing ozone with a higher level of stability. PFOA is also considered to be capable of adsorbing hydrophobic organic molecules, resulting in high degradation rates of organic contaminants present in water. The working principle of this solid catalyst is similar to perfluorocarbon solvents, with ozone solubility of 10-12 times that of water, and ozone systems, which have exhibited higher removal efficiency of pharmaceuticals when compared with aqueous phase ozonation [39]. Results obtained from the ozonation of nitrobenzene, chlorobenzene, cumene, and toluene [40], gasoline compounds [10], natural organic matter [41], and humic acid [42] in the presence of PFOA indicated that the O_3/PFOA system was capable of providing higher efficiency of ozonation process and a significant degradation of water pollutants in comparison with ozonation alone. Since contribution of •OH reactions become negligible at acidic pH levels, high efficiency of catalytic ozonation assisted by PFOA has notably been observed only in acidic aqueous solutions. Similarly, under these conditions the performance of this ozonation process is not markedly affected by the presence of radical scavenger [43].

Contribution of Hydroxyl Radicals

In ozonation systems where the production of •OH is dominated by the presence of NOM or presence of catalysts, and the concentration of micropollutants or intermediates is low enough to influence the transformation of ozone into •OH, the contribution of hydroxyl radicals can be used as a method of characterizing ozonation systems. As explained in previous sections, ozone can react with micropollutants through direct reaction by molecular ozone and indirect reaction by hydroxyl radicals and elimination of a micropollutant by ozone and hydroxyl radicals can be described by a set of two second-order reactions. However, concentration of hydroxyl radicals is difficult to measure directly in aqueous solution because reactivity of hydroxyl radicals towards components in the water matrix leads to a relatively low steady-state concentration, typically $< 10^{-12}$ M. An alternative method to indirectly measure the concentration of •OH has been developed by Elovitz and von Gunten [27]. According to this approach, for a particular ozonation system the ratio of [•OH] to $[O_3]$, denoted as R_{ct} parameter, is a constant value, Eq. (2.15). It can be noticed that higher values of R_{ct} indicate that a greater fraction of the ozone is being converted into •OH. In conventional water ozonation systems, R_{ct} parameter value varies between 10^{-6} and 10^{-9}.

$$R_{ct} = \frac{[\bullet\mathrm{OH}]}{[\mathrm{O_3}]} \tag{2.15}$$

After substituting R_{ct} into Eq. (2.14) and integrating, the rate equation describing the removal of M becomes:

$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = -\left(k_{O_3} + k_{OH}R_{ct}\right)\int [\mathrm{O_3}]dt \tag{2.16}$$

Since a plot of $\ln\left([\mathrm{M}]/[\mathrm{M}]_0\right)$ versus $\int [\mathrm{O_3}]dt$ gives a straight line, R_{ct} value can be readily calculated from the slope of the straight line. Thus, from the experimentally measured decrease in concentration of micropollutant (M) and ozone and using rate constants for the reactions of M with molecular ozone and hydroxyl radical, R_{ct} values for a particular ozonation process can be estimated.

Of special interest is also to investigate the contributions of molecular ozone and hydroxyl radical to the removal of the target micropollutant. Once R_{ct} parameter is calculated, the fraction of micropollutant degraded by •OH can also be estimated by replacing [•OH] by R_{ct} $[O_3]$ into Eq. (2.14). Thus, the fraction of micropollutant degraded by •OH is defined by:

$$f_{\mathrm{OH}} = \frac{k_{OH}[\bullet\mathrm{OH}][\mathrm{B}]}{k_{O_3}[\mathrm{O_3}][\mathrm{B}] + k_{OH}[\bullet\mathrm{OH}][\mathrm{B}]} = \frac{k_{OH}R_{ct}}{k_{OH}R_{ct} + k_{O_3}} \tag{2.17}$$

Observed Reaction Rate

The reaction kinetic information available for the individual reaction steps during ozonation allows one to predict the trend of the kinetics of the chain reaction in cases where the concentrations of well-defined solutes are varied. However, formation of several intermediates during ozonation of a particular micropollutant makes the kinetics of the radical-initiation reactions too complex to perform a detailed kinetic analysis by considering kinetic parameters for the ozonation of single reaction intermediates. In addition, the observed micropollutant removal in the presence of certain catalysts results in a combination of simultaneous homogeneous and heterogeneous reactions, taking place in the bulk liquid and on alumina surface. In this regard, kinetics of catalytic ozonation systems could be described by a simplified second-order rate equation. Thus, the overall contribution of homogeneous and heterogeneous reactions to micropollutant removal by various ozonation systems is established using Eq. (2.14).

$$-\frac{d[\mathrm{M}]}{dt} = k_{obs}[\mathrm{O_3}][\mathrm{M}] \tag{2.18}$$

where k_{obs} is the apparent or observed second-order rate constant. Integrating Eq. (2.14) with respect to time and 2,4-D concentration, the rate equation describing 2,4-D removal becomes:

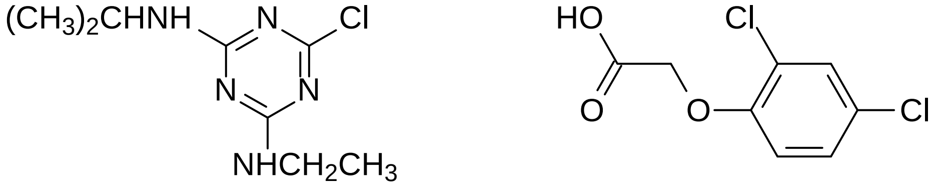
$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = -k_{obs}\int[\mathrm{O}_3]dt \tag{2.19}$$

Often, only the disappearance of the target compound is of interest so that intermediate reactions are neglected in the chemical model. In addition, direct reactions do no play a significant role in the oxidation of the target compound. Instead, the indirect reactions and the catalytic reactions involved in the production of •OH have a major effect. In this case, since R_{ct}, as well as k_{O3} and k_{OH}, is a constant value, an overall or observed second-order (first-order in micropollutant and first order in ozone) rate constant, k_{obs}, can be obtained as represented by Eq. (2.20) to describe the general kinetics of the ozonation process.

$$k_{obs} = k_{O_3} + k_{OH}R_{ct} \tag{2.20}$$

2.4. Properties of Model Compounds and Previous Ozonation Studies

The chemical structures of atrazine and 2,4-dichlorophenoxyacetic acid are shown in Figure 2.1. Atrazine has relatively low water solubility, and is therefore hydrophobic with high adsorption potential on organic matter. 2,4-D has a much higher water solubility than atrazine (890 compared to 33 mg/L [44]), and thus poses a greater threat of leaching and transport in surface runoff and groundwater. The average half-lives in environment are 10 and 60 day for 2,4-D and ATZ, respectively [44]. Therefore, these two herbicides are poorly biodegradable. Atrazine, being used in Canada since 1960, is the most frequently detected herbicide in sources of potable water in the Great Lakes Region and Lower Fraser Valley Region of British Columbia [11, 45], whereas 2,4-D, the most extensively used herbicide in the Northern Prairies for more than 50 years, has the highest concentration levels, above 1.850 μg L^{-1}, in sources (reservoirs) of potable water [13].



(a) (b)

Figure 2.1. Chemical structures of (a) atrazine and (b) 2,4-D.

Previous studies on ozonation of atrazine showed high conversion, but relatively slow rate of reaction of atrazine with ozone as compared with other pesticides. However, atrazine exhibits a high reactivity toward hydroxyl free radicals [46]. Atrazine reaction constants with molecular ozone (k_{O3}) and hydroxyl radicals (k_{OH}) range from 6.0 to 6.4 $M^{-1}s^{-1}$ and 2.4×10^{9} to 3.0×10^{9} $M^{-1}s^{-1}$, respectively [2]. Prado and Espuglas [47] compared different ozone-based AOPs to eliminate atrazine. They found that the combined O_3/H_2O_2/UV process showed a synergistic effect on the degradation rate of atrazine. For a 7×10^{-5} M (15 mg L^{-1}) atrazine concentration, complete conversion was achieved in about 40 min by both UV/O_3 and O_3/H_2O_2 systems while by using O_3/H_2O_2/UV process ATZ was decomposed in 15 min. These experiments were carried out at a neutral pH and using 0.025 M H_2O_2 and 253.7 nm, 1.85×10^{-6} einstein s^{-1} UV irradiation. Ma et al. [48] showed that the addition of Mn^{2+} also enhanced the decomposition of ozone and improved the conversion of atrazine. The authors reported complete conversion of 3×10^{-6} M (0.64 mg L^{-1}) atrazine in 4 min using a concentration of 9.1×10^{-6} M (0.5 mg L^{-1}) Mn^{2+}.

Degradation of 2,4-D by ozonation and ozone-based AOPs has also been well documented. 2,4-D reaction rate constants with molecular ozone and hydroxyl radicals are 1.46 and 5.1×10^{9} $M^{-1}s^{-1}$, respectively [49]. Meijers et al. [50] reported 95% conversion of 0.9–6.4 mg L^{-1} 2,4-D by using O_3/H_2O_2 system. Brillas et al. [51] compared the effects of O_3/UV, O_3/Fe^{2+}, and O_3/Fe^{2+}/UV systems on degrading 2,4-D. For a 230 mg L^{-1} 2,4-D concentration at 3.0 pH, 95% conversion was achieved in 6, 8, and 4 min by O_3/UV, O_3/Fe^{2+}, and O_3/Fe^{2+}/UV systems, respectively. In these experiments, and concentration of 1.0×10^{-3} M Fe^{2+} and 8.3×10^{-7} einstein min^{-1}, 250-500 nm UV irradiation were employed. In addition to the fast 2,4-D removal rates, more than 95% TOC reduction for 1.5 hours reaction was reported.

Only three works have been documented on the degradation of atrazine and 2,4-D involving heterogeneous catalysis of ozonation. Sanchez-Polo et al. [52] examined the combined effect of activated carbon and ozone in removal of atrazine. The authors reported that the main process responsible for ATZ removal was the adsorption on the surface of activated carbon, due mainly to the hydrophobic nature of ATZ. By using an ATZ stock solution of 1.02×10^{-6} M (0.22 mg L^{-1}) and a granular activated carbon dose of 0.5 g L^{-1} at pH 7 and in the presence of 8×10^{-5} M tert-butyl alcohol, a radical scavenger, ATZ was completely adsorbed within 5 min. Hu et al. [8] investigated the catalytic effects of cobalt oxide supported on ordered mesoporous zirconia for 2,4-D degradation. Although 2,4-D was hardly adsorbed on the surface of the catalyst, this catalyst was found to be highly effective not only for decomposing the parent compound, but also for mineralizing 2,4-D in aqueous solution with ozone. The authors reported a 94% TOC reduction in 20 min using an initial 2,4-D concentration of 4.52×10^{-5} M (10 mg L^{-1}) at pH 7 and 2 g L^{-1} catalyst dose (2 wt% Co). With an observed decrease over 75% in 2,4-D conversion in the presence of 1×10^{-2} M TBA, the authors concluded that the radical scavenger could trap •OH both in solution and on the surface of the catalyst. Chu et al. [53] examined the degradation of ATZ by ozonation and photo-assisted ozonation (O_3/UV) in the presence of a non-ionic surfactant (Brij 35). At pH level of 7 and an ATZ concentration of 10×10^{-5} M (22 mg L^{-1}), the degradation rates were increased by 17% for ozonation and 52% for photo-assisted ozonation by using a concentration of Brij 35 of 6.81×10^{-7} M. However, addition of only 6.6×10^{-8} M bicarbonate had a notable impact on the generation of hydroxyl radicals, which resulted in 25% reduction in atrazine removal rate at the same pH level.

None of the studies reported in homogeneous catalytic ozonation considered the negative effect of radical scavengers, and the works in heterogeneous catalytic ozonation indicated a significantly negative impact on micropollutant removal. In this regard, the present work considers the ability of the catalyst to accelerate the ozone transformation into hydroxyl radicals as well as the affinity of micropollutants for adsorption under various operating conditions, including the presence of a radical scavenger. Thus, the efficiency of activated carbon, alumina, and perfluorooctyl alumina in removing atrazine and 2,4-D is investigated.

3. EXPERIMENTAL

In this chapter, properties of the materials used in the present work are listed, and illustration of their preparation or pre-treatment is provided. In addition, experimental procedures and analytical methods performed on the reacting materials are described.

3.1. Materials

3.1.1. Model Compounds

Atrazine and 2,4-dichlorophenoxyacetic acid PESTANAL® were obtained from Sigma-Aldrich Inc. Other chemicals, supplied by Alfa Aesar, were either reagent grade or analytical, when available, and were used without further purification. Stock solutions were prepared in ultrapure Milli-Q water (18 MΩ cm^{-1}). Depending on the ozonation system, solution pH was adjusted using a mixture of hydrochloric acid/potassium hydroxide or phosphate buffer. The buffer solution was prepared using potassium hydroxide and phosphoric acid so that, after addition to the reactor, the ionic strength of the reaction solution was kept at a constant concentration of 0.10 M.

3.1.2. Catalysts Preparation

Perfluorooctyl alumina catalyst was synthesized by interaction between gamma alumina and perfluorooctanoic acid following the method described by Ebadi and coworkers [54]. Accordingly, 5 g of perfluorooctanoic acid was dissolved in 100 mL of ultrapure water, added to 10 g of gamma alumina (Al_2O_3), and stirred for 4 h at 60 °C. The solids were filtered and washed with 100 mL of 0.1 M $NaHCO_3$ solution and 200 mL of Milli-Q water. Then, the catalyst was dried at 60 °C for 4 h. Gamma alumina, 1/8" pellets, was crushed to reduce its particles size to approximately 0.5-1 mm Then the catalyst was washed with ultrapure water and dried at 60°C before use. Activated carbon, Norit ROW 0.8 mm pellets, was used without any additional treatment. Gamma alumina, perfluorooctanoic acid, and activated carbon were also provided by Alfa Aesar.

3.2. Experimental Procedures

3.2.1. Adsorption of Atrazine and 2,4-Dichlorophenoxyacetic Acid

Adsorption tests of model micropollutants on different catalysts were carried out in an 800 mL closed glass flask at room temperature. 770 mL of micropollutant solution was contacted with various masses of catalyst (60 min for atrazine and 30 min for 2,4-D). Initial concentration of atrazine and 2,4-D were 4.64×10^{-4} M and 2.26×10^{-4} M, respectively. A magnetic stirrer was used to keep the solid phase suspended in aqueous phase. Samples (2.0 mL) were withdrawn at specific intervals, and the solution was separated from the catalyst by filtration through 0.45-μm cellulose nitrate membrane and analyzed for micropollutant content. No measurable loss of pesticide on membranes was observed.

The solution pH was set at 5 using phosphate buffer with an ionic strength of 0.05M. In tests involving alumina, pH was fixed using hydrochloric acid and potassium hydroxide due to the possibility of blocking active centers on the surface of the catalyst by phosphates ions. In 2,4-D adsorption experiments, tert-buytl alcohol was added to the system at a fixed concentration of 1×10^{-4} M to maintain consistent conditions as those used for ozonation experiments.

3.2.2. Ozone Decomposition

Ozone decomposition experiments were conducted in the experimental set-up shown in Figure 3.1, at room temperature. The reactor was operated in batch mode and consisted of the same 800 mL glass flask used for adsorption tests. 770 mL of ultrapure water, taken from a Millipore system and at an adjusted pH level (phosphate or HCl/KOH), was placed in the reactor for each catalytic and non-catalytic (blank) experiment. Ozone was generated from pure oxygen feed with a laboratory ozone generator (HTU-500G, BiOzone Corp.). After the generator reached steady state, ozone gas was bubbled into the ultrapure water in the reactor until reaching the desired dissolved ozone concentration. The initial aqueous ozone concentration used was 1.04×10^{-4} M (5 mg L^{-1}) for each experiment. In catalyzed ozone decomposition experiments, catalysts were quickly introduced into the reactor, and the reactor was instantly closed. Concentration of ozone in water was continuously measured using the electrochemical (amperometric) method [1] for 30 min.

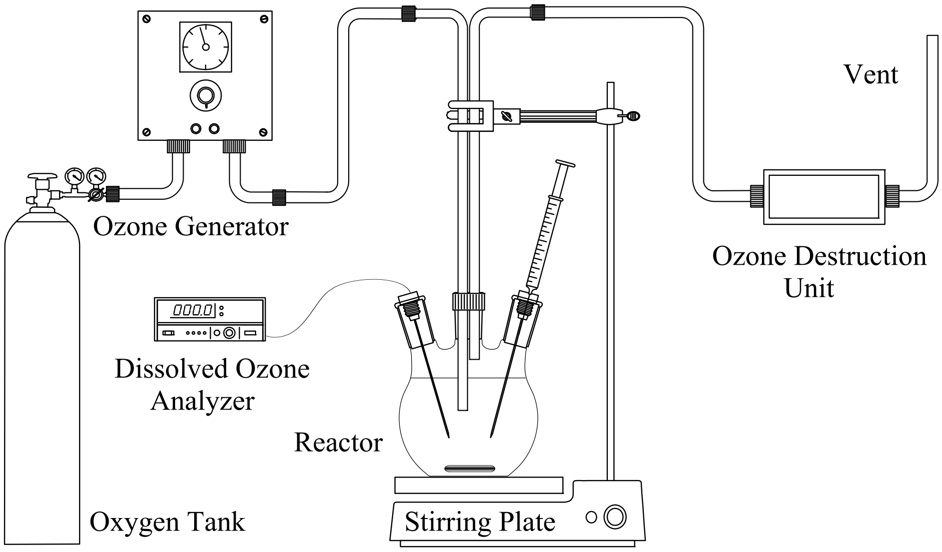


Figure 3.1. Experimental setup for ozonation experiments on model micropollutants

Ozone decomposition experiments were conducted using various amounts of catalyst. In contrast to adsorption experiments, ozone decomposition tests were run at three different pH levels (i.e. 3, 5, and 7). In addition, some ozone decomposition experiments were performed in the presence of 1×10^{-4} M TBA for each catalyst to evaluate the inhibition effect of this radical scavenger.

Ozone decomposition tests were used to determine the minimum stirring speed required to limit external mass transfer effects. For this purpose, various ozone decomposition experiments in the presence of the various catalysts were conducted with varying mixing speeds. It was observed that above 275 rpm mixing speed, agitation does not affect the rate of catalytic ozone decomposition. Thus, a stirring speed of 275 rpm was used for adsorption, ozone decomposition, and ozonation experiments.

3.2.3. Ozonation of Atrazine and 2,4-Dichlorophenoxyacetic Acid

Ozonation experiments were carried out in the same 800 mL laboratory-scale slurry reactor used for adsorption and ozone decomposition testes, operated in batch mode at room temperature (23.5±0.5°C) and 275 rpm mixing speed (Figure 3.1). These experiments were similar to the adsorption experiments except for the addition of ozone. Ozone gas was continuously fed into the reactor containing ultrapure water, at the prescribed pH level, until the desired dissolved ozone concentration was achieved. Then, micropollutant stock solution was added into the reactor so that initial ozone concentration was 1.042×10^{-4} M (5 mg L^{-1}). In atrazine ozonation experiments, the initial micropollutant concentration was 4.64×10^{-5} M (10 mg L^{-1}), whereas 2,4-D initial concentration was 2.26×10^{-5} M (5 mg L^{-1}) in ozonation tests. In catalytic ozonation experiments, a given amount of catalyst was introduced into the reactor immediately after the addition of the micropollutant. Samples (1.7 mL) were collected at different time intervals, quenched with 0.3 mL of 0.05 M Na_2SO_3 solution, and filtered through a 0.45-μm membrane.

In order to determine suitable experimental conditions, non-catalytic ozonation experiments of 2,4-D were carried out with varying the initial concentration of tert-butyl alcohol. This compound has the potential to terminate the chain reaction of ozone decomposition when reacts with hydroxyl radicals. As TBA is not significantly adsorbed on either the surface of alumina [9] or activated carbon [30], this compound is a suitable radical scavenger to inhibit the action of hydroxyl radical in the bulk liquid. As a result, other ozonation experiments were run using a relatively low initial concentration of TBA (1×10^{-4} M). In the case of atrazine, to investigate the scavenging effect on micropollutant degradation, ozonation experiments were also conducted in the presence of 0.05 M TBA.

As it was described in the Ozone Decomposition Procedure, the reaction medium was stirred with a relatively high speed. Therefore, the external mass transfer resistance was negligible. To assess internal mass transfer effects due to the intraparticle diffusion resistance, the Weisz-Prater criterion was used [24]. The Weisz-Prater parameter (*E*), defined as the ratio between the observed reaction rate and the maximum internal diffusion rate in the pores of the catalyst particles [54], is expressed by:

$$E = \frac{\left(-r_A\right)_{obs} L_p^2}{D_{eA} C_{As}} \tag{3.1}$$

where $\left(-r_A\right)_{obs}$ (M s^{-1}) is the observed catalytic reaction rate, L_p (cm) is a dimensional parameter of the catalyst particle, and D_{eA} (cm^2 s^{-1}) is the effective diffusivity. C_{As} (M) is assumed to be the concentration of reactant in the bulk solution. According to this criterion, when $E \ll 1$ the internal mass transfer is negligible and the surface reaction is the controlling step. Otherwise, internal diffusion is the controlling step of the catalytic reaction rate. Weisz-Prater parameters obtained for the different catalytic ozonation systems were at least one order of magnitude smaller than one. Thus, it was confirmed that the diffusion rate of the reactants were not controlling the overall reaction rate (for details on the calculation of Weisz-Prater parameters for the various reacting systems see Appendix C).

3.3. Analytical Methods

3.3.1. Micropollutant Concentration

Atrazine and 2,4-D concentrations were determined by high performance liquid chromatography (HPLC) (1100, Agilent Technologies Inc.) using a 150 mm × 4.6 mm C-18 column (Waters Corp.) and a diode array detector set at 226 and 239 nm, respectively. For atrazine an acetonitrile-water mixture (60:40, v/v) was used as the mobile phase at a constant flow rate of 1 mL min^{-1}, whereas for 2,4-D a methanol-phosphoric acid buffer mixture (70:30, v/v) was the carrier phase also at a isocratic flow rate of 1 mL min^{-1}.

3.3.2. Ozone Concentration, pH and Temperature

Dissolved ozone concentration was monitored using an ozone microsensor (MS-O_3, AMT Analysenmesstechnik GmbH) providing an accuracy of approximately 2% of the measuring value and with a response time of less than 5 seconds. Solution pH was measured using a high accuracy (±0.02 pH) single junction pH combination electrode (Cole-Parmer Inc.) calibrated with two standard solutions. During ozonation experiments, a data acquisition system continuously recorded the aqueous ozone concentration, pH, and temperature every two seconds (cDAQ-9172, National Instruments).

3.3.3. Catalyst Properties

Catalysts specific surface areas and average pore size were determined by physisopriton of N_2 at 77 K with an ASAP 2000 apparatus (Micromeritics Instrument Corp.). Elemental analysis of alkyl groups on PFOA was performed with a Vario EL-III CHNS instrument (Elementar Analysensysteme GmbH). The surface charge properties of activated carbon and gamma alumina were characterized by their point of zero charge (pH_{PZC}) following the mass titration method described by Noh and Schwarz [55]. Accordingly, three different initial pH solutions, varying from 3 to 11, were prepared using HNO_3 and KOH. KNO_3 was used to set a constant ionic strength of 0.01 M. For each initial pH, various containers were filled with 30 mL of the solution, and different (increasing) amounts of activated carbon, or gamma alumina, were added (ranging from 0.5 to 20 weight percent). The equilibrium pH was measured after 24 h.

3.4. Repeatability of Experimental Measurements

To evaluate the repeatability of ozone concentration measurements, ozone decomposition tests, without micropollutant, were run 3 to 5 times for the catalytic and non-catalytic systems. Although variations of ±0.1 mg L^{-1} in the initial ozone concentration were observed, changes in the pseudo firs-order ozone decomposition rate constant were in a range of ±5% the constant value for a reaction period of 30 min. In addition, non-catalytic ozonation experiments, with micropollutant, were conducted three times for both atrazine and 2,4-D. In this case, ozone decomposition rate constants were also observed to vary ±5%.

Atrazine and 2,4-D samples were analyzed in duplicate, and an average of the levels found in each of the duplicate analysis were reported. For each set of samples taken during ozonation experiments, validity of the HPLC calibration method was evaluated using standard solutions within the concentration range of the samples. These standards were always observed to vary less than ±3%. In non-catalytic ozonation experiments for atrazine and 2,4-D run in triplicate series, variations in micropollutant concentration were less than ±7%.

4. CATALYST PROPERTIES

Determining catalyst properties is crucial to ensure high catalytic activities and proper operating conditions. As a result of their high catalytic activity, ozone may either be quickly decayed into hydroxyl radicals or stabilized to enhance molecular ozone reactions. On the other hand, catalyst ability to adsorb a target micropollutant may play an important role in the reaction mechanism. Thus, degradation pathway of an organic compound may be elucidated, or the catalyst performance in removing a catalyst may be anticipated.

4.1. Catalyst Characterization

Textural and surface chemistry properties of AC, Al_2O_3, and PFOA are summarized in Table 4.1. It can be noticed that activated carbon has the largest specific surface area, which suggests lower doses may be required to achieve high ozone decomposition rates and, thus, a high •OH production rate. However, since functional groups, responsible for AC catalytic activity, are different from those present on alumina surface or PFOA, neither mass nor surface area basis provide an accurate criterion for comparative purposes. On the other hand, alumina exhibited the largest average pore diameter of 75 Å, in contrast to activated carbon's pore diameter of 44 Å. The reduction in surface and pore size of PFOA was to be expected due to the attachment of perfluorooctyl groups on alumina surface and partial pore blockage.

Table 4.1. Characterization of AC, Al_2O_3 and PFOA

Catalyst	S_{BET} (m^2 g^{-1})	Pore Size (Å)	pH_{PZC}	Surface coverage (μmol m^{-2})
PFOA	201	60	NA	4.2
Al_2O_3	223	75	7.7	NA
AC	925	19	9.8	NA

The pH of point of zero charge (pH_{pzc}) was used to characterize the catalytic activity of AC and alumina, and to ensure catalyst properties and process conditions were suitable for high ozone decomposition rates. Experimental results obtained for the determination of pH_{PZC} of activated carbon (a) and alumina (b), by mass titration (as described in the Experimental Section), are presented in Figure 4.1. It can be observed that the point of zero charge of activated carbon is notably higher than that of alumina. However, pH_{PZC} values for these two catalysts have different interpretations.

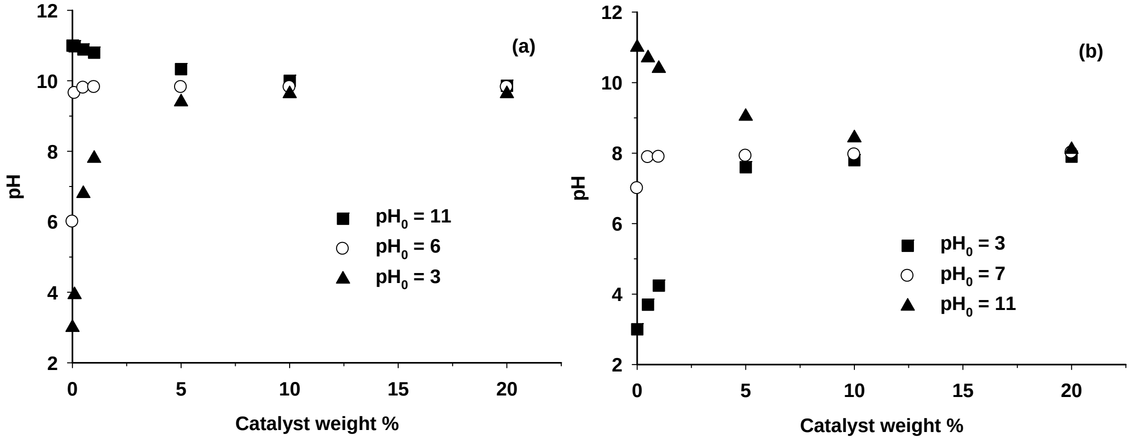


Figure 4.1. Determination of point of zero charge for activated carbon (a) and alumina (b)

The significance of the pH_{PZC} in the catalytic activity of activated carbon can be understood from the mechanism of interaction between ozone and activated carbon surface, proposed by Rivera-Utrilla and coworkers [32]. According to the authors, the electrons of the carbon basal planes and the oxygenated basic groups (chromene- and pyrone-like), Figure 4.2, acting as Lewis bases and present on the surface of activated carbon, are mainly responsible for the fast ozone decomposition in aqueous medium [26, 32]. Experimental evidence indicate that in connection with the density of basic oxygenated groups, activated carbons with high pH_{PZC} values exhibit a stronger catalytic activity to convert ozone into •OH radicals [5, 6, 28]. Therefore, selection of an activated carbon with highly basic character, such as Norit^{TM}, allowed for a proper evaluation and comparison with other catalysts.

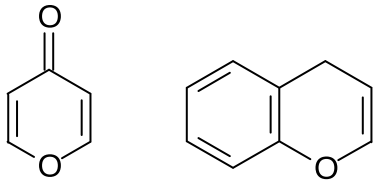


Figure 4.2. Pyrone (left) and chromene (right) structures

Because of the nature of AC active sites, the catalytic activity of activated carbon to transform ozone into hydroxyl radicals is greatly influenced by the solution pH [6, 7]. Beltran et al. [7] studied the effect of solution pH on the ozone decomposition promoted by a commercial activated carbon, and found that in the pH range of 2 to 6, the apparent first-order rate constant is practically independent of the pH value without production of •OH. Whereas at pH>6 the apparent first-order rate constant increases significantly with the increase of pH that leads to the generation of •OH. Similar results were reported by Alvarez et al. [6] using activated carbon produced from cherry stones. However, experimental results of ozonation in the presence of activated carbon at low pH levels have shown significant increase of micropollutant removal when compared with non-catalytic ozonation and adsorption, indicating the existence of a catalytic reaction mechanism under acidic conditions [30, 33].

With regard to alumina, hydroxyl groups (OH) present on alumina surfaces are thought to be the catalytic centers [3]. When aluminum oxide is introduced into water, it strongly adsorbs H_2O molecules. This chemisorption process of water on aluminum oxide surfaces involve a reaction between the aluminum ion, an electron acceptor (Lewis acid), and the hydroxyl ion, its electron donor (Lewis base). Therefore, the activity of aluminum oxide in catalyzing ozone decay is related to the surface acid–base properties of aluminum oxide [9]. Thus, surface hydroxyl groups play an important role in the acid–base properties of aluminum oxides as it relates to pH_{PZC}.

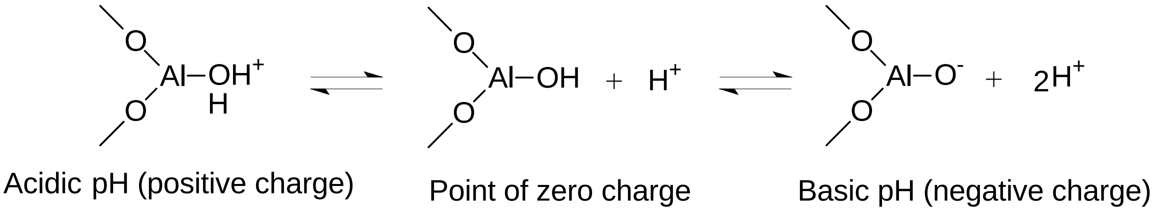


Figure 4.3. Effect of point of zero charge on the surface hydroxyl groups on alumina [56]

Experimental evidence indicates that in a solution with a pH about the same as alumina pH_{PZC}, alumina exhibits its maximum activity [9]. This observation can be explained by the fact that at pH_{PZC} the amount of non-dissociated hydroxyl groups, which are responsible for alumina activity, reaches a maximum value, as shown in Figure 4.3. However, decrease of density of hydroxyl ions on the surface starts from the pH_{PZC} in both acidic and basic directions. Hence, at pH levels far below or above pH_{PZC} hydroxyl groups are in ionized forms [56]. In view of the value of pH_{PZC} of the catalyst selected, the strongest activity of gamma alumina to decompose ozone into hydroxyl radicals is expected to be at about neutral pH. It should be noticed however that some inorganic anions in the aqueous phase can adsorb on the surface of aluminum oxide through ligand exchange with surface hydroxyl groups. In this case, high concentrations of inorganic anions, such as phosphates, should be avoided to prevent the blockage of alumina active centers.

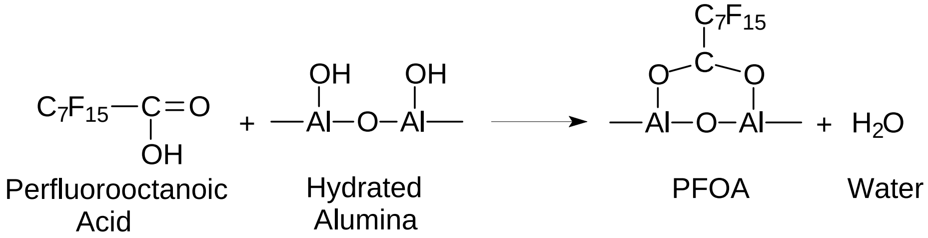


Figure 4.4. Illustration of perflurrooctyl alumina preparation [54]

PFOA was prepared by binding perfluorooctanoic acid to the surface of alumina, which prevents perfluorinated molecules from dissolution into an aqueous phase (Figure 4.4). These perfluorinated groups are thought to adsorb ozone and thus enhance ozone stability and solubility. Since these alkyl groups act as an ozone-stabilizing agent, they do not decompose ozone. It is believed that oxidation reactions take place on the surface of PFOA. Micropollutants are adsorbed on the PFOA surface, and subsequently oxidized by molecular ozone adsorbed on PFOA or dissolved in the aqueous solution [40]. Therefore, the higher the surface coverage (α), the larger the amount of ozone adsorbed and micropollutant adsorption capacity. The α value was determined using a material balance based on the carbon content and the number of carbon atoms per perfluorooctyl group (for details on the calculation of perfluorooctyl groups on PFOA see Appendix A). The perfluorooctyl surface coverage obtained of 4.2 μmol m^{-2} is in agreement with previous catalysts showing marked catalytic activity [43, 54].

4.2. Adsorption of Atrazine and 2,4-Dichloropehnoxyacetic Acid on Catalysts

In addition to their frequent detection in sources of drinking water, atrazine and 2,4-D exhibit contrasting adsorption properties, which is of great utility to discern the role that micropollutant adsorption plays in catalytic ozonation**.** While 2,4-D dissociates completely in water at a pH above 2.65, atrazine retains its molecular form in the wide range of pH under investigation (3<pH<7). Thus, these two micropollutants may exhibit different affinity towards adsorbents, particularly alumina and modified alumina (PFOA). Under the experimental conditions examined, alumina acts as an anion exchanger, whereas PFOA tends to adsorb non-polar species. On the other hand, activated carbon is an excellent adsorbent of organic micropollutants, showing a strong affinity for a great variety of organic functional groups.

To quantify and compare the adsorption tendency of catalysts towards model micropollutants, uptake of atrazine and 2,4-D on the different catalysts surface was studied and expressed using second-order kinetics (first-order with respect to micropollutant concentration and first-order with respect to catalyst dose):

$$-\frac{d[\mathrm{M}]}{dt} = k_a[\mathrm{M}]\ \mathrm{W} \tag{4.1}$$

where k_a (L g^{-1} s^{-1}) is the adsorption rate constant, [M] is the concentration of micropollutant (M), and W is the mass of adsorbent per litre of solution (g L^{-1}).

Results obtained for adsorption of atrazine and 2,4-D using a wide range of catalyst doses are presented in Table 4.2. It can be noticed that atrazine is more rapidly adsorbed on activated carbon when compared with alumina and perfluorooctyl alumina. Accordingly, the adsorption rate constant for activated carbon is about three and two orders of magnitude higher than those of alumina and perfluorooctyl alumina, respectively. It is interesting to note that modification of alumina surface results in a new material with a notable affinity towards atrazine. This observation can be explained by the fact that atrazine is a hydrophobic compound, which does not dissociates in water at moderate pH levels. Thus, although atrazine adsorbs significantly on activated carbon and perfluorooctyl alumina, its uptake on alumina surface is practically negligible.

Table 4.2. First-order adsorption rate constants of atrazine and 2,4-D on the different catalysts. $[ATZ]_0 = 4.65\times10^{-5}$ M (10 mg L^{-1}), $[2,4\text{-}D]_0 = 2.26\times10^{-5}$ M (5 mg L^{-1}), pH = 5.

Catalyst	Catalyst	Dose range (g L^{-1})	k_a (L g^{-1} s^{-1})
ATZ	AC	0 – 1	2.13×10^{-4}
	Al_2O_3	0 – 8	2.06×10^{-7}
	PFOA	0 – 8	6.88×10^{-6}
2,4-D	AC	0 – 1	2.56×10^{-4}
	Al_2O_3	0 – 8	8.28×10^{-5}
	PFOA	0 – 8	1.46×10^{-7}

Results obtained for the adsorption of 2,4-D on AC, Al_2O_3, and PFOA are also presented in Table 4.2. It can be observed that, as opposed to atrazine, 2,4-D is more rapidly adsorbed on alumina. This is to be expected as at pH levels beyond its pK_a 2,4-D forms anions that exhibit great affinity for alumina surface. For the same reason, uptake of 2,4-D on PFOA hydrophobic surface is negligible. Similar to atrazine adsorption, activated carbon was found to be the adsorbent with the fastest adsorption rate of 2,4-D.

These observations about catalyst adsorptive properties, with respect to atrazine and 2,4-D, is valuable to understand the role of micropollutant adsorption on the reaction pathway. However, micropollutant removal, ability to transform ozone into •OH, and effect of radical scavenger are also crucial in elucidating the kinetics of catalytic ozonation, as discussed in the next three chapters.

5. OZONE DECOMPOSITION

As mentioned in the Background Section, some catalysts are believed to enhance the transformation of ozone into hydroxyl radicals. However, their ability to accelerate ozone decomposition is affected by various factors, especially solution pH. Since removal of micropollutants via hydroxyl radicals may have a major contribution, the influence of major operating parameters on the ozone decomposition rate is crucial to determine their significance to target pollutant degradation. Thus, ozone decomposition experiments, in absence and presence of catalyst, were conducted under various conditions. In the present chapter, the results obtained for different ozonation systems are presented and discussed separately.

5.1. Ozone Self-Decomposition

In order to assess the influence of the catalysts under investigation in transforming ozone into •OH, self-decomposition of ozone in water was studied under various operating conditions. The major factors affecting the ozone decay chain reaction were solution pH, presence of phosphate buffer, and presence of radical scavenger. Due to fast ozone depletion observed under neutral pH conditions, duration of ozone decomposition experiments was 30 min over the pH range 3-7.

5.1.1. Effect of pH

Ozone self-decomposition at three different pH levels is presented in Figure 5.1. It can be seen that ozone decomposition rate increases with increasing pH. As described in the Background Section, in pure water hydroxyl ions, which act as initiators of ozone decay, are responsible for ozone decay into •OH. Therefore, as the pH of the medium is raised, the rate of ozone decomposition is expected to increase. However, from pH 5 to 7 a sudden increment of ozone depletion rate was observed (Figure 5.1). This can be explained by the fact that the radical-type chain reaction of ozone decomposition also involves the formation of H_2O_2 (Equations (2.1)-(2.3)), which remains mostly in its molecular form under acidic conditions. At pH levels above 6, an increase in pH results in significantly higher concentrations of HO_2- (and OH-), and therefore higher rates of •OH production [22]. As a consequence, at neutral pH values H_2O_2 is an important initiator for the free-radical chain-reaction which leads to accelerated decomposition of aqueous ozone [25].

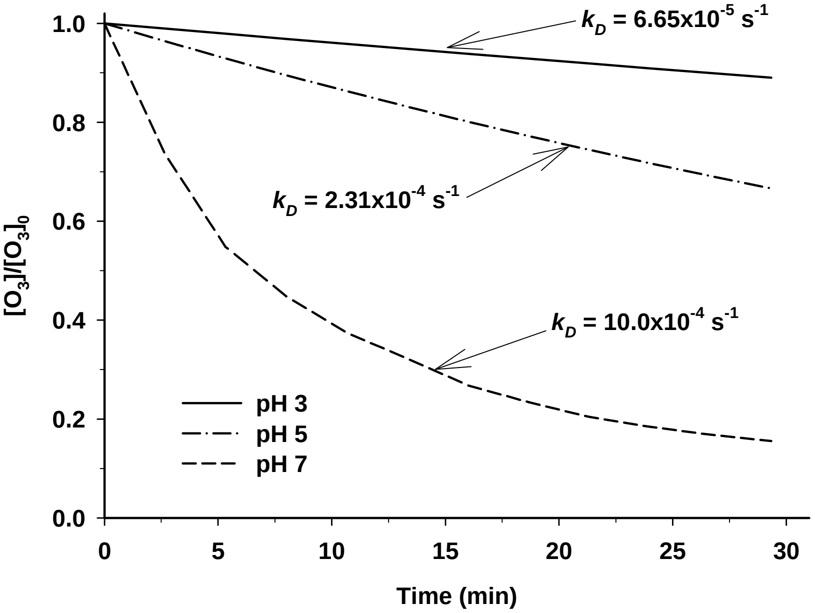


Figure 5.1. Effect of pH on self-decomposition of ozone in non-buffered ultrapure water. $[O_3]_0 = 1.042\times10^{-4}$ M (for details on the determination of pseudo first-order rate ozone decomposition constants see Appendix B)

5.1.2. Effect of Phosphate Buffer

In order to assess the influence of pH control by buffering on the ozone decomposition rates, ozone decomposition experiments were performed with two different pH control solutions: HCl/KOH and phosphate buffer. As illustrated in Figure 5.2, phosphate buffer had a marked effect on ozone decay at pH 7. Under these conditions, ozone decomposition is accelerated by OH^- and HO_2^- formed in the radical-type chain reaction, resulted in a high production of •OH. Phosphate species ($H_3PO_4/H_2PO_4^-/HPO_4^{-2}$) do not consume ozone, and thus are commonly used as buffers in ozonation systems [57]. However, it should be noticed that they react with •OH, thus acting as a hydroxyl radical scavenger [57].

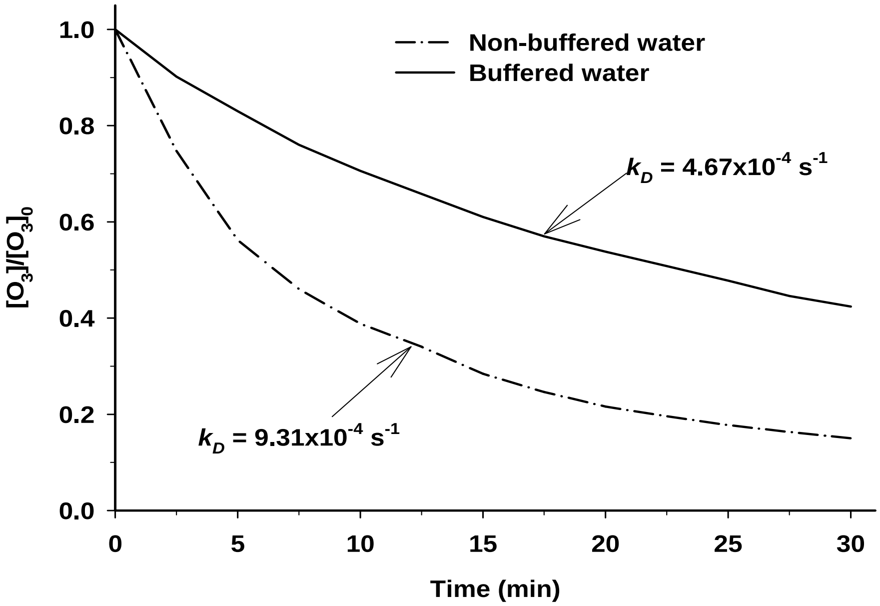


Figure 5.2. Effect of buffer on ozone self-decomposition. $[O_3]_0 = 1.042\times10^{-4}$ M, ionic strength (buffer) = 0.05 M, pH = 7

For consistency of the experimental results, the buffering of the medium at various pH levels was established using a constant ionic strength of 0.05 M, when required. On the other hand, chloride (Cl^-) consumes ozone with an apparent rate constant of only 0.003 M^{-1} s^{-1} when measured above pH 2, and •OH produced from decomposed ozone cannot oxide Cl^- in acidic or neutral medium [57].

5.1.3. Effect of Radical Scavenger

Radical scavengers are species that remove hydroxyl radicals produced during ozone decomposition without generating the key free radical (ozone-selective) superoxide ion radical ($O_2^{\bullet-}$), therefore terminating the radical chain reaction. In the present study, tert-butyl alcohol (TBA) has been used as an effective radical scavenger, which is scarcely adsorbed on activated carbon [30] and alumina [4]. In addition, TBA was observed not to affect solution pH.

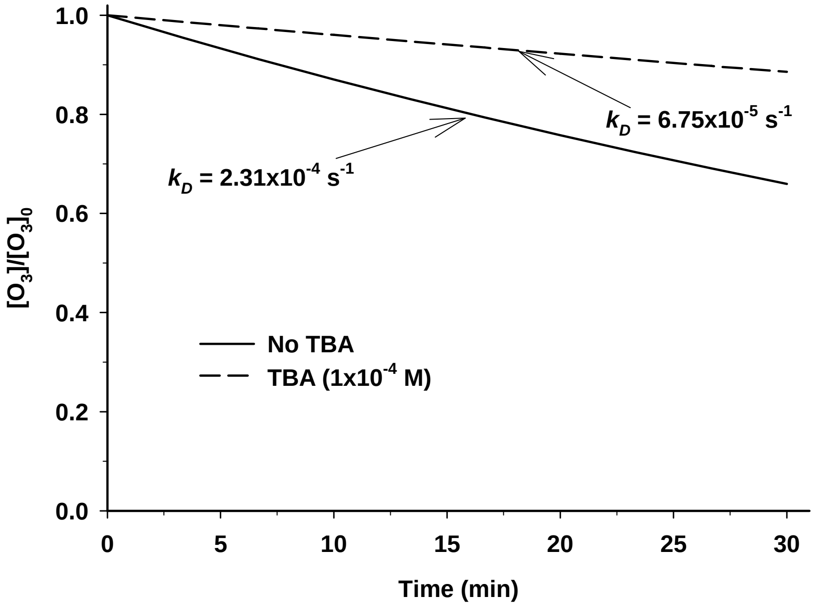


Figure 5.3. Effect of radical scavenger on ozone self-decomposition in non-buffered ultrapure water. $[O_3]_0 = 1.042\times10^{-4}$ M, $[TBA]_0 = 1\times10^{-4}$ M, pH = 5, ionic strength (buffer) = 0.05 M

The influence of the presence of TBA on ozone self-decomposition rate at pH 5 is illustrated in Figure 5.3. As can be observed, an initial concentration of 1×10^{-4} M TBA is sufficient to reduce ozone depletion from 30% to less than 10% after 30 min of reaction time. It should be noticed that as the solution pH is raised, the inhibition effect of radical scavenger is more significant, as production of hydroxyl radicals is accelerated.

5.2. Ozone Decomposition in the Presence of Activated Carbon

In addition to impurities commonly found in natural waters, catalysts may also be able to enhance ozone decay. Thus, the catalytic ability of a catalyst to convert ozone into hydroxyl radicals is an important aspect that must be studied to anticipate its performance in a particular ozonation process. Previous studies indicate that the main variables that affect the ability of activated carbon to transform ozone into •OH are solution pH, the presence of radical scavenger, and catalyst dose [6, 7, 28]. Since activated carbon exhibited a great activity towards ozone decomposition, doses ranging from 0.25 to 1.0 g L^{-1} were selected so that •OH production rate was notably high, and enough dissolved ozone ($[O_3]_0 = 1.04 \times10^{-4}$ M (5 mg L^{-1})) was available for reaction periods between 10 and 30 min at pH levels of 3, 5, and 7. As phosphate buffer did not significantly affect activated carbon active sites, and this catalyst rapidly altered the solution pH, experiments involving activated carbon were performed in a buffered medium.

5.2.1. Effect of pH

Effect of pH on ozone decomposition catalyzed by activated carbon (0.5 g L^{-1}) is illustrated in Figure 5.4. It can be observed that the production of •OH was enhanced by the presence of activated carbon at all pH levels. However, a clear relationship between pH and catalytic activity was not observed. As can be seen in Figure 5.4, at pH 5 ozone is depleted at a lower rate than at pH 3 and 7. This observation suggests that ozone interaction with the activated carbon active sites follows different mechanism depending on the solution pH. According to Beltran and coworkers [7], in acidic medium and in the presence of activated carbon the initiation step of ozone decomposition is the same as in gas phase and does not depend on the concentration of OH^- ions, whereas in neutral and basic media ozone decomposition rate constant is a strong function of solution pH. As a result, at low pH level, molecular ozone is directly adsorbed on AC active sites, whereas at neutral and basic solutions ozone reacts with adsorbed hydroxyl groups.

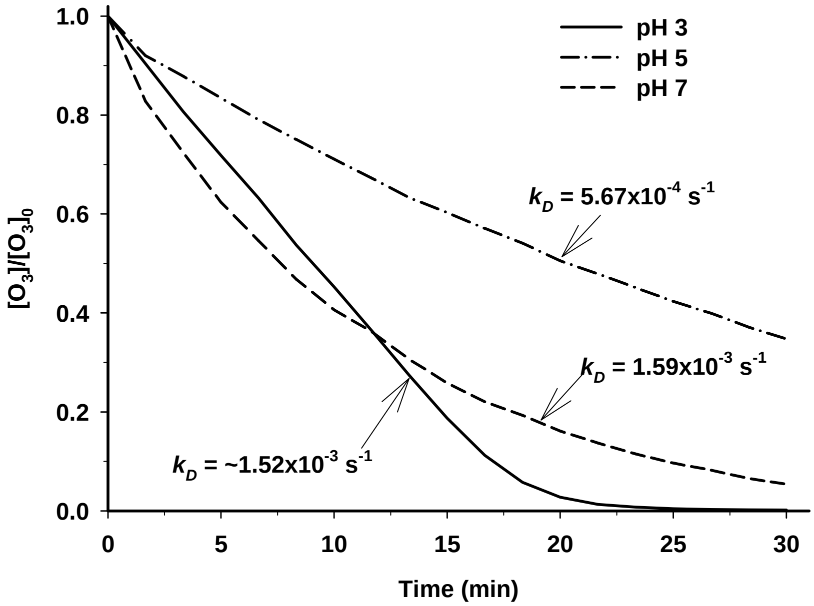


Figure 5.4. Effect of pH on ozone decomposition catalyzed by activated carbon. $[O_3]_0 = 1.042\times10^{-4}$ M, AC = 0.5 g L^{-1}, ionic strength (buffer) = 0.05 M

On the other hand, it has been proposed that the reduction of ozone on the activated carbon surface generates OH^- ions and H_2O_2 that initiate the ozone decomposition into •OH [26]. Therefore, the strong increase in catalytic activity of activated carbon observed from pH 5 to 7 can be explained by the presence of a higher concentration of HO_2^- resulting from the formation of H_2O_2 on surface active sites and its subsequent dissociation. This finding also suggests that for the strong catalytic activity observed at pH 3 a different mechanism must take place, therefore indicating the existence of two distinct mechanisms at neutral and highly acidic pH levels. Thus, the low catalytic activity observed at pH 5 may be attributed to the absence of a predominant mechanism and the hindrance produced by the combined action of two different reaction pathways.

5.2.2. Effect of Scavenger

Some impurities present in surface water may inhibit the action of hydroxyl radicals produced during ozone decomposition. Thus, a large fraction of •OH, being generated from ozone, may be trapped by radical scavengers present in the water matrix, and therefore they may not be available for micropollutant elimination. Of primary importance is the catalyst ability to maintain a high production rate of •OH or develop a more efficient reaction pathway through micropollutant adsorption.

As catalytic activity of activated carbon to convert ozone into hydroxyl radicals is greatly affected by solution pH, effect of radical scavenger was assessed a different pH levels. As can be seen in Figure 5.5, ozone decay rate at pH 3 and 7 was markedly inhibited by tert-butyl alcohol. However, only at pH 5, the rate of ozone decomposition is practically unaffected by the presence of the TBA. This observation relates to the previous finding that interaction of ozone with activated carbon catalytic centers follow different pathways at pH levels 3, 5, and 7. It should be noticed that as the inhibition effect of TBA on ozone decay is more significant at pH 3, it can be inferred that reactions in the bulk play a major role at this acidic levels.

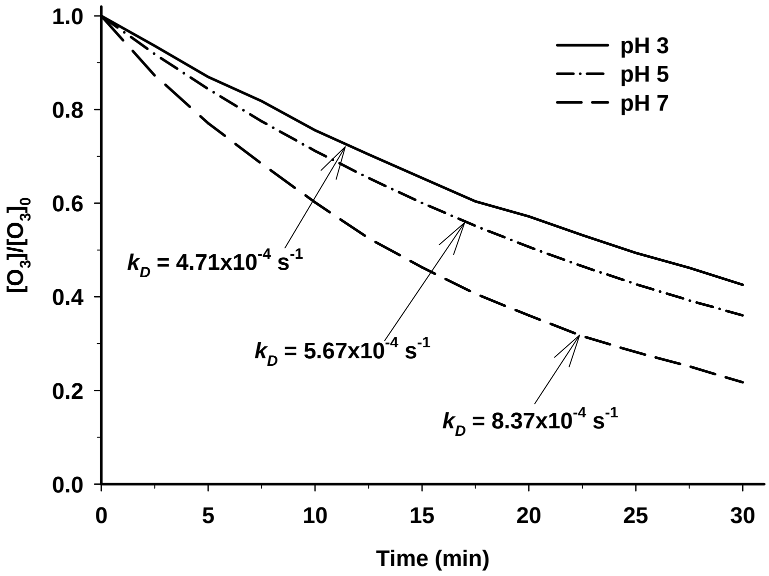


Figure 5.5. Effect of radical scavenger on the ozone decomposition catalyzed by activated carbon. $[O_3]_0 = 1.042\times10^{-4}$ M, ionic strength (buffer) = 0.05 M, $[TBA]_0 = 1\times10^{-4}$ M

5.2.3. Effect of Catalyst Dose

Previous studies suggest that a minimal AC dose or optimal dose range [6, 28] determines the performance of an ozonation process catalyzed by AC. It should be noticed that these findings were observed under various operating conditions. Minimal catalyst dose was required when introducing a radical scavenger into the reaction system [28], and optimal dose range was determined using a wide range of catalyst dose (0.1-2.0 g L^{-1}) [6]. For these reason, the effect of catalyst dose on ozone decay catalyzed by activated carbon in the range of 0.25 to 1.0 g L^{-1} was investigated at pH 7.

As shown in Figure 5.6, the pseudo first-order ozone decomposition rate constant increases linearly with increasing amounts of activated carbon. Thus, in this dose range AC catalytic activity is proportional to the surface area and availability of catalyst active centers.

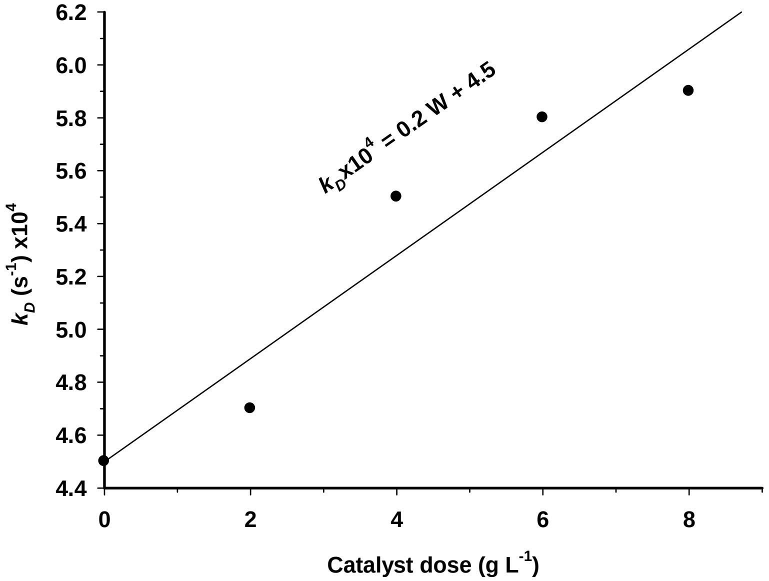


Figure 5.6. Effect of catalyst dose on ozone decomposition rate. $[O_3]_0 = 1.042\times10^{-4}$ M, ionic strength (buffer) = 0.05 M, pH = 7

5.3. Ozone Decomposition in the Presence of Alumina

Due to the special surface characteristics and structure of aluminum oxides, their applications in drinking water and wastewater treatment are increasing. Although alumina has also been used as a support for catalysts in ozone applications [58, 59], in some cases it has been found that the real role of the deposit metal on alumina is not clear and alumina as a support alone may be responsible for the improvement of the ozonation process [18]. It is believed that ozone decomposes on alumina as a result of ozone interaction with the metal oxide surface producing free radicals [3]. However, experimental evidence indicates that the ability of alumina to convert ozone into hydroxyl radical is strongly affected by the presence of inorganic anions such as phosphates, solution pH, inhibition of radical scavengers, and catalyst dose [9].

5.3.1. Effect of Phosphate Buffer

Anions such as F^- and PO_4^{3-} strongly adsorb on the surface of alumina through the formation of complexes. It is therefore suspected that hard Lewis bases such as fluoride and phosphate might, due to their high adsorption affinity towards alumina, lower the activity of the catalyst [37]. For this reason, the effect of pH control with phosphate buffer on ozone decomposition catalyzed by alumina was examined.

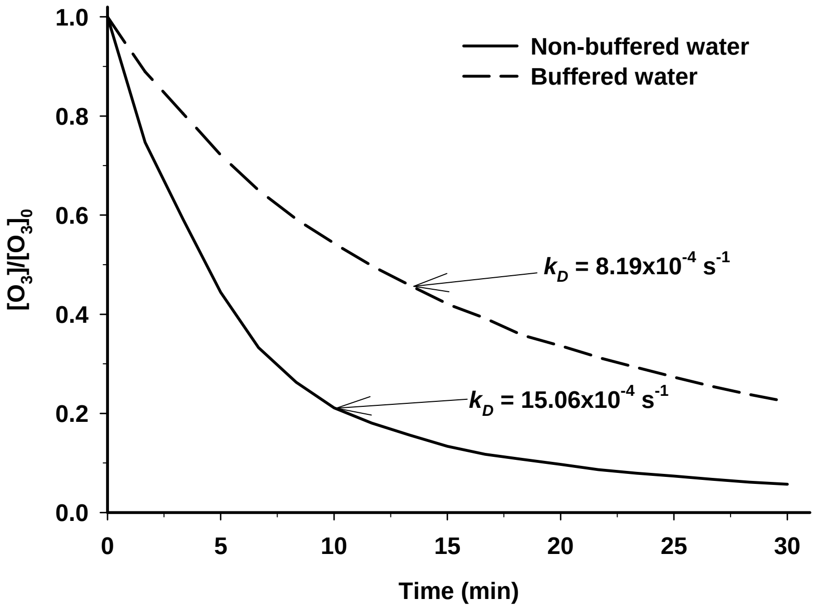


Figure 5.7. Effect of phosphate ions on ozone decomposition catalyzed by alumina. $[O_3]_0 = 1.042\times10^{-4}$ M, $Al_2O_3 = 4$ g L^{-1}, ionic strength (phosphate) = 0.05 M, pH = 7

As can be observed in Figure 5.7, the presence of phosphate buffer notably reduces ozone decay rate. This is to be expected as phosphate ions exhibit high affinity towards alumina surface, which results in blocking alumina active centers for interaction with ozone [60]. Therefore, in experiments on ozone decomposition and ozonation of model micropollutants in the presence of alumina, solution pH was controlled using an HCl/KOH solution instead of phosphate buffer.

5.3.2. Effect of pH

As the density of hydroxyl groups on alumina surface dictates its ability of transform ozone into hydroxyl radicals, solution pH plays a major role in its catalytic activity. Reduction of ozone concentration with time in the presence of 4 g L^{-1} at pH 3, 5, and 7 is depicted in Figure 5.8. When comparing with ozone self-decomposition at various pH levels (Figure 5.1), it can be noticed that the rate of ozone decomposition did not increase significantly with the addition of alumina and increasing pH level, except at neutral pH.

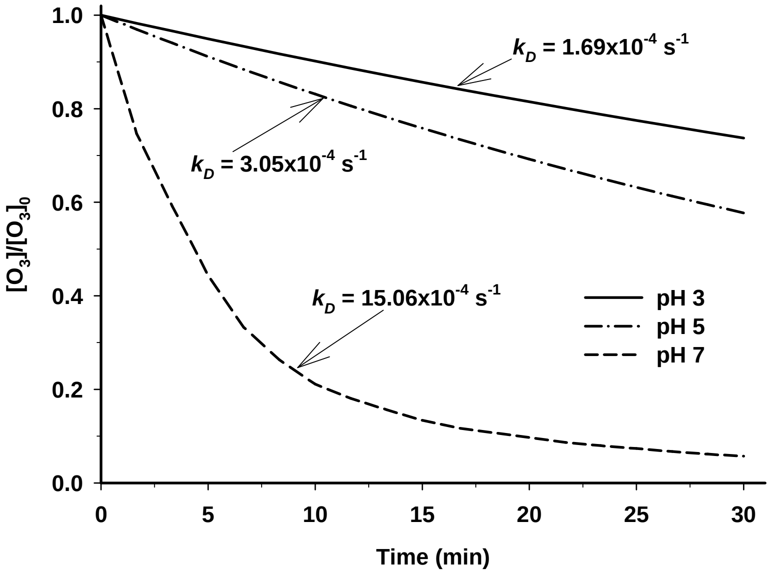


Figure 5.8. Effect of pH on ozone decomposition catalyzed by alumina. Al_2O_3 = 8 g L^{-1}

This significant increase in ozone decay rate at neutral pH can be explained by changes on alumina surface.

$$AlOH_2^+ \rightleftharpoons AlOH + H^+ \rightleftharpoons AlO^- + 2H^+ \tag{5.1}$$

At a solution pH close to alumina pH_{PZC} (7.7), the surface charges of aluminum oxide achieved proton balance, i.e. the net surface charge is approximately zero. As shown in Equation (5.1), under acidic conditions ($pH<pH_{PZC}$), the surfaces of metal oxides are

electro-positive, whereas under basic conditions ($pH>pH_{PZC}$), the surfaces of metal oxides are electronegative [35]. Although in the present work only acidic and neutral conditions were examined, the great improvement in ozone decay rate at pH 7 indicates the strong influence of solution pH on alumina hydroxyl groups.

5.3.3. Effect of Radical Scavenger

Influence of TBA on alumina catalytic activity to decompose ozone was examined at pH 5. As shown in Figure 5.9, the presence of a radical scavenger greatly affects the efficiency of alumina to transform ozone into hydroxyl radicals.

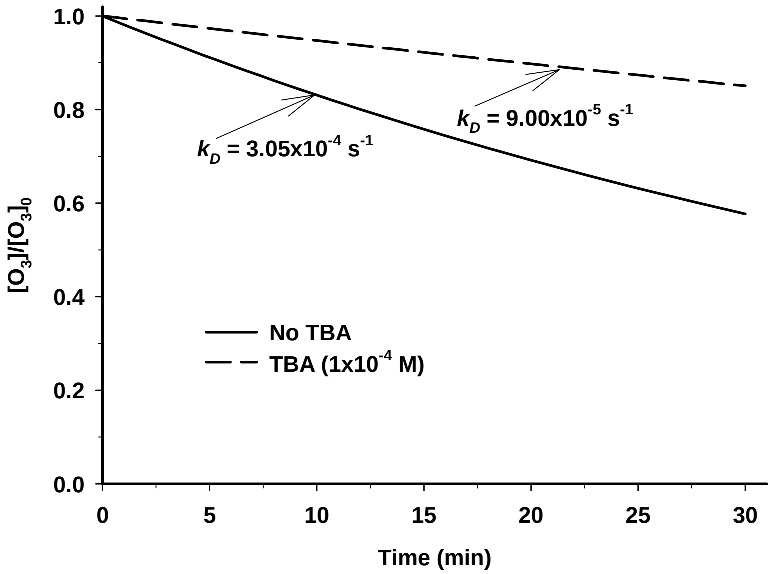


Figure 5.9. Influence of TBA on the ozone decay catalyzed by alumina. $[O_3]_0 = 1.042\times10^{-4}$ M, $Al_2O_3 = 8\ g\ L^{-1}$, pH = 5

As TBA scarcely adsorbs on alumina, this observation does not relates to the blockage of alumina active sites by the radical scavenger. Instead, it indicates the central importance of the ozone decomposition radical-type reaction, which develops in the aqueous solutions.

5.3.4. Effect of Catalyst Dose

At pH 7, alumina exhibited a superior performance, and increasing amounts of catalyst showed a trend towards high ozone decay rates. As can be seen in Figure 5.10, in the dose range from 2 to 8 g L^{-1} pseudo firs-order zone decay rate constant clearly increased linearly with increasing catalyst dose. Interestingly, the intercept of the resulting straight line give a k_D value practically the same as the one obtained for self-decomposition under identical conditions. In a previous work, a linear relation between catalyst dose and k_D was also reported for various aluminum oxides [9, 35].

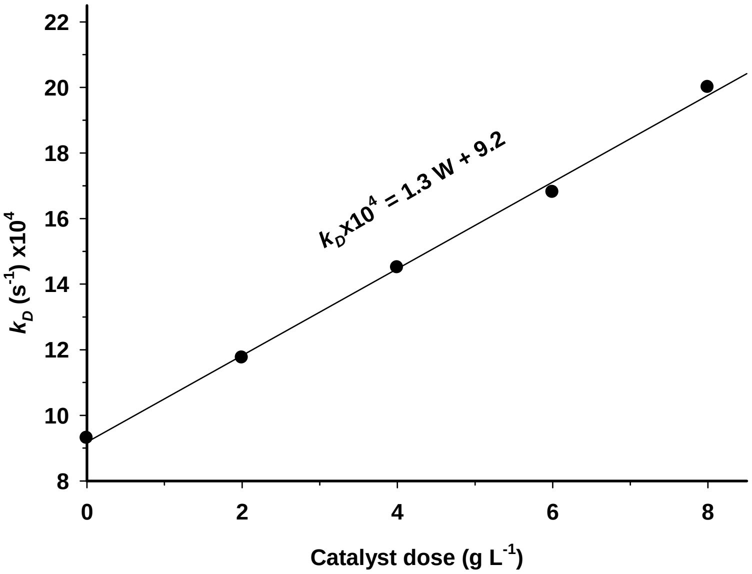


Figure 5.10. Effect of alumina dose on the pseudo first-order ozone decomposition rate constant. $[O_3]_0 = 1.042\times10^{-4}$ M, pH = 7

5.4. Ozone Decomposition in the Presence of Perfluorooctyl Alumina

Alumina covered with a monomolecular layer of non-polar perfluorinated alkyl chains is not expected to significantly increase ozone decay rates. Conversely, perfluorinated groups are expected to adsorb ozone and enhance its stability. However, uptake of ozone on PFOA surface and/or alumina bare surfaces may induce ozone disappearance at relatively low but noticeable rates. Experimental results on kinetics of ozone decomposition catalyzed by PFOA, in batch systems, have not been previously reported so that the effect of operating parameters is unknown. Therefore, for consistency the effects of solution pH, presence of radical scavenger, and catalyst dose on ozone decay were examined.

5.4.1. Effect of pH

Results of ozone decomposition in the presence of PFOA at various pH levels are depicted in Figure 5.11. It can be noticed that ozone decomposition rate increased with increasing pH value of the medium.

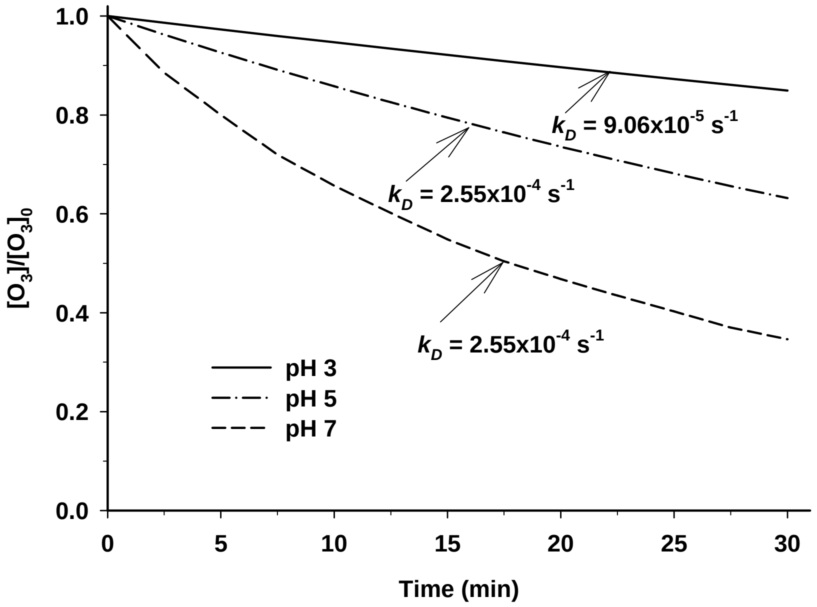


Figure 5.11. Effect of solution pH on ozone decomposition in the presence of PFOA. $[O_3]_0 = 1.042\times10^{-4}$ M, PFOA = 8 g L^{-1}, ionic strength (buffer) = 0.05 M

When compared with results shown in Figure 5.1, it is evident that PFOA did not significantly enhance the transformation of ozone into hydroxyl radicals. However, a close examination of the pseudo first-order rate constants indicates a slight increase in the ozone disappearance.

5.4.2. Effect of Radical Scavenger

Reduction of ozone concentration in the presence of TBA and using a dose of 4 g L^{-1} PFOA is shown in Figure 5.12. When compared with Figure 5.3, no noticeable difference in ozone concentration profiles can be appreciated. This is to be expected as PFOA is thought not to promote ozone decomposition, and ozone decomposition radical-type chain reaction is governed by reactions taking place in the bulk liquid. Therefore, ozone decay rates remain almost unaffected in the presence of this catalyst.

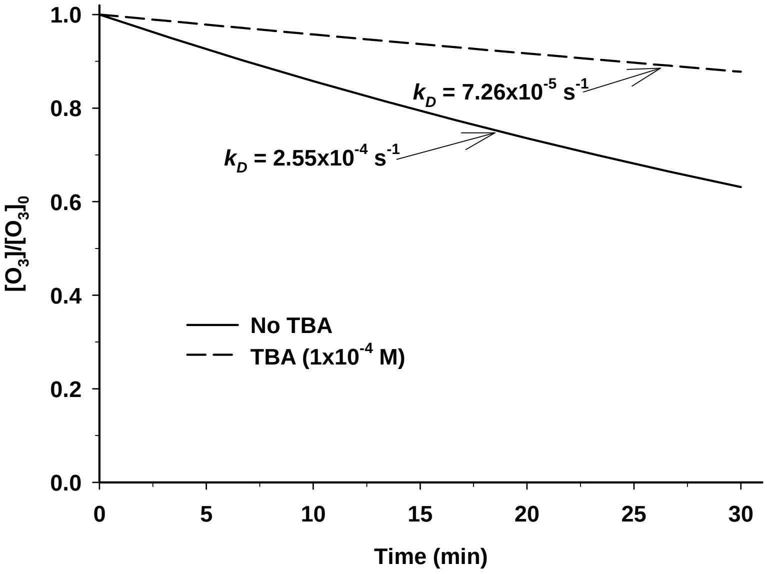


Figure 5.12. Influence of radical scavenger on the decomposition of ozone in the presence of PFOA. $[O_3]_0 = 1.042\times10^{-4}$ M, PFOA = 8 g L^{-1}, ionic strength (buffer) = 0.05 M, pH = 5

5.4.3. Effect of Catalyst Dose

Influence of catalyst dose was investigated using a dose range between 2 and 8 g L^{-1} at pH 7. Kinetics presented in Figure 5.13 shows that as catalyst dose is raised, pseudo first-order ozone decay rate constant increases. However, when compared with activated carbon and alumina catalysts, the ability of PFOA to reduce ozone concentration into the reacting system is negligible. The minor influence on ozone decay rate may be explained by two different phenomena: decomposition of ozone on alumina bare surfaces or gradual uptake of ozone on perfluorinated groups.

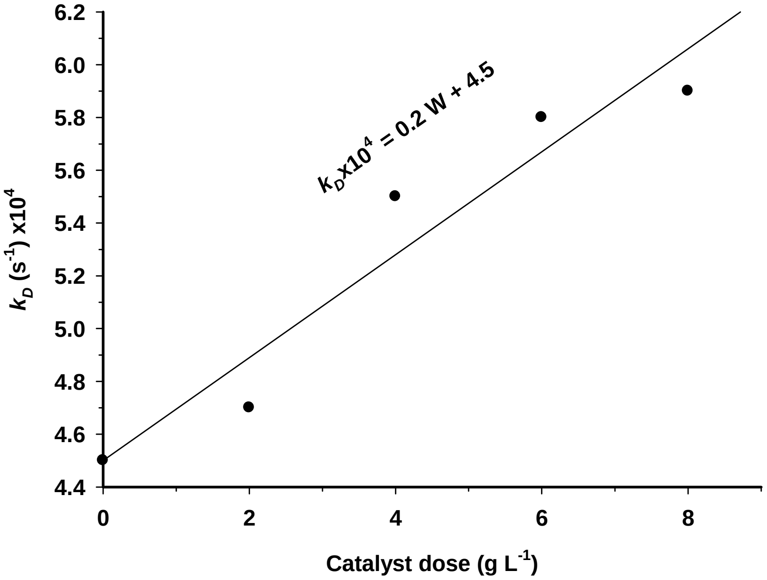


Figure 5.13. Effect of catalyst dose on the pseudo first-order ozone decomposition rate constant in the presence of PFOA. $[O_3]_0 = 1.042\times10^{-4}$ M, ionic strength (buffer) = 0.05 M, pH = 7

5.5. Conclusions

In this chapter, the factors affecting ozone decomposition performance by various catalysts were investigated. Major conclusions can be summarized as follows:

- In pure water, ozone decay rate is largely dependent on the solution pH, which affects the production of ozone promoters and their acid/base equilibrium. Thus, in acidic medium, ozone decomposes at a relatively low rate, whereas at neutral pH it decays significantly fast. For this reason, the addition of radical scavengers and phosphate ions, also acting as inhibitors of ozone decay, results in a notable reduction in the rate of ozone disappearance, especially at pH > 5.
- Activated carbon markedly increases ozone decay rates at all pH levels, and its catalytic centers are not significantly affected by phosphate buffer. However, its catalytic activity is notably influenced by the solution pH. At a pH level of 5, activated carbon exhibited the lowest catalytic activity, whereas the highest ozone decay rates were observed at pH 3 and 7. Reduction in ozone decay rates in the presence of radical scavenger indicates the participation of hydroxyl radicals in the ozone decomposition mechanism, which develops in the bulk liquid.
- In contrast with activated carbon, phosphate ions markedly affect the ability of alumina to accelerate ozone decomposition, possibly by blocking its active sites. Solution pH also exerts a significant influence on the catalytic activity of alumina. Thus, the most significant increase in ozone decay rate was observed at neutral pH, while at low pH levels its catalytic activity decreases. The presence of a radical scavenger results in a considerable reduction in ozone decay rate, which suggests that development of the radical-type chain reaction has a major role in the ozone decomposition.
- In comparison with non-catalytic ozone decomposition and catalytic process in the presence of activated carbon and alumina, perfluorooctyl alumina slightly increases

the rate of ozone decay. It was suggested that its catalytic effect may be related to the presence of bare alumina surface or the gradual adsorption of ozone on its perfluorinated groups.

6. OZONATION OF ATRAZINE

After gaining a general insight into the performance of catalysts to decompose ozone into hydroxyl radicals and their affinity towards the two model micropollutants, one may be able to more clearly interpret experimental results from micropollutant ozonation. As ozone decays in water partly into reactive hydroxyl radicals, ozonation systems always involve the reactions of two species: molecular ozone and free hydroxyl radicals. To examine the contribution of direct and indirect reactions in micropollutant removal, ozonation of atrazine was investigated.

According to previous studies on atrazine ozonation, major intermediates evolved during ozonation include deisopropylatrazine, de-ethyl-atrazine, atra-imine, 2-chloro-4-ethylimino-6-isopropylamino-s-triazine, and 4-acetamido-2-chloro-6-isopropylamino-s-triazine [2, 61]. These organic species react slowly with molecular ozone, and therefore do not act as initiators or promoters of ozone decomposition. Instead, these compounds react more rapidly with hydroxyl radicals. However, reaction rate constants of these species with hydroxyl radicals are much lower than atrazine [2]. As a result, hydroxyl radicals will preferably react with abundant atrazine. In view of this fact, the effect of catalyst on the production of hydroxyl radicals from ozone was investigated based on the R_{ct} concept, as explained in the Background chapter.

In this chapter, results of non-catalytic ozonation are first presented and discussed. Subsequently, effect of the presence of each catalyst is examined. The experimental conditions examined were similar to those in the Ozone Decomposition and Adsorption Sections, i.e. room temperature and three pH levels (i.e. 3, 5, and 7). Thus, aspects of the catalytic mechanism for each ozonation system, such as the role of surface reactions or development of reactions in aqueous medium, can be related to the previous experimental results of ozone decomposition and micropollutant adsorption.

6.1. Non-catalytic Ozonation

As discussed before, atrazine reacts slowly with molecular ozone, whereas it exhibits remarkable reactivity towards hydroxyl radicals. Its strong refractory character towards direct ozone attack can be evidenced by carrying out ozonation experiments at various pH levels or adding a radical scavenger, which can trap hydroxyl radicals and thus restrict their availability to the target micropollutant.

Reduction of atrazine concentration with time, corresponding to ozonation experiments at pH 3 and 7 in the absence and presence of TBA, is shown in Figure 6.1. It can be noticed that as the solution pH is raised from 3 to 7, atrazine removal increases from about 50% to 90% in the first 20 min. Similarly, after 60 min ozone concentration has dropped less than 50% of its initial value at pH 3, whereas for the same reaction time ozone has almost been totally depleted at neutral pH. Therefore, it is clear that solution pH exerts a strong influence on atrazine ozonation. On the other hand, when hydroxyl radical is the dominant oxidizing species, the oxidation process is strongly inhibited by adding TBA. As depicted also in Figure 6.1, at pH 7 the presence of a radical scavenger leads to a reduction of approximately 50% in atrazine removal, whereas at pH 3 a drop of about 10% atrazine removal was observed. This experimental observation indicates that atrazine degradation takes place mainly via hydroxyl radical mechanism.

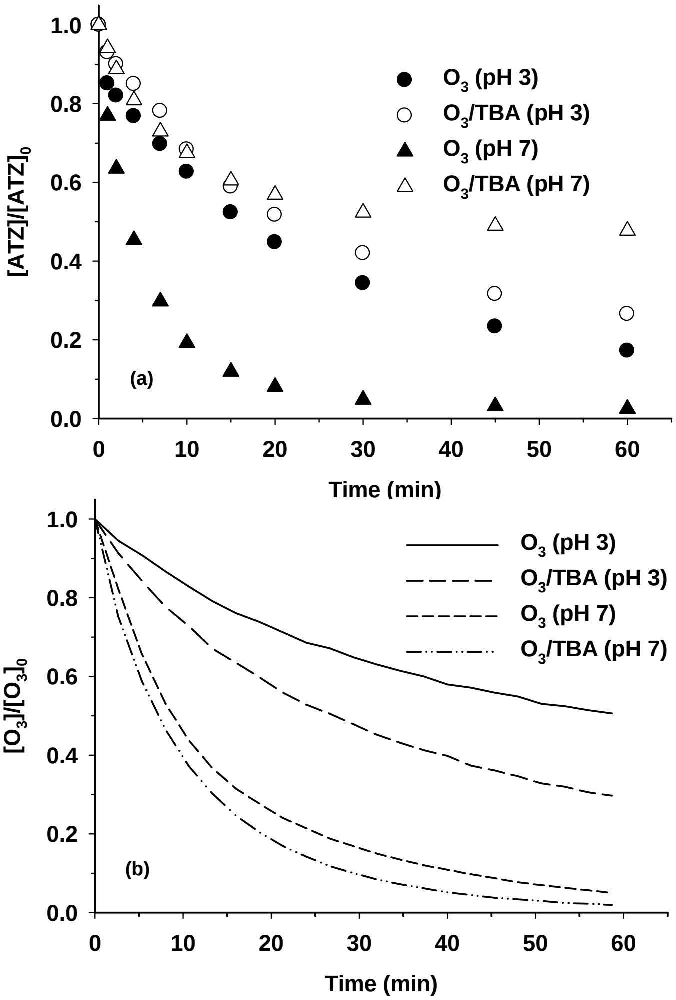


Figure 6.1. Effect of radical scavenger on non-catalytic ozonation of atrazine at various pH levels. $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, when applies $[TBA]_0 = 0.05$ M

Of great interest is to estimate the contribution of hydroxyl radicals, generated from ozone decomposition, to atrazine removal. For this purpose, the R_{ct} concept, explained in the Background chapter, can be used to indirectly determine the concentration of •OH and characterize the ozonation processes under investigation (for details on the determination of the R_{ct} parameter see Appendix B). Other parameters that can be used to describe ozonation process include ozone decomposition rate constant (k_D) and the observed or total removal rate constant (k_{obs}). Results obtained for non-catalytic ozonation under various conditions are summarized in Table 6.1. It can be noticed that the pseudo first-order ozone decomposition rate constant (k_D) increases with increasing pH, which is to be expected from the ozone radical-type chain reaction. Similarly, increase in solution pH leads to higher R_{ct}, k_{obs} and f_{OH} values. However, a close examination of R_{ct}, k_{obs} and f_{OH} values reveals that addition of TBA drastically reduces the contribution of hydroxyl radicals to the degradation of atrazine.

Table 6.1. R_{ct}, k_D, and k_{obs} values for non-catalytic ozonation of atrazine at various pH levels. $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, when applies $[TBA]_0 = 0.05$ M

pH	$[TBA]_0$ (M)	$k_D \times 10^4 (s^{-1})$	$R_{ct} \times 10^9$	k_{obs} $(M^{-1}s^{-1})$	f_{OH}
3	0	2.45	0.30	6.89	0.12
3	0.05	4.12	0.27	6.81	0.12
5	0	3.50	1.68	11.5	0.46
7	0	10.00	9.46	34.38	0.83
7	0.05	12.79	1.32	9.97	0.40

6.2. Ozonation Catalyzed by Activated Carbon

Ozone decomposition in the presence of activated carbon gives rise to a high production rate of hydroxyl radicals. In addition, this micropollutant exhibits a great affinity for adsorption on activated carbon. Therefore, ozonation in the presence of this catalyst may involve the competitive adsorption of atrazine and ozone. In case that oxidation of atrazine occurs mostly on the surface of the catalyst, addition of a radical scavenger will not significantly influence its reaction rate. However, if free hydroxyl radicals in the aqueous solution are mainly responsible for micropollutant degradation, its removal will be negatively affected.

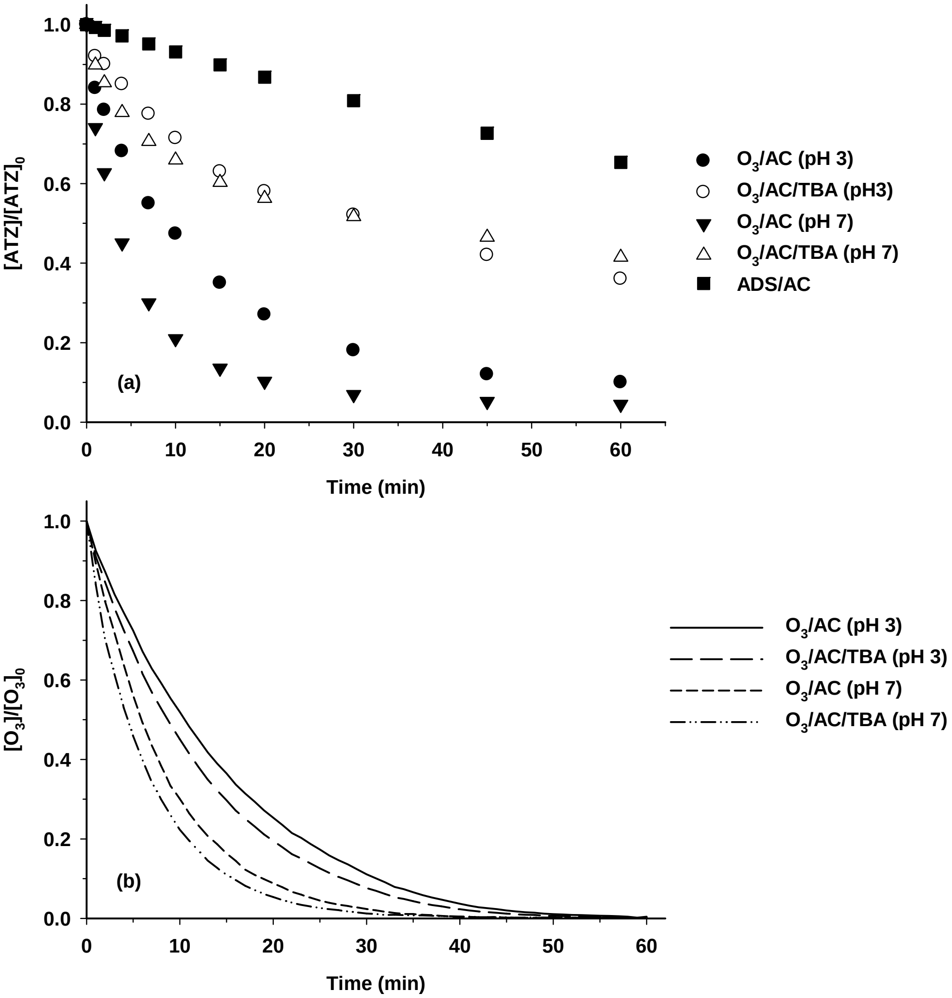


Figure 6.2. Adsorption and catalytic ozonation of atrazine by AC at various pH levels. AC = 0.5 g L^{-1}, $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, when applies $[TBA]_0 =$ 0.05 M

Figure 6.2 shows the reduction in atrazine concentration during adsorption and ozonation in the presence of activated carbon. As can be seen, atrazine shows high affinity for adsorption on the catalyst. Thus, after 60 min uptake of the micropollutant on the catalyst leads to approximately 30% and 60% reduction in concentration in the presence of 0.5 g L^{-1} and 1 g L^{-1} of activated carbon, respectively. However, the combined use of activated carbon and ozone results in fast removal rates of atrazine, achieving over 80% depletion after 30 min at pH 3 and 7. Also shown in Figure 6.2, ozone decay profiles indicate that fast generation of •OH occurred during the catalytic ozonation processes resulting in over 90% of ozone consumption after a 30 min period.

It should also be noticed that the presence of TBA markedly affects the micropollutant removal so that after 30 min less than 50% atrazine has been removed. Thus, a close examination of atrazine profile shows that this micropollutant was gradually removed in the first half hour at both pH levels. However, after this reaction period atrazine concentration starts an abrupt decreasing trend, even after complete ozone depletion. This observation suggests that two different phenomena were in effect before and after 30 min reaction time. In the absence of ozone, the role that adsorption plays on atrazine removal is evident, whereas in the presence of ozone a reaction taking place mainly in the bulk liquid is dominant.

If it assumed that atrazine is mostly degraded in the aqueous phase, and the effect of adsorption is neglected when dissolved ozone is available, the R_{ct} concept may be used to estimate the contribution of free hydroxyl radicals to the removal of the target micropollutant. For this purpose, a series of ozonation experiments were carried out at three different pH levels of 3, 5, and 7 with varying doses of activated carbon (0.25-1 g L^{-1}). In Figure 6.3, the ratio between •OH concentration and ozone concentration, R_{ct}, are plotted against the dose of activated carbon. As can be observed, ozone decomposition rate constant (k_D) and transformation of ozone into •OH (R_{ct}) were enhanced by increasing the dose of activated carbon. Over the entire range of doses, the experimental data fell on a straight line.

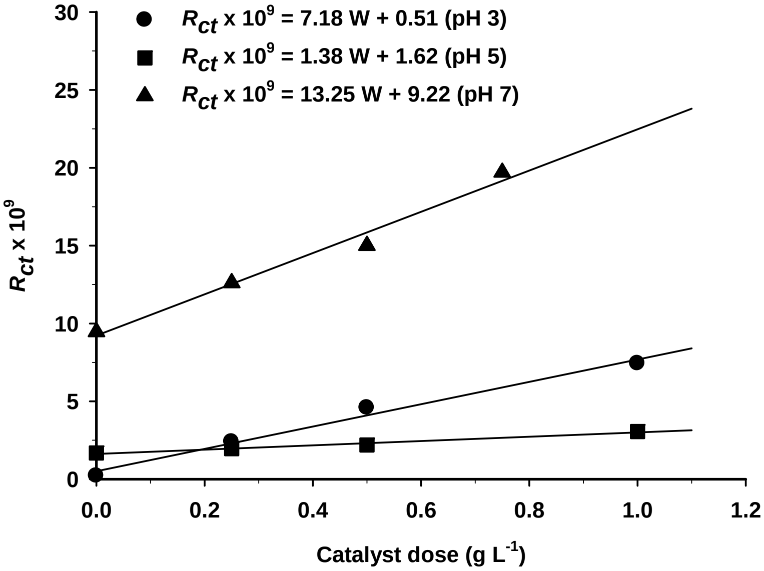


Figure 6.3. Effect of activated carbon dose on the R_{ct} parameter at three pH levels. $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M

Also shown in Figure 6.3, expressions for R_{ct} parameter as a function of catalyst dose are presented. It should be noticed that the line intercept corresponds to the R_{ct} value obtained for non-catalytic ozonation, and the slope of each line represents the contribution of the catalyst to the enhancement of generation of hydroxyl radicals from ozone. Although the production of •OH was enhanced by the presence of activated carbon at all pH levels, a clear relationship between pH and R_{ct} parameter was not observed. For instance at pH 5 a low slope was obtained than those at pH 3 and 7. This finding indicates that ozone interaction with the activated carbon active sites is largely dependent on solution pH.

R_{ct}, k_D , and k_{obs} values obtained for atrazine degradation by non-catalytic and catalytic ozonation in the presence of 0.5 g L^{-1} activated carbon are summarized in Table

6.2. It can be noticed that, when compared to non-catalytic ozonation results (Table 6.1), at all pH levels the presence of AC significantly increases the ozone decay rates and the production of hydroxyl radicals from ozone. For instance, at pH 3 the addition of AC to the system resulted in an increase in the R_{ct} value by approximately a factor of 13, whereas the ozone decomposition rate constant increased by a factor of 5. As a result, the fraction of hydroxyl radical contribution to atrazine removal increased from 0.12 for non-catalytic ozonation to 0.66 for the catalytic process. At the same time, this rise in •OH contribution represented an increase of over 2.5 times in the observed reaction rate constant. At higher pH levels, larger ozone decay rate constants and R_{ct} values as well as observed rate constants were determined in the non-catalytic ozonation process. However, at pH values of 5 and 7, the effect of the activated carbon catalytic activity exhibited a milder improvement in the contribution of •OH to atrazine degradation.

Table 6.2. R_{ct}, k_D, and k_{obs} values for catalytic ozonation of atrazine assisted by activated carbon at various pH levels. AC = 0.5 g L^{-1}, $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, when applies $[TBA]_0 = 0.05$ M

pH	$[TBA]_0$ (M)	$k_D \times 10^4 (s^{-1})$	$R_{ct} \times 10^9$	k_{obs} $(M^{-1}s^{-1})$	f_{OH}
3	0	11.95	3.91	17.73	0.66
3	0.05	14.00	0.77	8.32	0.28
5	0	6.28	2.54	13.64	0.56
7	0	20.87	13.25	45.75	0.87
7	0.05	23.91	2.55	13.65	0.54

6.3. Ozonation Catalyzed by Alumina

In contrast to activated carbon, atrazine does not exhibit affinity for alumina adsorption. As a result, reactions between this organic compound and the oxidizing species are limited to the homogeneous phase, instead of the catalyst surface. These facts suggest that atrazine ozonation catalyzed by alumina may be negatively affected by the presence of a radical scavenger.

Results of atrazine adsorption and catalytic ozonation in the presence of 8 g L^{-1} alumina at pH 3 and 7 are presented in Figure 6.4. It can be noticed that atrazine concentration remains constant throughout the adsorption process. When ozone is combined with alumina, atrazine removal rate is notably enhanced during the first 20 min at the two reaction pH levels. After this reaction period, reduction in micropollutant concentration is negligible. It should also be noticed that the presence of TBA markedly affects the efficiency of the catalytic ozonation process, especially at neutral pH. Under these conditions, less than 40% atrazine removal was observed, which contrasts with the approximately 50% removal obtained for non-catalytic ozonation and catalytic ozonation in the presence of activated carbon. On the other hand, also shown in Figure 6.4, ozone decomposition was observed to be accelerated by the catalytic action of alumina, even at acidic pH. From the fast ozone consumption and the marked inhibition effect, it can be inferred that reactions between atrazine and •OH are mainly responsible for micropollutant removal.

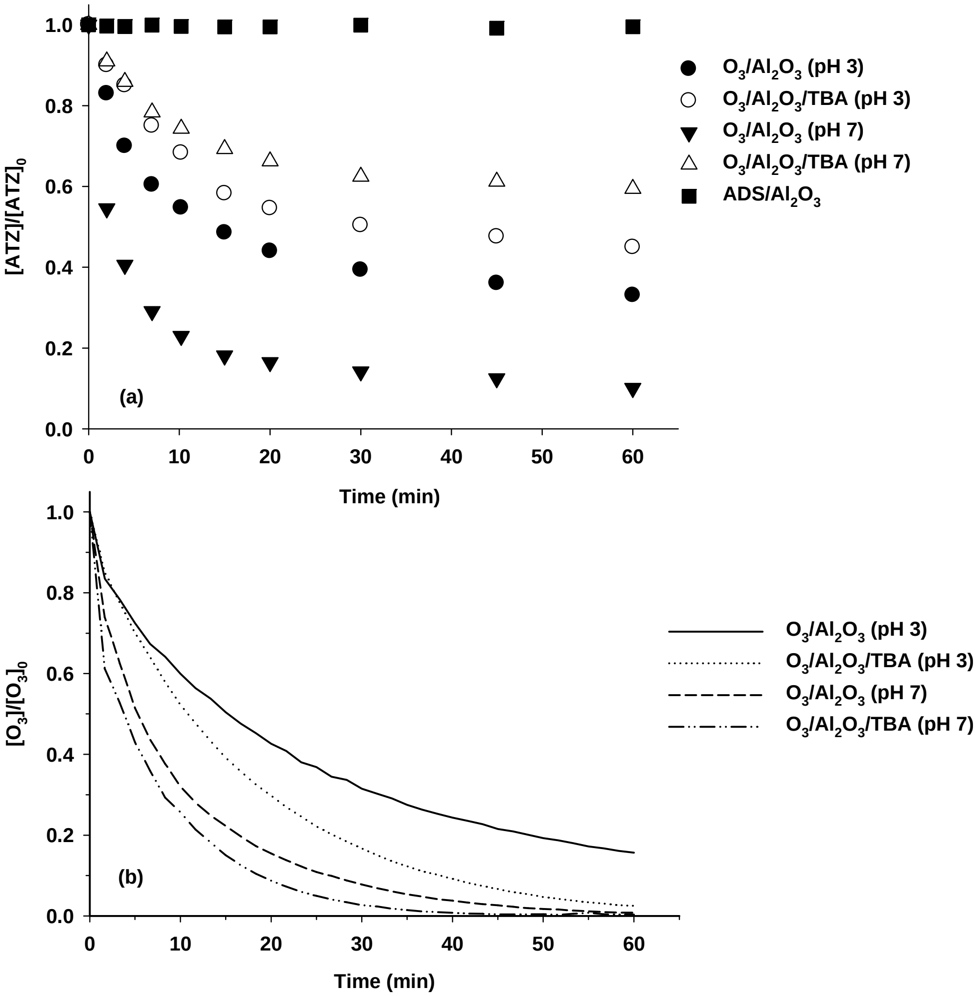


Figure 6.4. Adsorption and catalytic ozonation of atrazine by alumina at two pH levels. Al_2O_3 = 8 g L^{-1}, $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, when applies $[TBA]_0$ = 0.05 M

Since direct and indirect ozone reactions with atrazine presumably take place in the bulk liquid, R_{ct} concept represents a suitable method to evaluate the contribution of hydroxyl radicals to micropollutant removal. Results obtained for atrazine catalytic ozonation assisted by alumina are depicted in Figure 6.5. It can be noticed that as the mass of catalyst was increased, the ratio of hydroxyl radical concentration to ozone concentration increased. However, the most significant enhancement of ozone transformation into •OH was observed at neutral pH. At these conditions, a larger density of hydroxyl groups on alumina surface is expected, and therefore this catalyst exhibits a higher activity. Thus, the greatest potential of alumina to decompose the pollutant is limited to a narrow pH range close to its pH_{PZC}.

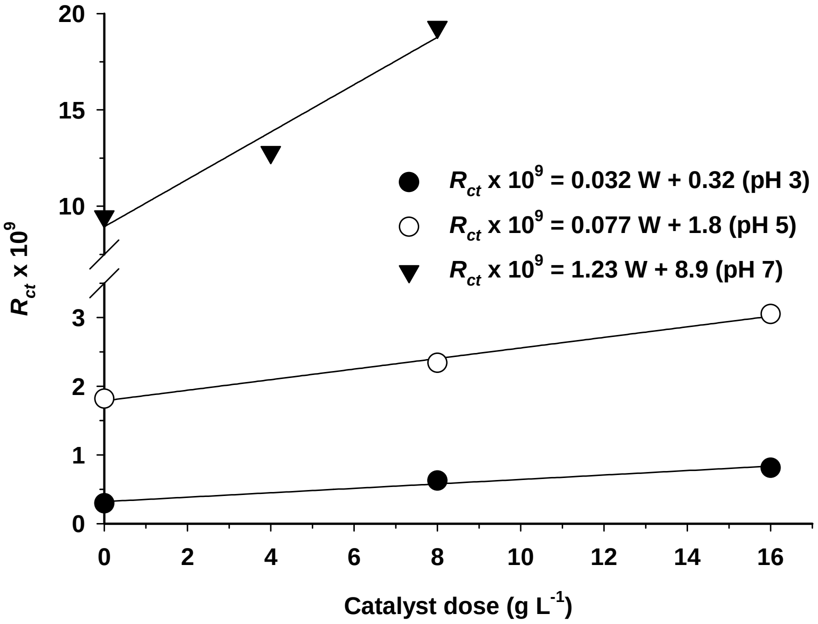


Figure 6.5. Effect of alumina dose on the R_{ct} parameters at three pH levels. $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M

A summary of R_{ct}, k_D, and k_{obs} values obtained for catalytic ozonation of atrazine assisted by alumina at various pH levels is presented in Table 6.3. When compared to non-catalytic ozonation results (Table 6.1), it is evident that the simultaneous action of ozone and alumina resulted in an increase in the generation of •OH. It is interesting to note that the most remarkable improvement was observed a neutral pH. At this pH level, R_{ct} value was increased by approximately a factor of 35, whereas the ozone decomposition rate constant increased by a factor of 7. As a result, the fraction of hydroxyl radical contribution to atrazine removal increased from 0.10 for non-catalytic ozonation to 0.79 for the catalytic process. At the same time, this rise in •OH contribution represented an increase of over 4 times in the observed reaction rate constant. It should also be noticed that, when TBA is introduced into the reaction system, the low contribution of •OH to atrazine removal reflects the significant influence of the radical scavenger on the process efficiency.

Table 6.3. R_{ct}, k_D, and k_{obs} values for catalytic ozonation of atrazine assisted by alumina at various pH levels. $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, $Al_2O_3 = 8$ g L^{-1}, when applies $[TBA]_0 = 0.05$ M

pH	$[TBA]_0$ (M)	$k_D \times 10^4 (s^{-1})$	$R_{ct} \times 10^9$	k_{obs} $(M^{-1}s^{-1})$	f_{OH}
3	0	5.80	1.41	10.23	0.41
3	0.05	9.60	9.63	8.89	0.32
5	0	6.35	2.34	13.0	0.54
7	0	19.86	18.89	62.66	0.90
7	0.05	21.91	1.51	10.54	0.43

6.4. Ozonation Catalyzed by Perfluorooctyl Alumina

The basic principle of enhancing molecular ozone reactions using solid catalysis involves the adsorption of both micropollutant and ozone. It is also required that the catalyst surface provides ozone with stability, thus resulting in a slow ozone decay rate and increase in ozone uptake. In the case of alumina as a support, modification of its surface with perfluorooctanoic acid improves the adsorption of hydrophobic micropollutants. On the other hand, it has been observed that ozone exhibits a significantly higher solubility in perfluorinated solvents than water. Thus, it is believed that PFOA may enhance direct ozone reactions of micropollutants with lower polarity, such as atrazine.

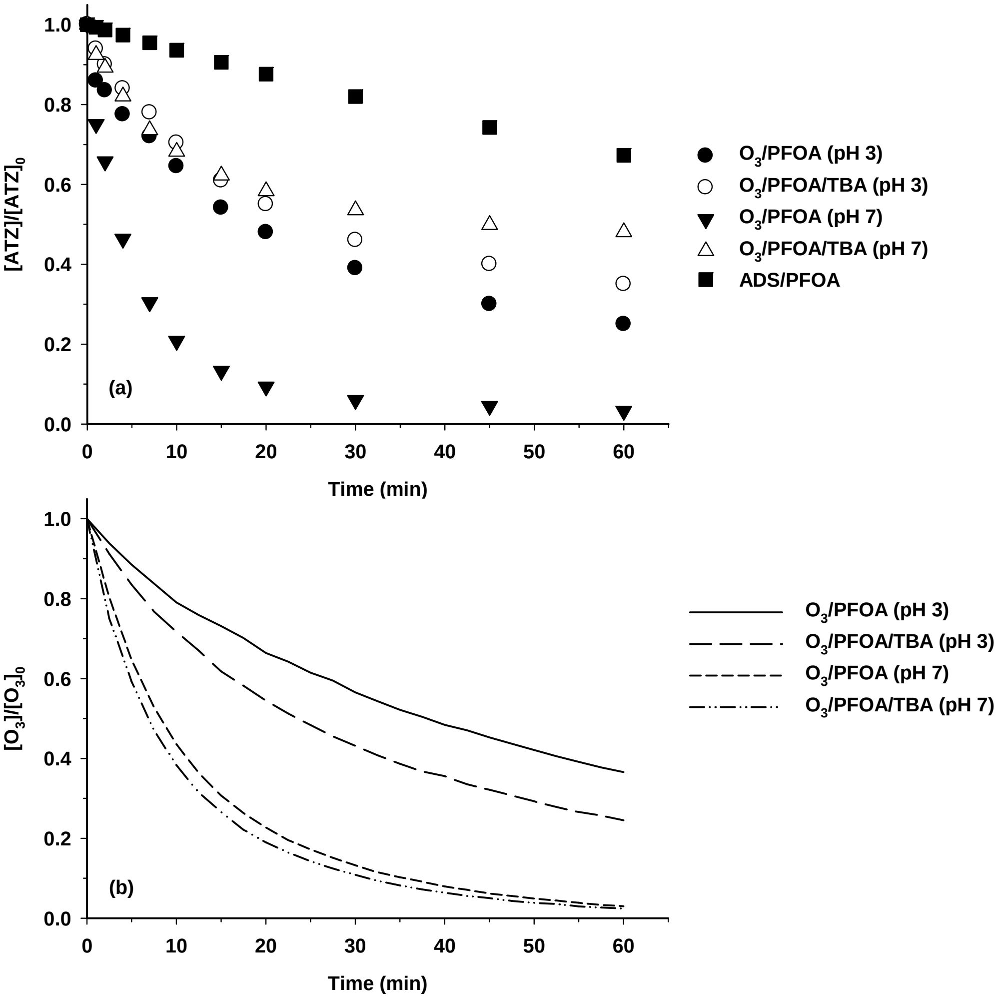


Figure 6.6. Effect of TBA on the removal of atrazine by PFOA-catalyzed ozonation at two pH levels. PFOA = 8 g L^{-1}, $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, when applies $[TBA]_0 = 0.05$ M

The ability of PFOA to enhance molecular ozone reactions with hydrophobic micropollutants was tested to check any catalytic action of PFOA on atrazine ozonation at various pH levels. As shown in Figure 6.6, modification of alumina surface to produce PFOA lead to a remarkable increase of atrazine affinity for adsorption. Thus, after 60 min, there was a 30% uptake of atrazine on PFOA surface. Figure 6.6 also depicts the results for ozonation experiments catalyzed by PFOA at two pH levels. When compared with non-catalytic ozonation experiments (Figure 6.1), it can be noticed that this catalyst neither increased the rate of ozone decay nor atrazine removal significantly. Thus, the addition of a radical scavenger strongly inhibits the removal of atrazine at neutral pH, whereas it is not notably affected at pH 3. A close examination indicates, however, that ozone concentration decrease slightly faster in the presence of PFOA. Although not very significant on Figure 6.6, this observation may be explained by a slow, but gradual, adsorption of ozone on the catalyst or ozone decomposition on alumina bare surface.

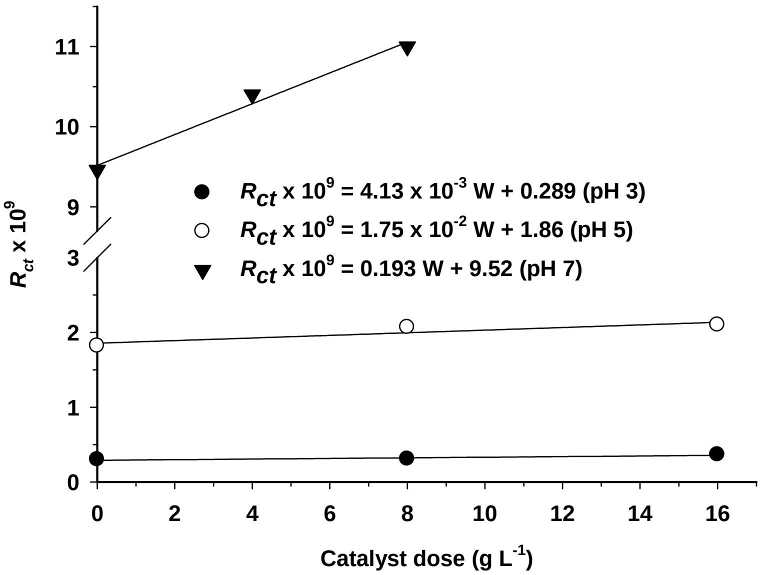


Figure 6.7. Effect of PFOA dose on the Rct parameter at various pH levels. $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M

To determine the influence of catalyst dose and solution pH, experiments on atrazine ozonation in the presence of varying masses of PFOA and different pH levels were performed. As depicted in Figure 6.7, at pH 3 and 5 the addition of PFOA into the ozonation system does not affect the ratio of hydroxyl radical concentration to ozone concentration notably. However, at neutral pH the introduction of PFOA in the reacting system leads to a significant increase in the R_{ct} value. It should be noticed that a similar behaviour was observed for the alumina-catalyzed ozonation process (Figure 6.5). Thus, the catalytic effect of alumina and PFOA leads to an increase in the production of •OH from ozone at neutral pH. This finding also suggests that the slight acceleration in ozone decay rate during ozonation experiments catalyzed by PFOA may be mainly due to bare alumina surface. For this reason, at pH 7 this catalysts exhibited its greatest ability to decompose ozone into •OH.

Table 6.4. R_{ct}, k_D, and k_{obs} values for catalytic ozonation of atrazine assisted by perflurooctyl alumina at various pH levels. PFOA = 8 g L^{-1}, $[O_3]_0$ = 1.042×10^{-4} M, $[ATZ]_0 = 4.62\times10^{-4}$ M, when applies $[TBA]_0 = 0.05$ M

pH	$[TBA]_0$ (M)	$k_D \times 10^4 (s^{-1})$	$R_{ct} \times 10^9$	k_{obs} $(M^{-1}s^{-1})$	f_{OH}
3	0	3.09	0.31	6.92	0.13
3	0.05	4.60	0.13	6.39	0.06
5	0	3.59	2.07	12.2	0.51
7	0	11.10	10.8	38.4	0.84
7	0.05	11.97	1.17	9.52	0.37

R_{ct}, k_D, and k_{obs} values and contribution of hydroxyl radicals to atrazine oxidation during PFOA-catalyzed ozonation re listed in Table 6.4. As can be noticed, as pH was raised the ozone decomposition into •OH was enhanced. When comparing with the results for non-catalytic ozonation system Table 6.1, the slight increase in k_D, R_{ct} and the contribution of hydroxyl radicals to micropollutant removal is evident. In addition, the presence of radical scavenger resulted in a marked reduction in the observed reaction rate constant as well as hydroxyl radical fraction reacting with atrazine.

6.5. Conclusions

In this chapter, performance of three different catalysts in removal of atrazine by ozonation was investigated at three pH levels. The following conclusions can be highlighted:

- As solution pH is raised, the contribution of hydroxyl radical to atrazine removal by non-catalytic ozonation is increased, leading to faster oxidation rates of the target micropollutant. Similarly, addition of a radical scavenger results in a marked reduction in atrazine reaction rates, especially at higher pH levels.
- The combined use of ozone and activated carbon results in a significant increase in atrazine removal rate. Although atrazine exhibited strong affinity for adsorption on activated carbon, fast ozone decay rates and markedly negative effect of a radical scavenger suggest that this micropollutant is mainly degraded by hydroxyl radicals in the bulk liquid. In addition, the larger reaction rate constants observed at pH 3 and 7, as compared with pH 5, also indicate that interaction between ozone and activated carbon active sites plays a more important role in the reaction mechanism than micropollutant adsorption.
- In contrast with activated carbon, atrazine did not show notable affinity for adsorption on alumina, and rates of atrazine removal were relatively low based on the catalyst dose. In addition, the presence of a radical scavenger greatly affected the reaction rate of the target pollutant. As related to the ozone decomposition catalyzed by alumina,

the highest catalytic activity was observed at pH 7, close to its pH_{PZC}. Thus, it is proposed that alumina catalyzes the generation of •OH from ozone, which reacts with atrazine in the bulk liquid.

- Modification of alumina surface to produce perfluorooctyl alumina resulted in a new catalyst capable of adsorbing atrazine at relatively high rates. However, its role in enhancing molecular ozone reactions was not clearly observed. In acidic media, catalytic effect of PFOA is negligible, whereas at neutral pH increase in catalyst dose resulted in a noticeable increase in the observed reaction rate constant. This observation indicates that PFOA exhibits partly properties of its support, which are pH dependent. Thus, acceleration of ozone transformation into •OH play a major role in the catalytic activity of PFOA, at least at neutral pH.

7. OZONATION OF 2,4-DICHLOROPHENOXYACETIC ACID

As explained in the Background chapter, 2,4-D is slowly degraded by direct ozone attack, whereas it exhibits a higher reactivity towards •OH. Thus, at low pH levels a minor contribution of •OH to 2,4-D removal is expected. This results in a slow reduction in 2,4-D concentration. However, ozonation of 2,4-D in aqueous solution develops through multiple reaction steps leading to various intermediates capable of enhancing ozone decomposition [51, 62]. Consequently, the degradation rate of 2,4-D is markedly increased and dependent on the evolution of these species, which can also give rise to competitive initiation due to radicals involved in the ozone decomposition mechanism. Since the production of hydroxyl radicals is not solely dependent on the catalyst and reacting conditions, R_{ct} concept does not provide an appropriate quantitative tool to characterize the various ozonation systems. Therefore, a general observed rate constant (k_{obs}) was found to be more suitable to describe the kinetics of the processes.

Since the rate of ozone transformation into •OH may be highly reduced by hindering the propagation of the radical-type chain reactions, a hydroxyl radical scavengers was added to the 2,4-D ozonation systems. Thus, with the purpose of setting up appropriate conditions to compare various ozonation systems, catalytic ozonation experiments were then conducted in the presence of an initial TBA concentration of 1×10^{-4} M. In addition, experimental conditions examined were similar to those used for the Ozonation of Atrazine Section, i.e. room temperature and three pH levels (i.e. 3, 5, and 7).

7.1. Non-catalytic Ozonation

In non-catalytic ozonation systems, transformation of ozone into •OH depends on solution pH and the presence of species that can initiate, promote, or inhibit ozone decomposition radical-type chain reaction. Species affecting the conversion of ozone into •OH may either be part of the impurities present in the water matrix being treated or evolve from the degradation path of oxidation of micropollutants [23]. Therefore, identification of reaction by-products formed during the ozonation process may provide a clear understanding of the kinetic process. In the case of 2,4-D, the two major intermediates identified during ozonation are 2,4-dichlorophenol (2,4-DCP) and glyoxylic acid [51, 62]. These two compounds are known to quickly react with ozone and enhance the transformation of ozone into •OH. In addition, as these compounds dissociate in water in a wide pH range, their reaction rates with ozone are strongly affected by solution pH [63].

In order to assess the influence of radical scavenger on 2,4-D degradation rate, ozonation experiments were conducted at varying TBA concentrations and pH 3. As can be seen in Figure 7.1, in the absence of TBA the reaction proceeds at a remarkably fast rate as observed by the almost complete disappearance of 2,4-D and ozone after 30 min of reaction time. However, addition of 1×10^{-4} M TBA scavenger markedly reduces the rate of 2,4-D and ozone disappearance, leading to a conversion of both ozone and 4,5-D of approximately only 40%. When a dose of 1×10^{-2} M TBA was used, 2,4-D and ozone decay rates also dropped notably, achieving a decomposition below 20%. Thus, addition of a hydroxyl radical scavenger reduces the ozone decomposition rate, as well as 2,4-D degradation rate, even at low initial TBA concentrations.

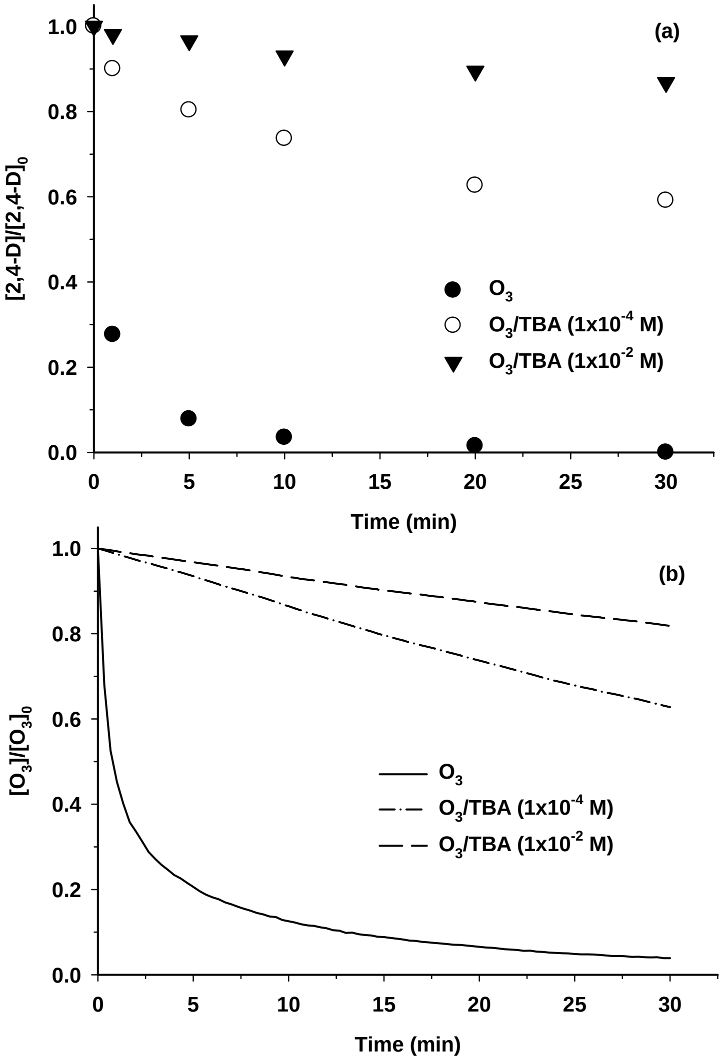


Figure 7.1. Effect of radical scavenger concentration on degradation of 2,4-D by non-catalytic ozonation. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, pH = 3

As the pH of aqueous medium is raised, decomposition of the ozone becomes accelerated, and therefore its conversion into •OH increases [22]. In addition, the solution pH influences acid/base equilibriums of some compounds and then the reaction speed of ozone. This also applies to the reaction with 2,4-DCP (pK_a = 7.8) and glyoxylic acid (pK_a = 3.2), whose reaction rate constants gradually increase with increasing solution pH below their pK_a [57].

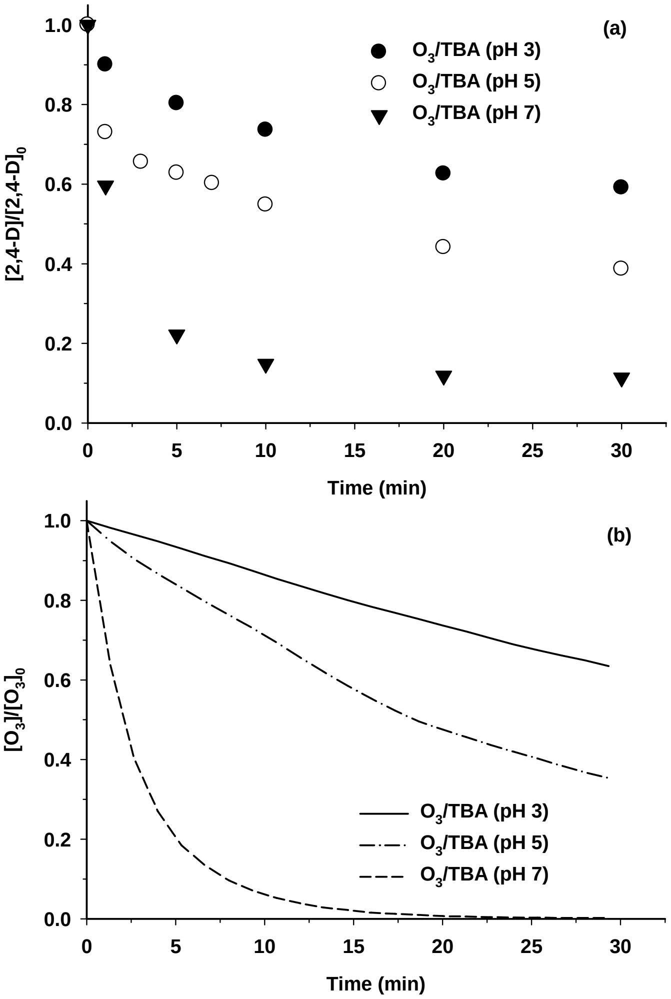


Figure 7.2. Effect of pH on 2,4-D degradation by non-catalytic ozonation. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26 \times10^{-4}$ M, $[\text{TBA}]_0 = 1\times10^{-4}$ M

To evaluate the influence of pH on 2,4-D degradation, ozonation experiments were conducted using an initial concentration of TBA of 1×10^{-4} M at three pH levels. As shown in Figure 7.2, after 5 min reaction time about 20 and 40 % of 2,4-D initial content has been removed at pH 3 and 5, respectively. However, in the same reaction time approximately 80% removal of 2,4-D was achieved at pH 7. The sudden increase in reaction rate from pH 5 to 7 may be explained by the formation of intermediates acting as promoters and the development of the radical-type ozone chain reaction under these conditions, as described in the Ozone Self-decomposition Section. It should also be noticed that hydrogen peroxide (H_2O_2) has been identified as a by-product during the ozonation of phenolic compounds [64], such as 2,4-DCP. H_2O_2, even when formed as a kinetically important intermediate, will only accumulate during the ozonation process if low pH values (pH <6) are maintained [22]. Thus, at neutral and basic pH levels, a significant degree of dissociation of H_2O_2 takes place, and therefore the decomposition of H_2O_2 by reaction of ozone with HO_2^- proceeds fast, increasing by a factor of 10 per pH unit increase [22].

Table 7.1. Effect of pH and initial TBA concentration on the non-catalytic ozonation of 2,4-D. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M

pH	$[TBA]_0$ (M)	$k_D \times 10^4 (s^{-1})$	k_{obs} $(M^{-1}s^{-1})$
3	0	61.87	186.5
3	1×10^{-4}	2.88	3.44
3	1×10^{-2}	1.12	0.815
5	1×10^{-4}	5.90	6.5
7	1×10^{-4}	46.01	101.1

Pseudo first-order ozone decay rate constants and observed 2,4-D reaction rate constants, at various initial concentrations of a radical scavenger and pH levels, for non-catalytic ozonation experiments are summarized in Table 7.1 (for details on the determination of the observed reaction rate constant see Appendix B). These results clearly show that k_D and k_{obs} decreased with increasing initial content of TBA at constant pH. Similarly, as pH was increased, the ozone decomposition rate constant and observed reaction rate increased.

7.2. Ozonation Catalyzed by Activated Carbon

In the present work, results of ozone decomposition indicate that activated carbon strongly accelerates the conversion of ozone into •OH. However, its catalytic activity depends largely on the solution pH. It has also been observed that in acidic medium activated carbon decomposes ozone more quickly at pH 3 than at pH 5, whereas at neutral pH, ozone decay rates are similar to those at pH 3. On the other hand, 2,4-D adsorbs rapidly on activated carbon, which may involve heterogeneous reactions between the micropollutant and the oxidizing species. Therefore, ozonation of 2,4-D in the presence of activated carbon may develop through a complex combination of various reaction pathways both in the aqueous solution and on the catalyst surface.

The extent of 2,4-D removal by adsorption and the influence of pH on the catalytic ozonation of 2,4-D assisted by activated carbon were examined. As shown in Figure 7.3, after 30 min only a reduction of 20% in the initial 2,4-D content was observed, whereas removals over 70% were achieved by the catalytic ozonation systems. It can be noticed that within 10 min about 70% of 2,4-D initially present disappeared at pH 7, and thereafter its concentration remained almost constant, which is not significantly different from the non-catalytic ozonation results (Figure 7.1). However, at pH 3 and 5 the addition of 0.5 g L^{-1} activated carbon into the ozonation system lead to markedly high removal rates of 2,4-D. It is interesting to note that in the first 5 min 2,4-D concentration dropped about 30% at both acidic pH levels, whereas at 20 min reaction time its concentration decreased about 60 and 80% at pH 5 and 3, respectively. On the other hand, at these acidic conditions ozone decay profiles were also found to exhibit different trends. This observation suggests the development of two different mechanisms of interaction between ozone and the catalyst active centers.

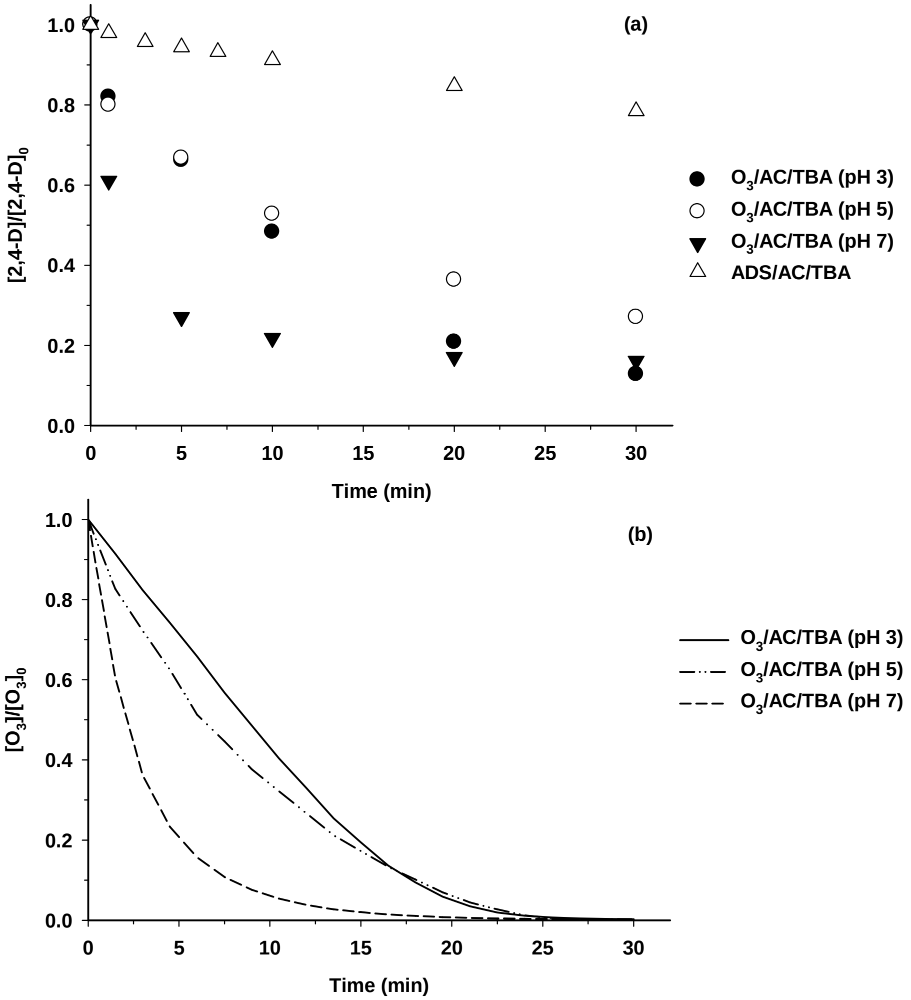


Figure 7.3. Effect of pH on the catalytic ozonation of 2,4-D assisted by activated carbon. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, $[TBA]_0 = 1 \times 10^{-4}$ M, AC = 0.5 g L^{-1}

Similar results obtained for non-catalytic ozonation and AC-catalyzed ozonation of 2,4-D at pH 7 indicate that homogeneous reactions play a major role in the total micropollutant removal. In the aqueous solution at this pH level, ozone transforms into

•OH through a radical chain reaction initiated mainly by OH^- and HO_2^- ions. However, dissociation of H_2O_2 to the initiator/promoter HO_2^-, which is a strong initiator of the transformation of aqueous ozone into hydroxyl radicals, is not favoured at very low pH levels. Therefore, at pH 3 and 5 the interaction between ozone and AC active sites may lead to an increased production of •OH, which boosts the degradation of 2,4-D and generation of intermediates. Some of these by-products, such as glyoxylic acid and 2,4-DCP, act as initiators and/or promoters also contributing to a faster ozone decay.

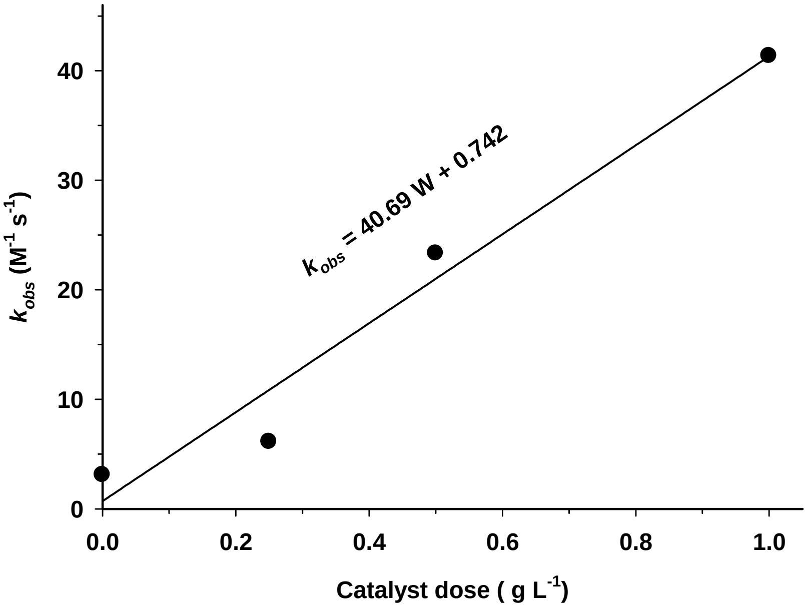


Figure 7.4. Effect of activated carbon dose on the observed removal rate of 2,4-D. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, $[TBA]_0 = 1\times10^{-4}$ M, pH = 3

Effect of activated carbon dose on 2,4-D degradation by catalytic ozonation was also examined. As depicted in Figure 7.4, the rate of 2,4-D removal increased linearly with the mass of activated carbon. It can also be noticed that by adding 0.5 g L^{-1} of catalyst to the ozonation system, 2,4-D is removed about four times faster than in the absence of AC.

In Table 7.2, k_D and k_{obs} values for 2,4-D ozonation experiments in the presence of 0.5 g L^{-1} activated carbon are shown. In comparison with the non-catalytic ozonation system (Table 7.1), the catalytic ozonation process exhibited significantly higher rate constants for both ozone decay and observed 2,4-D removal, especially in acidic medium. It is interesting to note that at pH 3 the reaction rates are slightly higher than those at pH 5. From the results described in the Ozonation Decomposition and Ozonation of Atrazine chapters, this is to be expected, since slower ozone decay rates were observed at pH 5 than pH 3. Similarly, ozone decomposition does not follow a first-order kinetic model at pH 3. This suggests that a different mechanism of interaction between ozone and active centres on activated carbon surface.

Table 7.2. Effect of pH on catalytic ozonation of 2,4-D by activated carbon. $[O_3]_0 = 1.042 \times 10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, $[TBA]_0 = 1\times10^{-4}$ M, AC = 0.5 g L^{-1}

pH	$k_D \times 10^4 (s^{-1})$	$k_{obs} (M^{-1}s^{-1})$
3	~23.33	23.51
5	21.43	18.47
7	40.17	83.66

7.3. Ozonation Catalyzed by Alumina

From the results of non-catalytic ozonation experiments, it is clear that the reason for enhanced 2,4-D removal, in the presence of 1×10^{-4} M TBA and at pH 7, is not the direct oxidation by molecular ozone but the production of hydroxyl radicals due to the formation of initiators and promoters, such as 2,4-DCP and H_2O_2. However, at pH 3 and

5 due to the presence of a heterogeneous phase, the adsorption of 2,4-D as well as of ozone on the catalyst surface may provide an alternative reaction pathway for higher removal rates. As deprotonated 2,4-D has a strong affinity for adsorption on alumina, surface reactions may play an important role in the catalytic ozonation of 2,4-D.

Results of 2,4-D adsorption and catalytic ozonation in the presence of 8 g L^{-1} of alumina are depicted in Figure 7.5. It can be noticed that 2,4-D is rapidly adsorbed on alumina, reaching about 70% removal after 30 min. However, introduction of alumina into the ozonation system leads to a notably higher removal rate. According to Figure 7.5 (for instance), after 10 min reaction time, over 80 and 90% of initial 2,4-D content has been reduced at pH 3 and 5, respectively. It is interesting to note that an initial fast ozone consumption at pH 7 results in lower conversion (80%) when compared to lower pH levels (>90%). It can also be seen that 2,4-D concentration remains practically constant after 3 min at pH 7. This observation indicates that 2,4-D is not being adsorbed, and probably competing with species formed during the ozonation process.

For an appropriate description of the mechanism, one important question is whether ozone attacks the organic compounds directly or indirectly via the radical mechanism in the presence of alumina. In a previous work, it has been assumed that as a result of ozone decomposition the acceleration of the indirect radical chain is started on alumina surface, and the involvement of the hydroxyl radicals in the catalyzed reaction was supported because the reaction is influenced by the presence of radical scavengers [4]. However, in other studies, the participation of hydroxyl radicals has been overlooked because the reaction was not affected by the presence of radical scavengers [18, 37]. Thus, it is possible that the enhancement of direct ozonation could be involved with heterogeneous catalysis in the presence of alumina [3].

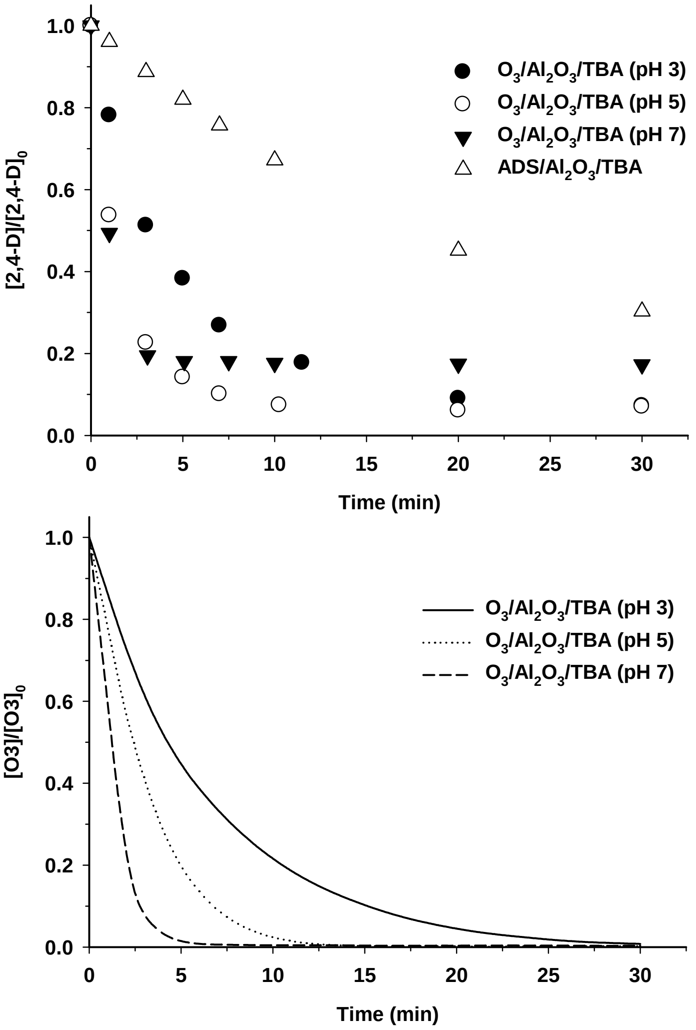


Figure 7.5. Effect of pH on the catalytic ozonation of 2,4-D assisted by alumina. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, $[\text{TBA}]_0 = 1\times10^{-4}$ M, $Al_2O_3 = 8$ g L^{-1}

In the present work, it has been observed that reactions taking place in the bulk liquid play an important role in the fast removal of 2,4-D. However, at low pH levels and in the presence of a radical scavenger, development of homogeneous reactions is restricted. On the other hand, in the Ozone Decomposition chapter it was noticed that alumina slightly enhances the transformation of ozone into •OH at pH 3 and 5, which suggests that hydroxyl radicals may be mostly formed in the aqueous phase. Therefore, it can be inferred that the quick adsorption of 2,4-D on alumina leads to direct ozone attack and rapid formation of intermediates that accelerate the decomposition of ozone into •OH, which initially reacts preferably with the most abundant 2,4-D.

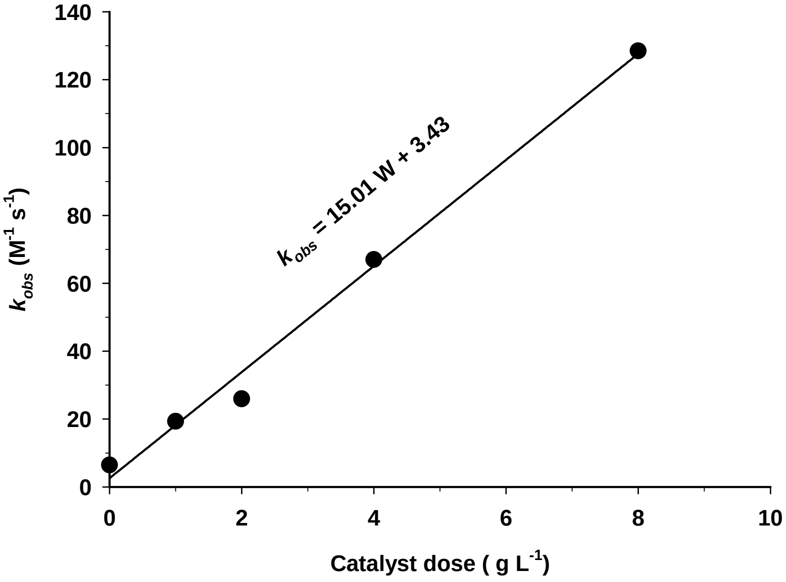


Figure 7.6. Effect of alumina dose on the observed removal rate of 2,4-D. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26 \times 10^{-4}$ M, $[TBA]_0 = 1\times10^{-4}$ M, pH = 5

The effect of the mass of catalyst on the reaction was investigated. As shown in Figure 7.6, the observed removal rate of 2,4-D increased linearly with the dose of alumina. This is to be expected as the larger catalyst surface leads to a faster adsorption rate of 2,4-D and initiation of reactions in the bulk liquid. It can also be observed that a catalyst dose of 4 g L^{-1} increases more than ten time the removal rate of 2,4-D.

k_D and k_{obs} values for ozonation experiments in the presence of 8 g L^{-1} of alumina, at various pH levels, are listed in Table 7.1. When comparing with ozone decay rate constants and observed reaction rate constants for the non-catalytic ozonation process

(Table 7.1), it can be clearly noticed that in the catalytic ozonation process 2,4-D was degraded at significantly high rates. Similarly, the markedly fast ozone decay rate observed indicates the existence of a catalytic mechanism, instead of simply uptake of micropollutant on the catalyst surface.

Table 7.3. Effect of pH on catalytic ozonation of atrazine by alumina. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, $[TBA]_0 = 1\times10^{-4}$ M, $Al_2O_3 = 8$ g L^{-1}

pH	$k_D \times 10^4 (s^{-1})$	$k_{obs}\ (M^{-1}s^{-1})$
3	25.33	58.91
5	60.17	128.5
7	141.7	190.4

7.4. Ozonation Catalyzed by Perfluorooctyl Alumina

As presented in the Adsorption Section, binding of perfluorinated groups on alumina surface results in an opposite effect on its adsorptive properties. Thus, while 2,4-D is extensively adsorbed on alumina, this micropollutant does not exhibit affinity for adsorption on PFOA. Therefore, based on the basic principle of enhanced molecular ozone reactions, ozonation in the presence of PFOA will have little or no influence on the direct ozone attack on 2,4-D.

Results obtained for 2,4-D adsorption and ozonation in the presence of PFOA at three pH levels are depicted in Figure 7.7. It can be seen that uptake of the micropollutant on the catalyst surface is negligible in the absence of ozone. When comparing with the non-catalytic ozonation system (Figure 7.2), no noticeable difference in 2,4-D removal or ozone decay rate could be observed. Thus, after a reaction period of 30 min about 40, 60, and 90% micropollutant conversion was observed at pH 3, 5, and 7, respectively.

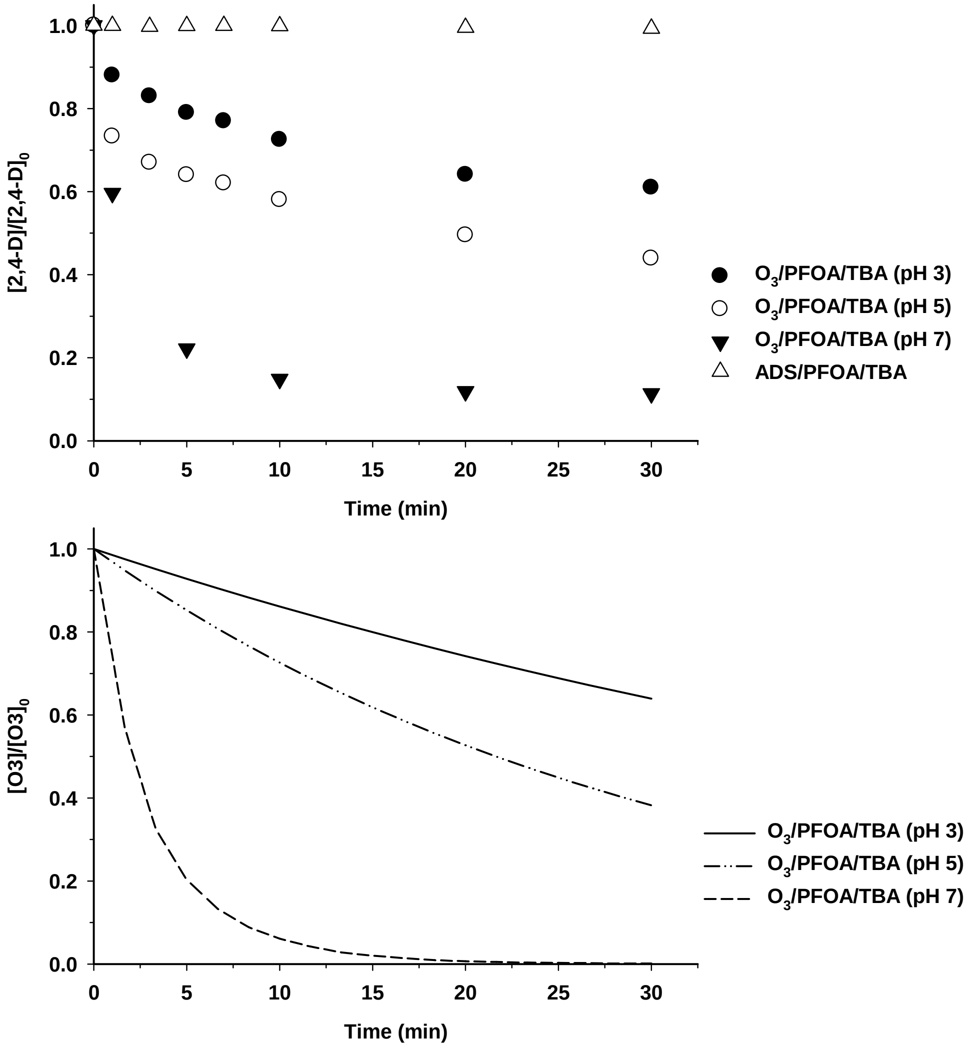


Figure 7.7. Effect of pH on the catalytic ozonation of 2,4-D assisted by PFOA. $[O_3]_0$ = 1.042×10^{-4} M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, $[\text{TBA}]_0 = 1\times10^{-4}$ M, PFOA = 8 g L^{-1}

From the results obtained for the ozonation of atrazine in the presence of alumina, this catalyst was also expected to exhibit a noticeable catalytic effect on the ozonation of 2,4-D at pH 7. However, at neutral pH level, decomposition of ozone into hydroxyl radicals, promoted by 2,4-D oxidation intermediates, is significantly fast for the bare alumina surface on the catalyst to influence the reacting system. At low pH levels no detectable difference in micropollutant degradation was observed between the catalytic and non-catalytic ozonation processes. This observation suggests that the catalyst does not play a major role by either adsorbing the micropollutant and ozone or generating hydroxyl radicals from ozone.

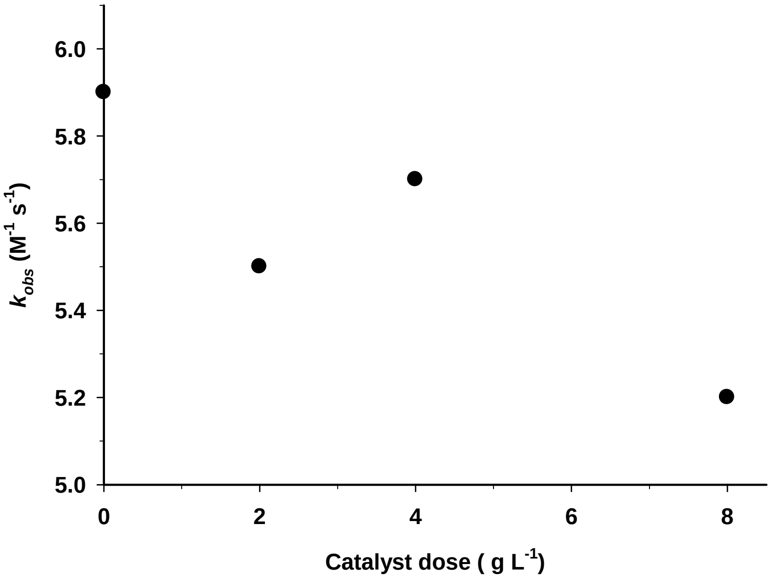


Figure 7.8. Effect of PFOA dose on the observed removal rate of 2,4-D. $[O_3]_0$ = 1.042×10^{-4} M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, $[TBA]_0 = 1\times10^{-4}$ M, pH = 5

To assess the influence of catalyst dose on the observed 2,4-D removal, ozonation experiments were performed in the presence of varying amounts of catalyst. As shown in Figure 7.8, ozonation in the presence of 1 g L^{-1} of PFOA did not notably increase the removal rate of the micropollutant, whereas addition of 1 g L^{-1} activated carbon (Figure 7.4) or 1 g L^{-1} alumina (Figure 7.6) resulted in observed reaction rate constants, respectively, over four or nine times higher than the non-catalytic process. This again suggests that the catalytic effect of PFOA is negligible.

k_D and k_{obs} values obtained from ozonation experiments in the presence of 8 g L^{-1} PFOA at different pH levels are shown in Table 7.4. Significant differences are not noticeable, when compared with results for the non-catalytic ozonation process (Table 7.1). In addition, 2,4-D does not exhibit affinity for adsorption on PFOA. Therefore, this observation suggests that PFOA does not affect the reacting system.

Table 7.4. Effect of pH on catalytic ozonation of atrazine by activated carbon. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, $[TBA]_0 = 1\times10^{-4}$ M

pH	$k_D \times 10^4$ (s^{-1})	k_{obs} ($M^{-1}s^{-1}$)
3	2.49	3.62
5	5.34	5.20
7	51.00	104.72

7.5. Conclusions

In this section, performance of the combined use of ozone and three solid catalysts to degrade 2,4-D was examined in the presence of a radical scavenger. From the presented results, the following conclusions can be drawn:

- At a very low solution pH (3), the degradation of 2,4-D is accelerated by the transformation of ozone into •OH as a result of the formation of by-products that act as initiators/promoters of ozone decomposition. Thus, addition of low doses of a radical scavenger leads to a marked reduction in the target micropollutant removal at these conditions. However, as solution pH is raised, higher doses of TBA are required to decrease the reaction rate. This observation suggests that solution pH affects the acid/base equilibrium of by-products as well as the radical-type ozone decay chain reaction.

- The catalytic effect of activated carbon on 2,4-D ozonation leads to a significant increase in 2,4-D removal at pH 3 and 5. In spite of the notable 2,4-D uptake on activate carbon, the higher reaction rate observed at pH 3, as compared with pH 5, suggests that acceleration of ozone transformation into •OH by activated carbon plays a major role in the mechanism of the reaction. At pH 7, with reductions in 2,4-D and ozone concentrations of about 80%, influence of catalyst on micropollutant was not clearly observed.
- In contrast to atrazine, 2,4-D exhibits a strong affinity for adsorption on alumina, which is suspected to be crucial to the catalytic ozonation of this micropollutant. Alumina does not significantly increase the rate of ozone decomposition at low pH levels, and formation of 2,4-D ozonation by-products is reduced by TBA. Therefore, the enhanced 2,4-D removal must be the result of surface reactions between adsorbed micropollutant and the oxidizing species present in the bulk liquid. In addition, the fast production of 2,4-D intermediates, acting as initiators/promoters, maintains a high rate of ozone transformation into •OH, which are not completely trapped by the TBA radical scavenger. Thus, hydroxyl radicals are available for degradation of the target micropollutant.
- Since affinity of 2,4-D for adsorption on PFOA is practically negligible, this catalyst is not expected to enhance molecular ozone reactions with micropollutant on the catalyst surface. In addition, at pH 7 in the non-catalytic ozonation process 2,4-D

removal rate is too high for the catalyst to significantly accelerate the transformation of ozone into •OH, as observed in atrazine catalytic ozonation process.

8. GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

In this work, application of activated carbon, alumina, and perfluorooctyl alumina catalysts in the process of ozonation of atrazine and 2,4-dichlorhophenoxyacetic acid in pure water was examined using a laboratory-scale reaction system over a range of operating conditions. The effects of solution pH, presence of a radical scavenger, pesticide adsorption on catalyst, and catalyst dose on micropollutant removal were investigated. Solution pH was found to significantly influence the catalyst ability to decompose ozone into free hydroxyl radicals, which, in some cases, were markedly inhibited by the radical scavenger resulting in a negative impact on pesticides degradation. In general, the removal rate of pesticides was found to increase with increasing doses of catalyst, while micropollutant adsorption had varying effects on the reaction pathways.

Activated carbon exhibited great adsorption ability with respect to atrazine and 2,4-D. However, it was found that the catalytic activity of activated carbon was mainly related to its ability to decompose ozone into hydroxyl radicals, which was notably influenced by the solution pH. When compared to the non-catalytic ozonation process, atrazine removal rates were four times higher at pH 3 and two times higher at pH 7 when using a catalyst dose of 0.5 g L^{-1}, whereas observed reaction rates for 2,4-D increased over 5 times at pH 3 using the same mass of catalyst and in the presence of 1×10^{-4} M TBA radical scavenger.

Alumina catalyst slightly increased ozone decay rates at acidic pH levels. However, its catalytic activity to produce hydroxyl radicals from ozone was markedly improved at neutral pH levels. Atrazine did not show a significant affinity for adsorption on alumina, whereas 2,4-D was extensively adsorbed. Thus, catalytic ozonation of atrazine involved mainly reactions between micropollutant and hydroxyl radicals in the bulk liquid, which were greatly affected by the presence of a radical scavenger. When using a catalyst dose of 8 g L^{-1}, the observed reaction rate constant was about two times higher than non-catalytic ozonation process. In the case of 2,4-D, adsorption of the micropollutant played an important role in the reaction pathway in acidic media. For this pesticide, the observed removal rate using 8 g L^{-1} was over ten times higher than that for the non-catalytic ozonation process at pH 5 and an initial concentration of tert-butyl alcohol of 1×10^{-4} M.

Modification of alumina to produce perfluorooctyl alumina resulted in a catalyst with different adsorptive properties. Thus, this catalyst was able to significantly adsorb atrazine, while 2,4-D did not exhibit affinity for adsorption. Perfluorooctyl alumina was found to enhance neither molecular ozone reactions nor ozone decomposition into hydroxyl radicals. However, at neutral pH a noticeable increase in hydroxyl radicals production was observed, as the dose of catalyst was increased. In the presence of 8 g L^{-1}, the observed removal rates for atrazine and 2,4-D did not increase significantly.

These encouraging results and the feasible implementation of catalytic ozonation systems in current water treatment facilities warrant more detailed study. In this regard, the following recommendations for future work are suggested:

- Current water facilities using ozone for disinfection purposes operate in continuous mode. Thus, it is proposed to run a continuous catalytic ozonation system to investigate mass transfer limitations that may occur.
- For feasible operation of a catalytic ozonation system, change in catalyst activity with time must be assessed. Thus, catalyst regeneration must be considered or costs of catalyst replacement must be determined.
- Since reaction by-products may induce ozone decomposition or negatively affect the toxicity of the water matrix, identification and evolution of the reaction intermediates are important to clarify the catalyst role or modify the operating conditions. On the other hand, detailed kinetics of the system allows for prediction of the process efficiency.
- For realistic modeling of catalytic ozonation applications, removal of water micropollutants must be assessed using different water matrices, such as river water. Similarly, in addition to single target micropollutant degradation, mixtures of micropollutants can be tested.

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APPENDIX A. Determination of the Surface Coverage of Perfluorooctyl Groups on Perfluorooctyl Alumina

The surface coverage of perfluorooctyl groups on alumina surface was determined based on the carbon content and surface area of the catalyst. The carbon content per mol of perfluorooctanoic acid reacting with alumina is 96.086 g. Thus, from the weight percent of carbon of several samples of perfluorooctyl alumina catalyst, the number of moles of perfluorooctyl groups attached to the surface of alumina can be determined. Table A. 1 summarizes the elemental analysis obtained for five samples of catalyst.

Table A. 1. Elemental analysis of perfluorooctyl alumina

Run	Nitrogen (wt. %)	Carbon (wt. %)	Sulphur (wt. %)	Hydrogen (wt. %)
1	0.000	6.623	0.036	0.664
2	0.005	6.689	0.123	0.651
3	0.009	6.656	0.134	0.568
4	0.008	6.591	0.134	0.498
5	0.007	6.688	0.552	0.464
Average	0.0058	6.649	0.196	0.569

On the other hand, to calculate the surface area of catalyst available in a certain amount of catalyst, the mass of perfluorooctanoic acid added to alumina must be subtracted. It should be noticed that when aluminum oxide is added in water it adsorbs water, which leads to the formation of hydroxyl groups. Thus, according to the reaction shown in Figure 4.4, addition of each perfluorooctyl group to the surface of alumina results in an increase of the mass of alumina, equivalent to eight carbon atoms and fifteen fluorine atoms. Therefore, the mass of catalyst will increase 381.06 g per mol of perfluorooctyl groups attached.

The surface area measured for alumina catalyst was 223 $\mathrm{m^2\ g^{-1}}$ (Table 4.1). Thus, selecting a 100 g of perfluorooctyl alumina catalyst as the basis of calculation we have that the number of moles of perfluorooctyl groups is:

$$n = \frac{6.649\ \mathrm{g}}{96.086\ \mathrm{g\ mol^{-1}}} = 0.06920\ \mathrm{mol} \tag{A.1}$$

Thus, the mass of alumina contained in a 100 grams sample of PFOA is:

$$m = 100\ \mathrm{g} - 0.06920\ \mathrm{mol} \times 381.06\ \mathrm{g\ mol^{-1}} = 73.631\ \mathrm{g} \tag{A.2}$$

and the surface area available is then:

$$S = 73.631\ \mathrm{g} \times 223\ \mathrm{m^2 g^{-1}} = 16419.71\ \mathrm{m^2} \tag{A.3}$$

Therefore, the surface coverage of perfluorooctyl groups (α) obtained is:

$$\alpha = \frac{0.06920\ \mathrm{mol}}{16419.71\ \mathrm{m^2}} = 4.214 \times 10^{-6}\ \mathrm{mol\ m^{-2}}\ \text{or}\ 4.214\ \mu\mathrm{mol\ m^{-2}} \tag{A.4}$$

APPENDIX B. Examples of Experimental Data Fitting of Linear Models used to Describe the Kinetics of Ozonation Processes

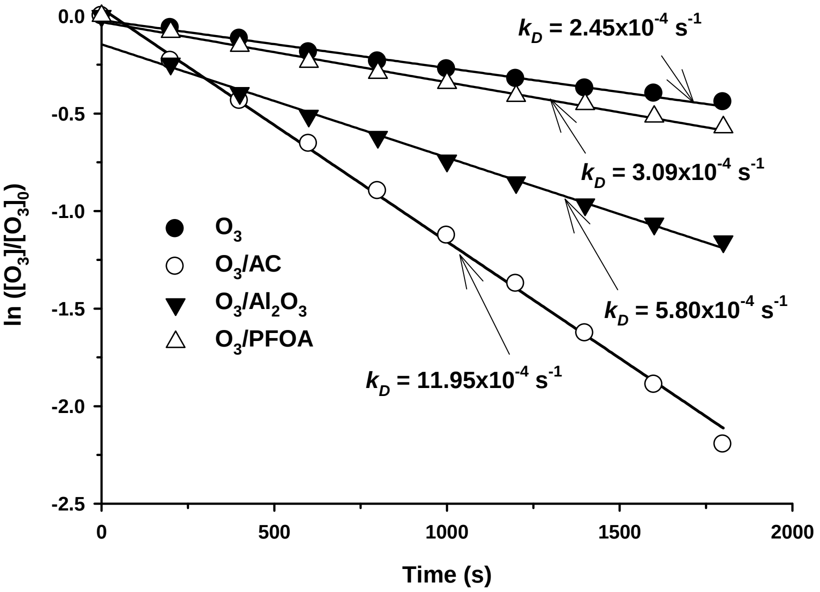

Figure B. 1. Determination of pseudo first-order ozone decomposition rate constants for atrazine ozonation experiments. $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, AC = 0.5 g L^{-1}, Al_2O_3 = 8 g L^{-1}, PFOA = 8 g L^{-1}, pH = 3

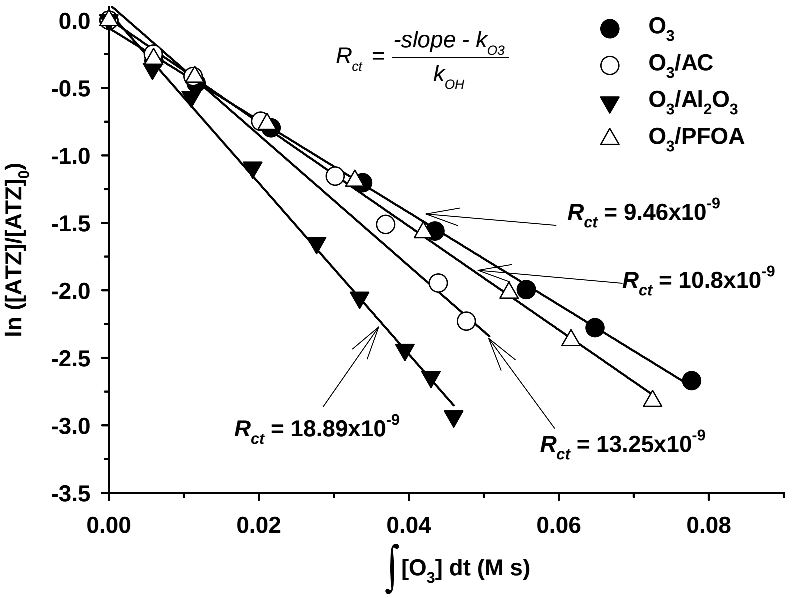

Figure B. 2. Determination of Rct parameter for atrazine ozonation experiments. $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, AC = 0.5 g L^{-1}, Al_2O_3 = 8 g L^{-1}, PFOA = 8 g L^{-1}, pH = 7

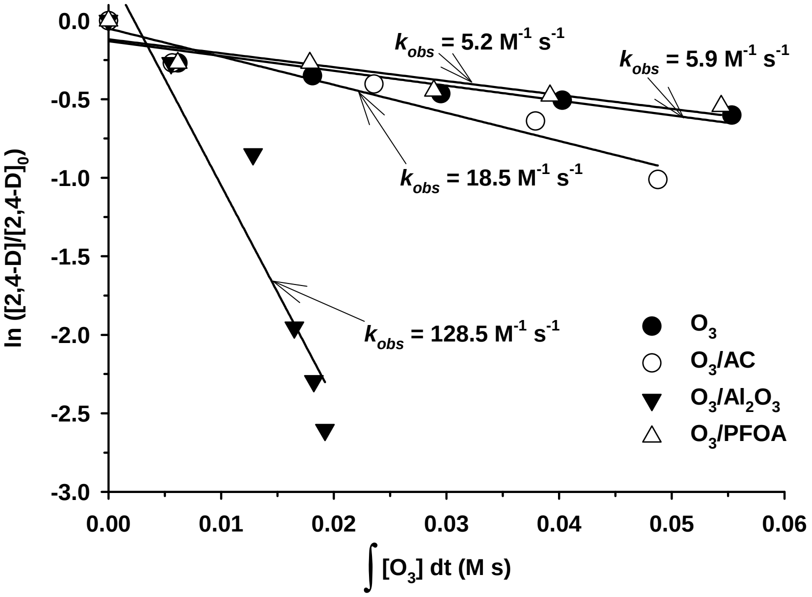

Figure B. 3. Determination of the observed rate constant for 2,4-D ozonation experiments. $[O_3]_0 = 1.042\times10^{-4}$ M, $[2,4\text{-}D]_0 = 2.26\times10^{-4}$ M, $[TBA]_0 = 1\times10^{-4}$ M, AC = 0.5 g L^{-1}, Al_2O_3 = 8 g L^{-1}, PFOA = 8 g L^{-1}, pH = 5

APPENDIX C. Determination of Intraparticle Diffusion Effects on Catalytic Ozonation Reaction Rates

To evaluate intraparticle diffusion resistance in catalytic ozonation processes, the Weisz-Prater criterion was used according to Eq. (3.1) [24]. Molecular or Fick's diffusivity of ozone (D_{O3}) in water was determined using the experimental correlation developed by Johnson and Davis [65] and expressed by Eq. (C.1). Atrazine and 2,4-D molecular diffusivities (D_A) were estimated using Wilke-Chang equation for solutes in aqueous solutions [66], represented by Eq. (C.2).

$$D_{\mathrm{O3}}\left(\mathrm{cm}^2\ \mathrm{s}^{-1}\right)=1.10\times10^{-2}\exp\left(-\frac{1896}{T}\right) \tag{C.1}$$

$$D_A\left(\mathrm{cm}^2\ \mathrm{s}^{-1}\right)=7.4\times10^{-8}\left(2.6M_{water}\right)^{0.5}\frac{T}{\mu_{water}V_A^{0.6}} \tag{C.2}$$

In these equations, T (K) is the solution temperature, V_A (cm^3 mol^{-1}) is the molar volume of the diffusing species, and μ_{water} (cP) and $\mathrm{M_{water}}$ (g mol^{-1}) are viscosity and molar mass of water, respectively. The effective diffusivity for all diffusing species can then be calculated using Eq. (C.3). The porosity, ε, and tortuosity factor, τ, of the catalysts particles were approximately taken as 0.5 and 1.5, respectively. Effective diffusivities of ozone, atrazine, and 2,4-D calculated are listed in Table C. 2.

$$D_{eA}=\frac{D_A\varepsilon}{\tau} \tag{C.3}$$

The bulk liquid concentrations (C_{As}) of ozone, atrazine, and 2,4-D are 1.042×10^{-4} M, 4.62×10^{-4} M, and 2.26×10^{-4} M, respectively. The dimensional parameter of catalyst particles ($L_p = R/3$) were 0.013 cm, 0.01 cm, and 0.01 cm for activated carbon, alumina, and perfluorooctyl alumina, respectively. The observed catalytic reaction rates, $\left(-r_A\right)_{obs}$, for atrazine and 2,4-D were calculated based on the observed reaction rate constants and the initial concentrations of ozone and micropollutants, whereas for ozone it was determined using the ozone decomposition rate constant. As ozone decay rates were faster in 2,4-D ozonation tests, Weisz-Prater parameters for ozone were determined for catalytic ozonation systems with 2,4-D.

Table C. 1. Molecular and effective diffusivities of ozone, atrazine, and 2,4-D in water

Solute	D_A (cm^2 s^{-1})	D_{eA} (cm^2 s^{-1})
Ozone	1.90×10^{-5}	6.33×10^{-6}
Atrazine	7.45×10^{-6}	2.48×10^{-6}
2,4-D	8.64×10^{-6}	2.88×10^{-6}

Weisz-Prater parameters for ozone, atrazine, and 2,4-D are summarized in Table C.2. As can be noticed, all *E* values obtained for the different catalytic ozonation processes were at least one order of magnitude smaller than one. However, the Weisz-Prater parameter estimated for 2,4-D in the ozonation system catalyzed by activated carbon was 0.128. Although this value is still much lower than one, it could have been reduced by decreasing the catalyst particle size. It should also be noticed that activated carbon was the catalyst exhibiting the higher removal rates of micropollutant removal on a catalyst dose basis. Thus, it is evidenced that mass transfer effects due to intraparticle diffusion did not play a major role in controlling the overall reaction rate.

Table C. 2. Weisz-Prater parameters for ozone, atrazine and 2,4-D in the different catalytic ozonation systems studied. $[O_3]_0 = 1.042\times10^{-4}$ M, $[ATZ]_0 = 4.62\times10^{-4}$ M, and $[2,4\text{-D}]_0 = 2.26\times10^{-4}$ M, pH = 3

Catalyst	Species	$\left(-r_A\right)_{obs}$ (M s^{-1})	E
AC	Atrazine	5.22×10^{-7}	8.09×10^{-2}
	2,4-D	4.68×10^{-7}	1.28×10^{-1}
	O_3	2.13×10^{-7}	5.74×10^{-2}
Al_2O_3	Atrazine	2.01×10^{-8}	4.87×10^{-3}
	2,4-D	1.63×10^{-7}	6.97×10^{-2}
	O_3	2.92×10^{-8}	1.23×10^{-2}
PFOA	Atrazine	1.81×10^{-10}	4.37×10^{-5}
	2,4-D	5.30×10^{-10}	2.26×10^{-4}
	O_3	5.08×10^{-10}	2.14×10^{-4}