UNIVERSITAT DE
BARCELONA

Contribution to Performance Characterization and Kinetic Modelling of Micropollutants Abatement in Water and Wastewater by Ozone-based Oxidation Processes

Alberto Cruz Alcalde

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UNIVERSITAT DE BARCELONA

Programa de doctorat d’Enginyeria i Ciències Aplicades

Contribution to Performance Characterization and Kinetic Modelling of Micropollutants Abatement in Water and Wastewater by Ozone-based Oxidation Processes

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La Dra. CARME SANS MAZÓN, professora titular del Departament d’Enginyeria Química i Química Analítica de la Universitat de Barcelona i el Dr. SANTIAGO ESPLUGAS VIDAL, Catedràtic del mateix departament:

CERTIFIQUEN QUE:

El treball de recerca titulat “CONTRIBUTION TO PERFORMANCE CHARACTERIZATON AND KINETIC MODELLING OF MICROPOLLUTANTS ABATEMENT FROM WATER AND WASTEWATER BY OZONE-BASED OXIDATION PROCESSES” constitueix la memòria que presenta l’Enginyer Químic Alberto Cruz Alcalde per a aspirar al grau de Doctor per la Universitat de Barcelona. Aquesta tesis doctoral ha estat realitzada dins del programa de doctorat “Enginyeria i Ciències Aplicades”, en el Departament d’Enginyeria Química i Química Analítica de la Universitat de Barcelona.

I per a que així consti als efectes oportuns, signen el present certificat a Barcelona, 15 de febrer de 2019.

Dra. Carme Sans Mazón i **Dr. Santiago Esplugas Vidal**

Directora i tutora de la tesi doctoral *Director de la tesi doctoral*

A mi familia

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Contents

Abstract

The increasing water scarcity is gradually forcing a switch from the classical wastewater management paradigm to a circular view in which wastewater is regarded as a precious resource and advanced tertiary treatments are required in order to make the most of it. But regardless of whether the final effluent is discharged or reused, there is a concerning aspect of wastewater pollution that still remain unregulated: the need of removing the so called micropollutants, especially those classified as priority substances and contaminants of emerging concern. If the aquatic environment is wanted to be preserved and safe water reuse practices established, these potentially harmful substances must be removed from wastewater.

Ozonation is nowadays a mature and competent technology for enhanced wastewater treatment. The combination of ozone, a strong and selective oxidant, with the even powerful and unselective hydroxyl radical, formed through ozone decomposition, is effective in the abatement of a number of organic compounds. However, there are still some points to be addressed for a more efficient application of ozone-based processes to wastewater treatment and reclamation.

Among micropollutants potentially present in wastewater effluents, there are several compounds that react very slowly with ozone. They are known as ozone-resistant micropollutants. If a high quality water is wanted to be obtained, these substances should be also removed from the effluent. In addition, modelling the abatement of micropollutants during wastewater ozonation is essential for process simulation, optimization and real-time control. To make this possible, performance characterization in terms of oxidation efficiency is required, as well as some kinetic information regarding the abatement of micropollutants. The first can be addressed by using normalizing parameters allowing the estimation, for instance, of hydroxyl radical availability as a function of the consumed ozone, or any other parameter whose measurement during the process is simple. The most accurate way of obtaining kinetic data of micropollutants oxidation is conducting individual studies on this chemicals degradation by ozone and hydroxyl radicals. Through these ones and some complementary tests, valuable data regarding the mechanisms of degradation and the potential ecotoxicological effects of formed transformation products can also be obtained.

This thesis was divided in two parts: first, individual batch ozonation studies of selected priority and emerging concern micropollutants were conducted. Particularly, the pesticides methiocarb, acetamiprid and dichlorvos were selected for that work. The second part consisted of the application of single ozonation and the combination of ozone and hydrogen peroxide (*i.e.*, peroxone process) was tested in the removal of ozone-refractory micropollutants from actual municipal wastewater effluents. The latter was done through semi-batch ozonation experiments. The objectives were, on one hand, obtaining kinetic, mechanistic and toxicological data of some priority/emerging concern chemicals. On the other, ozonation studies with real effluent samples were performed with the aim of exploring the removal of ozone-recalcitrant chemicals and potential strategies for the modelling and real-time control of this process. In addition, improvement strategies for peroxone process application were investigated.

Different kinetics were observed for pesticides reaction with ozone, being acetamiprid the most recalcitrant compound. In addition, toxicity of some of the pesticides transformation products was revealed, especially in the case of methiocarb degradation. Regarding ozone-based processes application to actual wastewater effluents, the removal of model ozone-recalcitrant compounds was found difficult, concluding that ozone doses higher than those corresponding to the immediate ozone demand value were required for a more effective abatement of these substances, regardless of the process employed. In the case of the peroxone process application, dosing hydrogen peroxide simultaneously to ozone bubbling was found to potentially entail important energy savings related to oxidants use. The oxidation performance of ozone-based processes and thus the abatement of ozone-refractory compounds could be effectively modelled using kinetic parameters, the monitoring of water quality parameters and empirical relationships obtained for each effluent. Furthermore, side reactions of involved oxidants with effluent organic compounds was found to increase the content in small and oxidized organic compounds in all cases. In the case of effluents containing suspended solids, ozone application also caused a net increase in the dissolved organic load.

Thesis directors' report and list of publications

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Drs. CARME SANS MAZÓN and SANTIAGO ESPLUGAS VIDAL, both professors at the Department of Chemical Engineering and Analytical Chemistry of the University of Barcelona and PhD thesis directors of Mr. Alberto Cruz Alcalde, issue the following report related with the participation of the PhD candidate in the publications derived from his predoctoral research and included in this dissertation:

All the major experimental work and results discussion of the contributions included in this thesis were entirely developed in the Department of Chemical Engineering of the University of Barcelona by Alberto Cruz Alcalde, under the supervision of his PhD directors. The publications included in this thesis and detailed below were not presented in other doctoral theses or doctoral theses presented as a summary of publications.

I. Cruz-Alcalde, A., Sans, C., Esplugas, S. (2017). Exploring ozonation as treatment alternative for methiocarb and formed transformation products abatement, *Chemosphere* 186, 725-732. DOI: 10.1016/j.chemosphere.2017.08.040.

II. Cruz-Alcalde, A., Sans, C., Esplugas, S. (2017). Priority pesticides abatement by advanced water technologies: The case of acetamiprid removal by ozonation, *Science of the Total Environment* 599-600, 1454-1461. DOI: 10.1016/j.scitotenv.2017.05.065.

III. Cruz-Alcalde, A., Sans, C., Esplugas, S. (2018). Priority pesticide dichlorvos removal from water by ozonation process: Reactivity, transformation products and associated toxicity, *Separation and Purification Technology* 192, 123-129. DOI: 10.1016/j.seppur.2017.09.069.

IV. Cruz-Alcalde, A., Esplugas, S., Sans, C. (2019). Abatement of ozone-recalcitrant micropollutants during municipal wastewater ozonation: Kinetic modelling and surrogate-based control strategies, *Chemical Engineering Journal*, in press. DOI: 10.1016/j.cej.2018.10.206

V. Cruz-Alcalde, A., Esplugas, S., Sans, C (2019). New insights on the fate of EfOM during ozone application for effective abatement of micropollutants in wastewater effluents, submitted to *Journal of Hazardous Materials*.

VI. Cruz-Alcalde, A., Esplugas, S., Sans, C (2019). Continuous H_2O_2 addition in peroxone process: performance improvement and modelling in wastewater effluents, submitted to *Chemical Engineering Journal* and currently under 2nd review.

Next, detailed bibliographic information of the journals in which the author of this thesis published or submitted the research studies is presented (data from *Journal Citation Reports*®, 2017):

- Chemosphere (IF: 4.427)

Category Name	**Quartile in Category**
Environmental Sciences	Q1

- Science of the Total Environment (IF: 4.610)

Category Name	**Quartile in Category**
Environmental Sciences	Q1

- Separation and Purification Technology (IF: 3.927)

Category Name	Quartile in Category
Engineering, Chemical	Q1

- Chemical Engineering Journal (IF: 6.735)

Category Name	Quartile in Category
Engineering, Chemical	Q1
Engineering, Environmental	Q1

- Journal of Hazardous Materials (IF: 6.434)

Category Name	Quartile in Category
Engineering, Civil	Q1
Engineering, Environmental	Q1
Environmental Sciences	Q1

Dr. Carme Sans Mazón and Dr. Santiago Esplugas Vidal

Barcelona, 15th February 2019

Nomenclature

The following is a list of the most used abbreviations, acronyms and symbols:

ACMP	Acetamiprid
AOP	Advanced Oxidation Process
ATZ	Atrazine
CAS	Conventional Activated Sludge
CEC	Contaminant of Emerging Concern
C*N* or C-*L*	It is referred to a wastewater effluent sample collected from a CAS system. It may be found followed by a number *N* or a location -*L*.
COD	Chemical Oxygen Demand, mg O_2 L^{-1}
DAD	Diode Array Detector
DDVP	Dichlorvos
DOC	Dissolved Organic Carbon, mg C L^{-1}
DOM	Dissolved Organic Matter
EC_{50}	Sample dilution causing a 50% reduction in bacteria light emission, % v/v
EfOM	Effluent Organic Matter
EQS	Environmental Quality Standard, µg L^{-1}
EU WFD	European Union Water Framework Directive (Directive 2000/60/EC)
Exposure	In ozone applications, the “exposure to an oxidant” (ozone or hydroxyl radical) or “oxidant exposure” is defined as the time-integrated concentration of an oxidant in the reaction medium (*e.g.*, ∫[•OHd*t* stands for the hydroxyl radical exposure). In this thesis, it is often called “availability”
GAV	Gavà-Viladecans, the location of a WWTP in Barcelona
H_2O_2	Hydrogen peroxide
HPLC	High-Performance Liquid Chromatography
IBU	Ibuprofen
IOD	Immediate or Instantaneous Ozone Demand, mg O_3 L^{-1} or mmol O_3 L^{-1}
K	Equilibrium constant, mol L^{-1}
k	Rate constant of reaction, s^{-1} (first order) or $M^{-1}s^{-1}$ (second order)
$k_{i,O3}$ or k_{O3}	Rate constant of ozone reaction with a compound *i*, $M^{-1}s^{-1}$
$k_{i,\bullet OH}$ or $k_{\bullet OH}$	Rate constant of hydroxyl radical reaction with a compound *i*, $M^{-1}s^{-1}$

k_La	Volumetric mass transfer coefficient, min^{-1}
K_{ow}	Octanol-water partition coefficient, dimensionless
LLA	La Llagosta, the location of a WWTP in Barcelona
MBR	Membrane Bioreactor
MC	Methiocarb
M*N* or M-*L*	It is referred to a wastewater effluent sample collected from an MBR system. It may be found followed by a number *N* or a location -*L*.
MP	Micropollutant
MPL	Metoprolol
MS	Mass Spectrometry
O_3	Ozone
•OH	Hydroxyl radical
pBZQ	*para*-Benzoquinone
pCBA	*para*-Chlorobenzoic acid
PH	Phenol
p*K*a	The decimal logarithm of the acid dissociation constant, *K*a.
PRA	El Prat de Llobregat, the location of a WWTP in Barcelona
PS	Priority Substance
PTFE	Polytetrafluoroethylene
R_{ct}	Ratio between •OH exposure and O_3 exposure, dimensionless
$R_{OH,O3}$	Ratio between •OH exposure and O_3 consumed, s
SEC-OCD	Size-Exclusion Chromatography with Organic Carbon Detection
SMX	Sulfamethoxazole
TOC	Total Organic Carbon, mg C L^{-1}
TOD	Transferred Ozone Dose, mg O_3 L^{-1} or mmol O_3 L^{-1}
TP	Transformation product
UV	Ultraviolet (also stands for “ultraviolet detector” in “HPLC-UV”)
UVA	Ultraviolet absorbance, cm^{-1} or m^{-1}
VAC	Vacarisses, the location of a WWTP in Barcelona
VAL	Vallvidrera, the location of a WWTP in Barcelona
WHO	World Health Organization
WWTP	Wastewater Treatment Plant
η_{tr}	Ozone mass transfer efficiency

1 Introduction

1.1 Water resources

1.1.1 Water demand and availability

Water use has increased about 500% over the last century, mainly as a result of the population growth and economic development [1]. Currently, the global water demand is estimated to be about 4600 km^3 per year, a number that is expected to become larger in the course of the next decades (Figure 1) [2]. The world population has been estimated to increase from 7700 million in 2017 to between 9400 and 10200 million in 2050, fact that is involving a rise in the water needs associated to food and energy production, in addition to domestic uses [3]. Moreover, the increasing industrialization and establishment of water supply services in developing regions of Africa, Asia and South America are significantly contributing to this inexorable growth in the water demand [4].

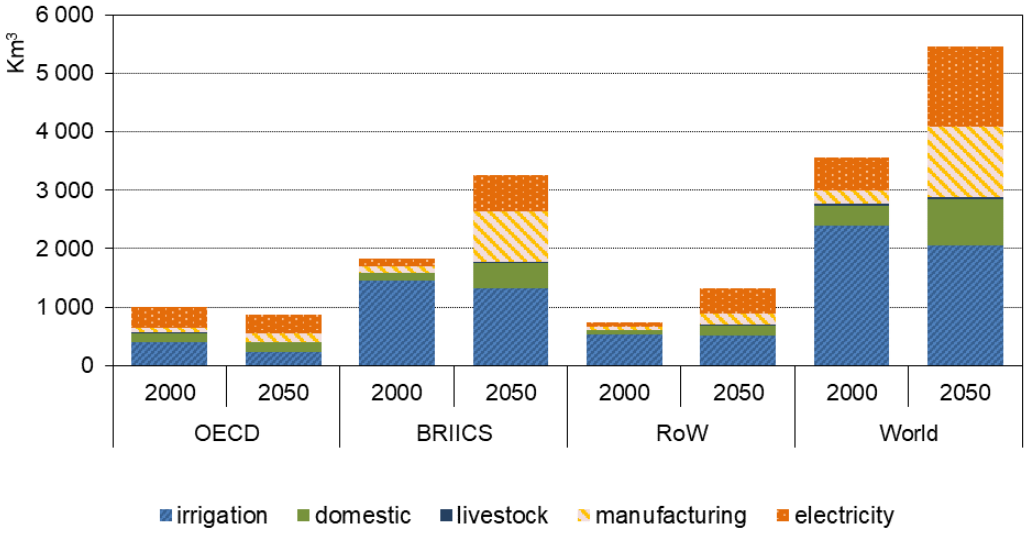


Figure 1. Global water demand (as freshwater withdrawals) in 2000 and 2050 (projection based on 2000 data) for different groups of regions in the world. OECD (Organization for Economic Co-operation and Development); BRIICS (Brazil, Russia, India, Indonesia, China, South Africa); RoW (rest of world) [4].

Only a 2.5% of the 71% of water covering the Earth surface is freshwater, and only a 1.2% of this mass constitutes an available resource for humans [5]. The world freshwater resources are renewed by the continuous cycle of evaporation, precipitation and runoff –the water cycle–, which dictates their distribution over the globe [6]. Since this is not uniform, indicators such as the water total renewable water per capita per year (Figure 2) can be helpful as a first estimate of the freshwater resources availability in a particular region of the world [7].

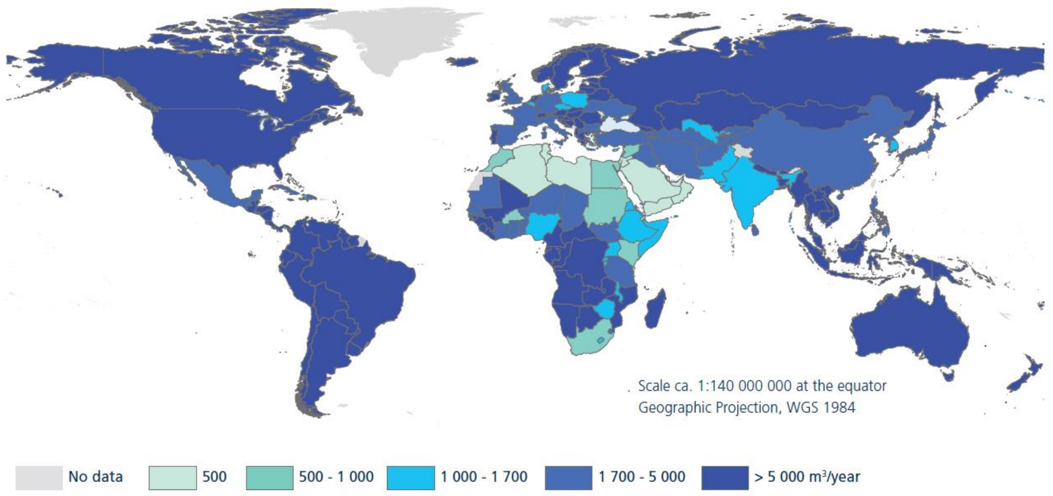


Figure 2. Total renewable freshwater (m^3 per capita and year) in 2014 [6].

According to this indicator, different levels of water scarcity –the other side of the coin– can also be defined. An area with renewable water levels between 1700 and 5000 m^3 of water per capita per year can suffer from occasional or local water stress. With less than 1700 m^3 of water per capita per year, an country is consider to suffer from regular water scarcity, whereas a region is under chronic and absolute scarcity when renewable water per capita per year drops below 1000 m^3 and 500 m^3, respectively [7]. In view of these data, therefore, it is quite clear that there are zones in the world in which renewable water resources are not physically available, triggering water stress situations. Moreover, other parts of the globe where freshwater is physically available can also suffer from water scarcity. In these cases, however, this situation is caused by economic constraints avoiding the establishment of the necessary infrastructures for the exploitation of these resources [6].

Water scarcity is an already demonstrated problem for humanity. The increasing demand of water, together with other issues such as the Climate Change –which directly affects the water cycle– are expected to contribute to worsen this situation over the next decades [6]. Throughout the 2010s, 1.9 billion people (around 30% of the world population) has lived in areas under potentially severe water scarcity. The projection for 2050 is about 2.7-3.2 billion.

However, if monthly variability is considered, between 4.8 and 5.7 billion people will suffer severe water scarcity at least one month per year [3].

In view of all these facts concerning freshwater scarcity, finding feasible solutions to this serious thread has become one of the most important 21st Century challenges. A partial solution –or at least an alternative to alleviate the situation– appears to reside in water reuse.

1.1.2 Wastewater treatment and reclamation

As a result of human uses of freshwater resources, huge amounts of wastewater are continuously generated. Due to the wide variety of potentially harmful contaminants that may contain, untreated wastewater cannot be discharged into natural water bodies without negatively impacting the quality of freshwater resources. However, it is estimated that near 80% of all industrial and municipal wastewater is released to the environment without any treatment [3]. This practice results in a growing deterioration of freshwater resources (Figure 3) that eventually might involve detrimental effects on human and environmental safety [3,8].

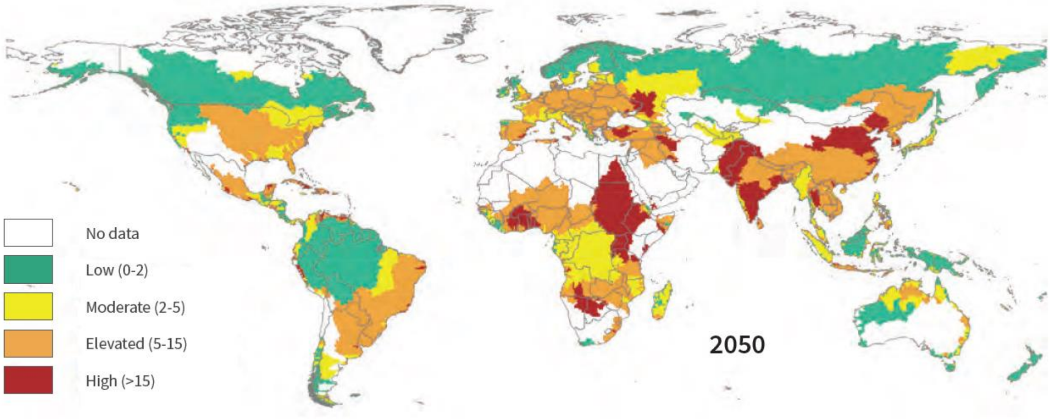


Figure 3. Water quality risk indices for major river basins in 2050 (projection based on the Commonwealth Scientific and Industrial Research Organization [CSIRO] *medium scenario*, which considers a drier future based on the CSIRO climate change model and a medium socio-economic growth) [8].

In a time in which water scarcity is increasingly becoming a problem, returning untreated wastewater to the water cycle may not be the wisest practice to preserve freshwater resources. Because of this, Wastewater Treatment Plants (WWTPs) are typically implemented in an attempt of minimizing the environmental impact of wastewater discharge into natural water systems [9]. Conventional wastewater treatment generally consists of a series of physicochemical (primary) and biological (secondary) treatment stages by means of which suspended solids, biodegradable organic matter and inorganic nutrients can be separated or removed. However, these processes are not effective in removing certain types of pollutants from wastewater, and therefore extra treatment steps are required if the quality of the final effluent is wanted to be further enhanced. These additional stages receive the name of tertiary treatments and are typically designed to remove nutrients (*e.g.*, phosphorus), pathogens, bio-recalcitrant chemicals, heavy metals and other suspended and dissolved solids [10].

Because WWTPs can be designed to meet the particular quality standards expected for a final effluent, treated wastewater is considered an alternative water resource. The objective behind waste reuse is to save important volumes of freshwater by reclaiming a wastewater that typically would have been released into the environment after treatment. Wastewater reclamation is currently a practice mainly established for non-potable applications, such as agricultural and landscape irrigation, industrial processes, environmental uses and urban cleaning, among others (Figure 4).

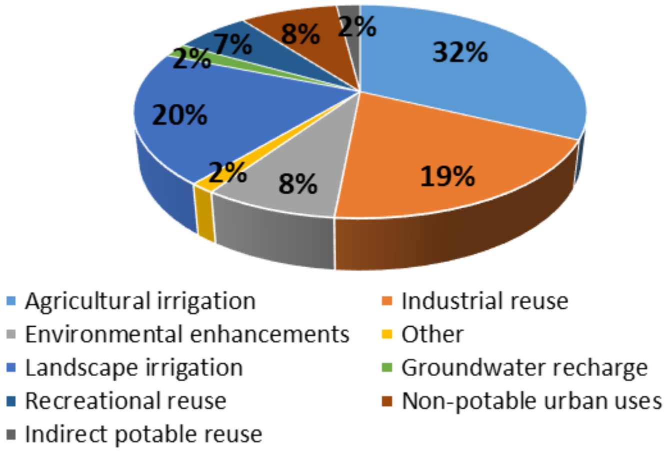


Figure 4. Worldwide water reuse by application [11].

However, and although more than 60 countries around the world practice various types of water reuse [12], reclaimed wastewater only represented 0.59% of the global water use in 2011, and it has been forecasted to represent 1.66% in 2030 [13]. In Europe, one of the most developed regions regarding wastewater infrastructures with near 80% of the population connected to a WWTP [12], only 2.4% of the treated wastewater is reused [14]. Considering that a 68.4% of urban wastewater treatment in Europe is performed at a tertiary level [15] and wastewater reclamation potential has been estimated to be 6 times the currently reused volume of water [16], this constitutes a clear case of unfulfilled potential.

The economic cost associated to advanced wastewater treatment is one of the critical factors avoiding further implementation of water reuse. Withdrawing of freshwater, especially in those zones with abundant reserves of this resource, is still more economically (and technically) attractive than wastewater reclamation. Another key barrier is related to the perception that this practice involves more health and environmental risks than benefits. This seems to be partly caused by the varying and insufficient legal frameworks regarding quality requirements for water reuse applications, which seems generate social mistrust and discourage investment in water reuse [17]. With the objective of revert this situation and stimulate and facilitate water reuse, the European Commission proposed on May 2018 a new regulation on minimum quality requirements for water reuse in Europe for agricultural irrigation [18].

Despite the current efforts aimed to promote enhanced wastewater treatment and water reuse, and the attempts made in order of regularizing such practices, a particular and increasingly concerning aspect of water pollution still remain poorly considered by laws, and consequently also in the planning stages of wastewater treatment or reclamation projects. We are referring to the presence in water resources (including treated wastewater) of organic micropollutants (MPs) and, particularly, the so called contaminants of emerging concern (CECs) and priority substances (PSs).

1.2 Micropollutants, contaminants of emerging concern and priority substances in water resources

The continuous development, production, use and disposal of an uncountable number of organic chemicals employed in daily human activities has caused, over the last decades, the widespread occurrence of many of such substances in the aquatic environment, including freshwater resources [19–21]. As they are typically detected at trace levels (ng L^{-1} to µg L^{-1}), these compounds are commonly known as micropollutants [22]. The sources of micropollutants in the aquatic environment are diverse, but in general they can be classified in six major groups namely pharmaceuticals, personal care products, steroid hormones, surfactants, industrial chemicals and pesticides (Table 1) [23].

Table 1. Main sources of micropollutants in the aquatic environment [23].

Group	**Main subclasses**	**Main sources**	
		Distinct	**Nonexclusive**
Pharmaceuticals	Non-steroidal Anti-inflammatory Drugs (NSAIDs), lipid regulator, anticonvulsants, antibiotics, β-blockers and stimulants	Domestic wastewater (from excretion) Hospital effluents Run-off from Concentrated Animal Feeding Operations (CAFOs) and aquaculture	Sources that are not exclusive to individual categories include: Industrial wastewater (from product manufacturing discharges) Landfill leachate (from improper disposal of used, defective or expired items)
Personal care products	Fragrances, disinfectants, UV filters and insect repellents	Domestic wastewater (from bathing, shaving, spraying, swimming and etc.)	
Steroid hormones	Estrogens	Domestic wastewater (from excretion) Run-off from CAFOs and aquaculture	
Surfactants	Non-ionic surfactants	Domestic wastewater (from bathing, laundry, dishwashing and etc.) Industrial wastewater (from industrial cleaning discharges)	
Industrial chemicals	Plasticizers and flame retardants	Domestic wastewater (by leaching out of the material)	
Pesticides	Insecticides, herbicides and fungicides	Domestic wastewater (from improper cleaning, run-off from gardens, lawns and roadways and etc.) Agricultural runoff	

Despite their low concentrations in water bodies, the presence of many MPs in the aquatic environment is thought to potentially involve a number of negative effects to both aquatic ecosystems and human health, including short-term and long-term toxicity, endocrine disrupting effects and antibiotic resistance of microorganisms [19,24]. However, and as recognized by international organisms such as the World Health Organization (WHO) or the

United Nations Educational, Scientific and Cultural Organization (UNESCO), scientific knowledge regarding the potential risks to human and environmental safety posed by the presence and continuous accumulation of micropollutants in water resources is still very scarce [25,26].

The fact that MPs can be detected in aquatic resources, in addition to their continuous production and disposal [27], is also attributed to the physicochemical properties of these chemicals, which in general make them certainly resistant to natural (biotic and abiotic) degradation processes taking place in the environment [21]. This, therefore, causes the persistence of MPs in water bodies, which may vary depending on the individual characteristics of each species. Moreover, and although many of these substances reach municipal WWTPs after their use, most of them are poorly removed and leave the plants to finally enter the environment (see Figure 5). Because of that, municipal WWTPs –which usually release treated water to the water bodies (see section 1.1.2)– are nowadays considered as one of the main pathways for MPs introduction into the aquatic environment [23,28].

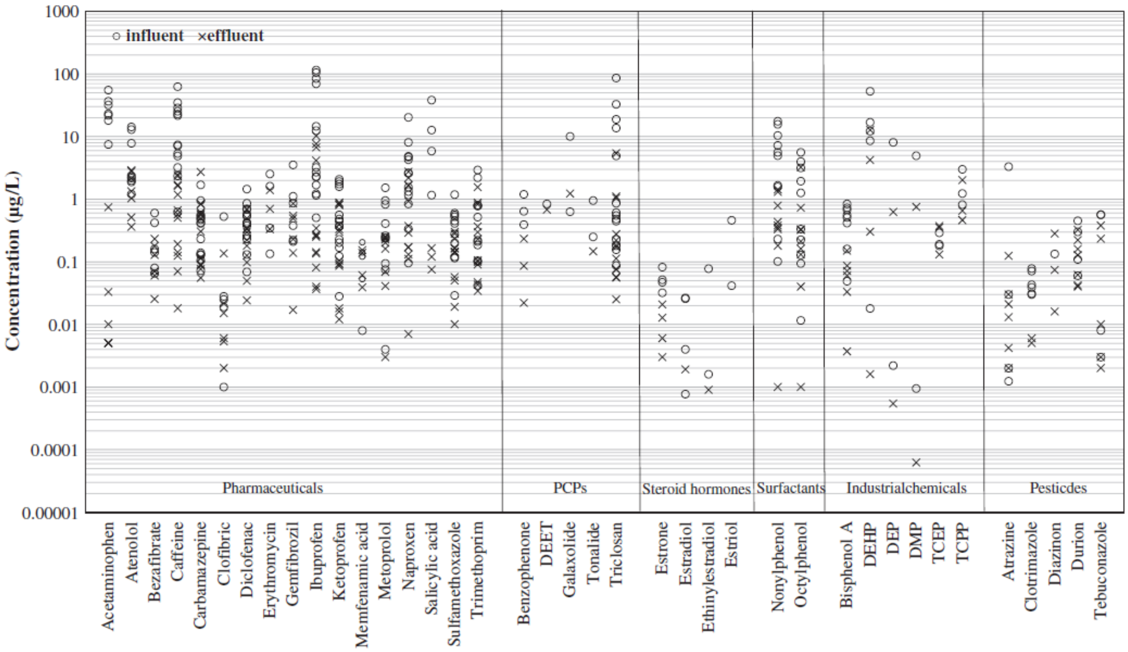


Figure 5. Average concentrations reported for selected micropollutants in WWTPs influents and effluents [23].

The potential risks of micropollutants linked to their presence in natural waters, together with their resistance to natural degradation mechanisms and to conventional wastewater treatments have led to the labelling of many MPs as contaminants of emerging concern (CECs). Although both terms (*i.e.*, MPs and CECs) are sometimes used interchangeably, *micropollutant* is perhaps a more general designation. CECs comprise three categories of compounds [29,30]: i) newly developed substances that have recently entered the environment; 2) chemicals whose presence is not new but recently recognized as potentially hazardous for humans and the environment; and iii) chemicals that have been recently detected due to the development of novel and more sensitive analytical methods. Furthermore, a common characteristic of CECs is that they are not covered by any regulation regarding water quality [27], whereas MPs may have been already regulated and included as priority substances (PSs) in related legislations.

1.2.1 European regulations on micropollutants in water resources

Although legal discharge limits for micropollutants are still inexistent, some regulations regarding their presence in water resources have been published over the last two decades. In the case of Europe, Directive 2000/60/EC –the so-called European Union Water Framework Directive (EU WFD)– laid the foundations for the establishment of a list of substances/groups or substances to be prioritized according to their relative risks to or through the aquatic environment [31]. The ultimate objective was defining EU Environmental Quality Standards (EQSs) representing the concentrations of particular pollutants or group of pollutants in aqueous compartments which should not be exceeded in order to protect human health and the environment. Being so, in 2001 Decision 2455/2001/EC set the first list of 33 PSs to be monitored at EU level, mainly based on the previous knowledge regarding their intrinsic hazards, environmental occurrence and volumes of production and use [32]. Some of these chemicals, designated as Priority Hazardous Substances (PHSs) were the same year listed in the Stockholm Convention on Persistent Organic Pollutants (POPs), which aimed to eliminate or restrict the production and use of these compounds [33]. POPs are defined as organic chemical substances possessing particular physicochemical properties that make them exceptionally persistent in the environment, bioaccumulative and toxic to both humans and wildlife. In 2008, after seven years since Decision 2455/2001/EC, Directive 2008/105/EC amended the EU WFD and finally published the EQS values for the 33 PSs and 8 additional pollutants [34]. EU countries must monitor these compounds in surface waters and compare these data with EQSs in order to determine the chemical quality of EU water bodies and if required, adopting measures to gradually reduce discharges, emissions and losses of PSs and PHSs. In 2013, Directive 2013/39/EU was launched and updated Directives 2000/60/EC and 2008/105/EC [35]. In this occasion, the PSs list was expanded to 41 organic compounds and 4 metals (cadmium, lead, mercury and nickel) (Table 2), and more restrictive EQS were set for some of the original PSs. Also, EQS values were considered for 8 additional compounds not considered as PSs. In addition, this regulation pointed out the need of developing alternative water treatment technologies that could be also effective for the removal of these chemicals.

Table 2. List of priority substances (PSs) in the field of water policy, established in Directive 2013/39/EU [35]. The symbol † in some groups of substances indicates that only certain compounds of the family are classified as PSs. Substances marked with an asterisk (*) are identified as priority hazardous substances (PHSs). Finally, two asterisks (⁑) in some groups of substances indicate that only some of their compounds are identified as PHSs. Further details regarding specific compounds can be consulted in Annex I of the Directive.

	Substance	**CAS number**	**Subclass**	**Class**
1	Alachlor	15972-60-8	Chloroacetanilides	Pesticides
2	Anthracene *	120-12-7	-	-
3	Atrazine	1912-24-9	Triazines	Pesticides
4	Benzene	71-43-2	Multiple applications	Industrial compound
5	Brominated diphenylethers * ⁑	-	Flame retardants	Industrial compound
6	Cadmium and its compounds *	7440-43-9	-	-
7	Chloroalkanes, C_{10-13} *	85535-84-8	Multiple applications	Industrial compounds
8	Chlorfenvinphos	470-90-6	Organophosphorus	Pesticides
9	Chlorpyrifos	2921-88-2	Organophosphorus	Pesticides
10	1,2-dichloroethane	107-06-2	Solvents	Industrial compounds
11	Dichloromethane	75-09-2	Solvents	Industrial compounds
12	Di (2-ethylhexyl) phthalate (DEHP) *	117-81-7	Plasticizers	Industrial compounds
13	Diuron	330-54-1	Phenylureas	Pesticides
14	Endosulfan *	115-29-7	Organochlorine	Pesticides
15	Fluoanthene	206-44-0	-	-
16	Hexachlorobenzene *	118-74-1	Organochlorine	Pesticides
17	Hexachlorobutadiene *	87-68-3	Organochlorine	Pesticides
18	Hexachlorocyclohexane *	608-73-1	Organochlorine	Pesticides

Table 2. (Continued)

	Substance	CAS number	Subclass	Class
19	Isoproturon	34123-59-6	Phenylureas	Pesticides
20	Lead and its compounds	7439-92-1	-	-
21	Mercury and its compounds *	7439-97-6	-	-
22	Naphtalene	91-20-3	-	-
23	Nickel and its compounds	7440-02-0	-	-
24	Nonylphenols * ⁑	-	Multiple applications	Industrial compounds
25	Octylphenols †	-	Multiple applications	Industrial compounds
26	Pentachlorobenzene*	608-93-5	Solvents	Industrial compounds
27	Pentachlorophenol	87-86-5	Organochlorines	Pesticides
28	Polyaromatic hydrocarbons (PAH) †*	-	-	-
29	Simazine	122-34-9	Triazines	Pesticides
30	Tributyltin compounds * ⁑	-	Organotin	Pesticides
31	Trichlorobenzenes	12002-48-1	Solvents	Industrial compounds
32	Trichloromethane (chloroform)	67-66-3	Solvents	Industrial compounds
33	Trifluralin *	1582-09-8	Dinitroanilines	Pesticides
34	Dicofol *	115-32-2	Organochlorines	Pesticides
35	Perfluorooctane sulfonic acid and its derivatives (PFOS) *	1763-23-1	Multiple applications	Industrial compounds
36	Quinoxyfen *	124495-18-7	Quinolines	Pesticides
37	Dioxins and dioxin-like compounds * ⁑	-	-	-
38	Aclonifen	74070-46-5	Diphenyl ethers	Pesticides
39	Bifenox	42576-02-3	Diphenyl ethers	Pesticides
40	Cybutryne	28159-98-0	Triazines	Pesticides
41	Cypermethrin	52315-07-8	Pyrethroids	Pesticides
42	Dichlorvos	62-73-7	Organophosphorus	Pesticides
43	Hexabromocyclododecanes (HBCDD) * ⁑	-	Flame retardants	Industrial compound
44	Heptachlor and heptachlor epoxide *	76-44-8/ 1024-57-3	Organochlorines	Pesticides
45	Terbutryn	886-50-0	Triazines	Pesticides

Furthermore, Directive 2013/39/EU proposed the first watch list of substances for Union-wide monitoring in the field of water policy, which was launched two years later in Decision 2015/495/EU [36]. The objective of the watch list was establishing monitoring programs on some contaminants considered to be of emerging concern (CECs), with the ultimate aim of gathering relevant information that could be used to support decisions in eventual prioritization procedures. It covered 17 CECs or groups of CECs. As this list must be revised periodically, Decision 2018/840/EU of 5 June 2018 has recently repealed Decision 2015/495/EU, updating the previous list of compounds according to monitoring and ecotoxicological data gathered during the period from 2015 to 2017 [37]. The current watch list comprises 15 CECs and is presented in Table 3.

Table 3. Watch list of substances for Union-wide monitoring in the field of water policy, established in Decision 2018/840/EU [37].

Substance	**CAS number**	**Subclass**	**Class**
17-α-ehinylestradiol (EE2)	57-63-6	17-α-Substituted estradiol derivatives	Steroid hormones
17-β-estradiol (E2)	50-28-2	Estradiol derivatives	
Estrone (E1)	53-16-7	Estrone derivatives	
Erythromycin	114-07-8	Macrolide antibiotics	Pharmaceuticals
Clarithromycin	81103-11-9		
Azithromycin	83905-01-5		
Amoxicillin	26787-78-0	Penicillin antibiotics	
Ciprofloxacin	85721-33-1	Fluoroquinolone antibiotics	
Methiocarb	2032-65-7	Carbamates	Pesticides
Imidacloprid	105827-78-9/ 138261-41-3	Neonicotinoids	
Thiacloprid	111988-49-9		
Thiametoxam	153719-23-4		
Clothianidin	210880-92-5		
Acetamiprid	135410-20-7		
Metaflumizone	139967-49-3	Semicarbazones	

As CECs included in the Watch List are still considered candidate substances for prioritization, EQSs have not yet been established for them. However, all the efforts are being currently made by researchers in order to boost the prioritization and inclusion in routine monitoring programs of all substances which must be there, according to scientific evidence. With this aim, the Working Group on Prioritization of Emerging Substances of the

NORMAN Association (an independent network of reference laboratories, research centers and related organizations for monitoring of emerging environmental substances [38]) has developed a common prioritization framework for emerging substances [39]. The objective of this scheme, which is completely in line with the aims of the EU WFD, is to provide decision-makers with the valuable information required to create and update lists of priority and emerging concern chemicals such as those established by Directive 2013/39/EU and Decision 2018/840/EU. So far, NORMAN has identified and included in its prioritization network more than 1000 emerging substances, which have been classified according to the available information mainly concerning their environmental occurrence and effects on living organisms [38].

1.2.2 The pesticides concern

Out of the 45 substances/groups of substances included in the PSs list, 23 are pesticides. Similarly, 7 out of 15 CECs in the watch list established in Decision 2018/810/EU also belong to this group of micropollutants. That represents a presence of pesticides in European priority and emerging concern substances lists of about 50%, which is not coincidence given the nature of these compounds.

Pesticides are substances designed and employed with the purpose of dissuade, incapacitate or simply killing living organisms considered to be harmful. They are typically used for crop protection in agriculture (around 85% of world production), although other important applications include livestock protection and human disease control [40]. Since its use became especially popular after World War II, synthetic organic pesticides have become essential to maintain the quality and increasing quantity of food required to satisfy human population [41,42]. However, and although specific legislation regulating the use of pesticides exists in some regions of the world such as Europe [43], this always involves risks to human and environmental safety. Concerns about pesticides use already started by the mid-1940s, with the first reports of harms to non-target organisms caused by exposure to the nowadays infamous dichlorodiphenyltrichloroethane (DDT), an organochlorine insecticide [44]. After further evidence on pesticides toxicity and a large public outcry, partly motivated by the divulgation made by Rachel Carson in her book *Silent Spring* of the disastrous impacts on the environment caused by the use of pesticides [45], DDT and other organochlorine pesticides were finally banned by 1970s in the United States and many other countries in the world [46]. Since then, other chemical classes of compounds, such as organophosphates, carbamates or pyrethroids, with apparent lower toxicity and persistence and a higher selectivity than organochlorines have been extensively used in agriculture as insecticides. Over the years, however, it has been demonstrated that even the use of these alternative compounds can negatively affect human health and the environment [40,47,48]. Thus, bans and restrictions on the use of several families of pesticides and particular compounds have gradually been imposed during the last decades, and the search for greener synthetic pesticides still continues these days [46].

One of the last chemical classes to be discovered and commercialized were neonicotinoid insecticides, which in 2013 surpassed organophosphates as the most widely used insecticides in the world [46]. Again, what apparently was a less toxic, more selective and less persistent class of pesticides than the preceding ones, started soon to raise concerns. An increasing number of reports relate the destruction of populations of birds, aquatic organisms and beneficial insects (*e.g.*, bees) to the presence of neonicotinoids in the environment [49,50]. These evidences, together with the uncertainty about risks posed to humans and other mammal species, have prompted regulating actions from the European Commission, which restricted on May 2018 the agricultural use of three of the most employed neonicotinoids, namely imidacloprid, clothianidin and thiametoxam [51–53].

Table 4. Occurrence of pesticides in water samples worldwide. Data collected between 1993 and 2017 [55].

Country	**Number of aquatic systems**	**Quantified pesticides**	**Sampling year**	**Average concentration [ng L^{-1}]**
Benin	1	6	2010	224.9
Egypt	2	12-13	1993	0.1
Ghana	2	4-11	2004	0.1-97.3
Kenya	1	2	-	9375
Mozambique	1	16	-	30.6
Nigeria	5	1-14	2014	190-2163
South Africa	5	4-15	1999-2002	35.2-77.9
China	11	5-30	1999-2014	1.5-7384
India	3	3-13	2009-2015	0.2-13166
Macau	1	18	2001	1.6
Russia	2	7	2003-2005	0.1
Vietnam	1	13	2012	398.5

Table 4. (Continued)

Country	Number of aquatic systems	Quantified pesticides	Sampling year	Average concentration [ng L^{-1}]
Central and Eastern Europe	1	9	2007	6.3
Belgium	2	6-7	2002-2004	48.4-312.1
Bulgaria	1	8	-	5.3
France	6	3-19	2003-2010	26.9-566.7
Germany	6	1-19	2001-2003	9.1-580
Greece	7	3-23	1996-2007	19.6-99.3
Hungary	1	2	2010	417.1
Italy	1	9	2008	1.9
Norway	1	12	2014	0.3
Poland	2	8-12	2002-2003	8.5-42
Portugal	7	8-48	2004-2012	31.2-17667
Romania	3	7	2004-2013	1.6-37.1
Spain	13	1-45	1996-2013	4-940
The Netherlands	-	13	2008	43.8
Australia	5	4-10	2006-2010	2.8-759.1
Argentina	2	3-8	2012	53.5-323.3
Brazil	2	10-11	1999-2005	12.9-23.6
Chile	1	8	2013-2014	2.6

Given the risks posed by pesticides to human and environmental safety, it becomes clear why the presence of these compounds in freshwater resources is of major concern. Moreover, some of the physicochemical properties of the pesticides/families of pesticides nowadays employed, such as relatively low hydrophobicity and high solubility, facilitate a higher distribution in water once they reach aqueous compartments via some of the typical transport mechanisms (*i.e.*, runoff, soil leaching and spray drifting) [54]. This is one of the causes of their widespread detection in water bodies worldwide (Table 4) [55].

Methiocarb

Methiocarb (MC, see chemical structure in Table 5) is one of the most employed carbamate pesticides worldwide. It can be used in agriculture as bird repellent, insecticide, acaricide and molluscicide. MC is poorly soluble in water (27 mg L^{-1}), moderately hydrophobic (log K_{ow} *ca.* 3) and does not dissociate in aqueous solution. As a carbamate, the MC mode of action is based on the inhibition of the vital enzyme cholinesterase, through what is known as cholinergic effect [56]. In short, MC molecules bind the enzyme molecule by carbamylation of the active site, and this prevents the degradation of acetylcholine neurotransmitter after synapsis [57]. If acetylcholine molecules are not degraded, they accumulate in the synaptic gap, leading to an overstimulation of the neurotransmitter receptor. Non-target organisms such as humans and aquatic species are also susceptible to the cholinergic effect [57]. Being so, MC is classified as a very toxic substance to human and aquatic life, with potential long lasting effects [58]. Moreover, MC is also classified by the WHO as a highly hazardous pesticide [59]. Notwithstanding, its use in Europe or the United States is still approved. Recently, it has been included in the watch list of substances established by Decision 2018/840/EU [37]. MC has been detected at concentrations up to a few ng L^{-1} in different surface waters of southern Europe [60–63].

Despite the risks posed by the presence of this pesticide in water resources, the search for advanced technologies for the degradation of MC from water matrices has been so far barely explored. Only a work describing the potential use of vacuum ultraviolet/ultraviolet (VUV/UV) process on that purpose has been recently published [64], in addition to three previous works dealing with the oxidation of this chemical by some conventional disinfectants [65–67].

Acetamiprid

Acetamiprid (ACMP, see chemical structure in Table 5) is one of the seven neonicotinoid insecticides that are currently commercialized [68]. ACMP is moderately soluble in water (4300 mg L^{-1}), presents low hydrophobicity (log K_{ow} = 0.8) and a pKa value of 0.7. Its mode of action –similar to all compounds included in this family of pesticides– is related to the disruption of cholinergic synapses, although in a different way than that for carbamate or organophosphate pesticides. Particularly, neonicotinoids act as agonists of the nicotinic acetylcholine receptors [68]. As they present similar characteristics than acetylcholine, neonicotinoids are able of miming this molecule, binding irreversibly to the nicotinic receptor. This union causes both, a blockage of the receptor and its permanent stimulation [68]. Since this specific neural pathway is more abundant in insects than in other organisms, neonicotinoids are in general more toxic to insects than mammals and other non-insect species [50,68]. However, there are studies relating negative impacts on human health due to the chronic exposure to this chemical [69–71]. Furthermore, it has been reported that ACMP can affect aquatic and other living species [72–75]. ACMP is currently classified at European level as harmful to both human and aquatic life [58]. Its use is approved worldwide, although recently it has been included as one of the neonicotinoids under surveillance in Europe, according to Decision 2018/840/EU [37]. As it appears to be less toxic to beneficial insects than it was initially though, the use of ACMP has not been restricted as happened with other compounds of the same family. Being so, an increase in the production and use of ACMP in the following years to the detriment of imidacloprid, clothianidin and thiametoxam should not be a surprise. ACMP has been frequently detected in different freshwater bodies worldwide, including some in Europe, at concentrations up to 380 ng L^{-1} [76–82].

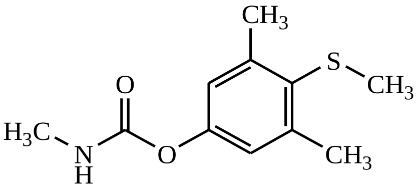
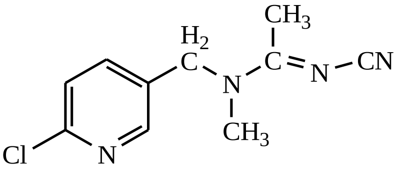
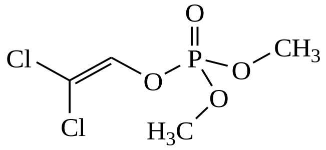
The removal of ACMP from water by means of advanced technologies has been frequently reported, including several recent works exploring UV irradiation, Fenton, photo-Fenton, heterogeneous photocatalysis and electrochemical oxidation processes as treatment alternatives [83–88]. However, the use with the same purpose of other well-established technologies such as ozonation has not yet been studied.

Dichlorvos

Dichlorvos (DDVP, see chemical structure in Table 5) is an organophosphate insecticide. It presents high solubility in water (*ca.* 10000 mg L^{-1}), moderate hydrophobicity (log K_{ow} about 1.5) and does not dissociate in aqueous solutions. As all pesticides belonging to this chemical family, DDVP acts inhibiting the acetylcholinesterase enzyme, in a similar way that carbamates do [56,57]. However, the binding due to phosphorylation of the enzyme active site is significantly stronger than that produced by carbamylation, which dramatically increases the potential negative impacts of organophosphate pesticides over non-target organisms [56], compared with carbamates. The exposure to DDVP has been related, among others, to serious health issues in humans and fish [89–93]. The European Commission categorized DDVP as a toxic substance for humans when exposure occurs via dermal or oral mechanisms, and fatal if inhaled. Moreover, it is classified as a very toxic chemical to aquatic life [94]. The WHO, on its part, recommended classifying DDVP as a highly hazardous pesticide [59]. The use of DDVP at European level is currently not approved, and since 2013 it is considered a priority substance, according to Directive 2013/39/EU [35]. In other regions of the world, such as the United States or Australia, the employment of this insecticide has been restricted but still continues. DDVP has been frequently detected in different water bodies worldwide, including some in European countries, at concentrations ranging from a few to 1100 ng L^{-1} [78,81,95–100].

DDVP removal by advanced treatment options has been previously reported, including some recent studies dealing with the use of Advanced Oxidation Processes (AOPs) on this purpose [101–103]. To the best of our knowledge, however, there are not previous studies on the degradation process of this pesticide through ozone-based processes.

Table 5. Names and chemical structures of pesticides methiocarb, acetamiprid and dichlorvos.

Compound name(s)	**Chemical structure**
Methiocarb (3,5-dimethyl-4-methylsulfanylphenyl) N-methylcarbamate	
Acetamiprid N-[(6-chloropyridin-3-yl)methyl]-N'-cyano-N-methylethanimidamide	
Dichlorvos 2,2-dichloroethenyl dimethyl phosphate	

1.3 Ozonation and ozone-based oxidation processes

The increasing preoccupation regarding the presence of priority substances and contaminants of emerging concern in water resources, together with the general consensus that conventional wastewater treatment plants are one of the main pathways for micropollutants introduction into the aquatic environment triggered, some decades ago, a search for advanced treatment options that were capable of removing these pollutants from water matrices [104]. These technologies should ideally destroy MPs without leaving no trace in water and without “passing the problem” to another medium, such as is typically done when applying membrane-based and other separation processes. Thus, emerging treatment technologies for MPs removal should be based on chemical oxidation. During the last years, and in view of the increasing problems related to water scarcity and the upward trend in considering wastewater as a water resource, this area of water research has received a massive boost.

Among the numerous, existing alternatives of treatment based on chemical oxidation, ozonation and ozone-based oxidation processes are some of the most mature technologies nowadays, with ample and demonstrated potential for MPs removal from aqueous matrices [104–107].

1.3.1 Chemistry of ozone in water and wastewater treatment

Ozone (O_3) is very reactive compound, fact that is attributed to the electronic configuration of its molecule (Figure 6). The lack and excess of electrons of one of the oxygen atoms in some of the possible resonance structures confers both electrophilic and nucleophilic character to this compound, respectively. Moreover, and also due to its electronic configuration and hybrid character, the ozone molecule presents some polarity (Dipole moment: 0.537 Debye).

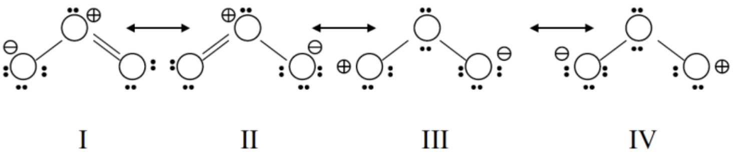


Figure 6. Resonance forms of the ozone molecule [108].

Because of its particular characteristics, ozone may be involved in different types of reactions with water constituents (including organic micropollutants), namely cycloaddition reactions, electrophilic substitution reactions and electron transfer reactions [107,108]. Nucleophilic addition reactions are also theoretically possible, although these have only been confirmed for non-aqueous systems [108].

Cycloaddition reactions with ozone are typical of unsaturated organic compounds, such as olefins [107]. Such reactions follow what is known as Criegee mechanism [109], which in aqueous solutions consists of the three following steps (Figure 7). First, a dipolar 1,3 addition between ozone and the double bound takes place, resulting in the formation of a cyclic structure called ozonide. This species is very unstable and it readily undergoes decomposition, giving rise to a carbonyl compound (aldehyde or ketone) and a zwitterion (step 2). The zwitterion, with certain polar character, interacts with water to give rise to a hydroxylalkylhydroperoxide, which decomposes to (and is in equilibrium with) another carbonyl compound and hydrogen peroxide [107].

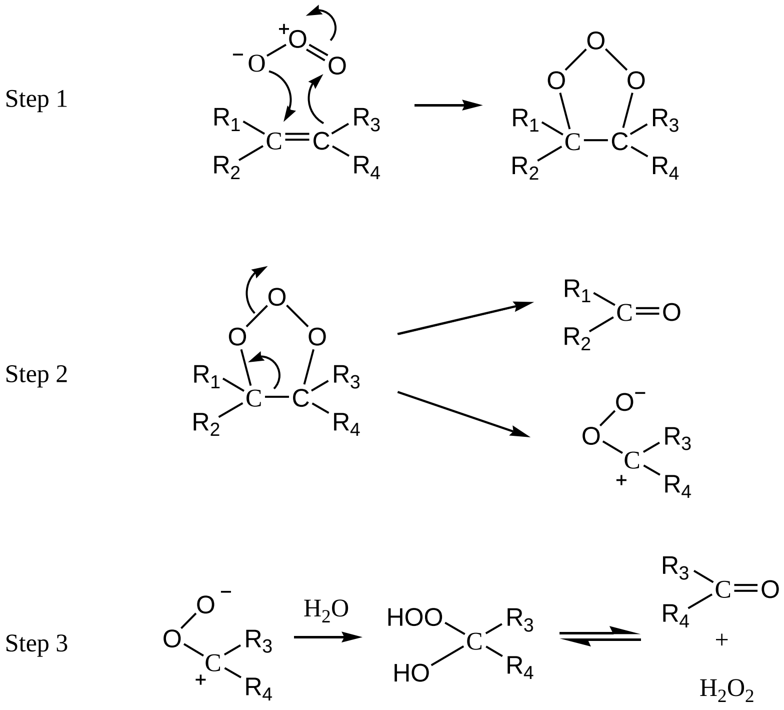


Figure 7. Ozone cycloaddition reaction: Criegee mechanism.

Ozone undergo electrophilic substitution reactions with moieties presenting a high electronic density [107]. Positions *ortho-* and *para-* in aromatic rings with electron-donating substituents, such as hydroxyl or amino groups, are especially susceptible to this type of reaction [108]. The example of Figure 8 illustrates this. First, a carbocation is formed. As the starting aromatic compound had an electron-donating group as substituent (D), electrophilic attack of ozone at *ortho-* and *para-* positions is favored. Then, oxygen is released from the formed carbocation and this is followed by a hydrogen shift, overall resulting in the hydroxylation of the starting compound [107].

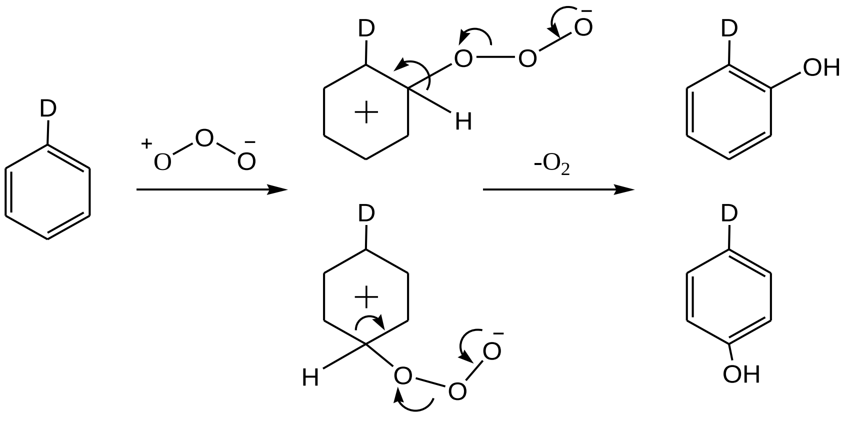


Figure 8. Electrophilic substitution reaction between ozone and aromatic compounds.

Table 6. Ozone decomposition mechanism in pure water. Initiation and radical chain evolution.

Reaction	**Rate constants**	**Reaction No.**	**References**
$O_3 + OH^- \rightarrow HO_4^-$	$k_1 = 70\ M^{-1}s^{-1}$	(1)	[111,112,116]
$HO_4^- \leftrightarrow HO_2^\bullet + O_2^{\bullet -}$	$k_2 \sim 10^7\ s^{-1}$	(2)	[116]
	$k_{-2} = 5\cdot10^9\ M^{-1}s^{-1}$		
$HO_2^\bullet + O_2^{\bullet -} \rightarrow HO_2^- + O_2$	$k_3 = 10^8\ M^{-1}s^{-1}$	(3)	[116]
$O_3 + HO_2^- \rightarrow HO_5^-$	$k_4 > 2.8\cdot10^6\ M^{-1}s^{-1}$	(4)	[111,117]
$HO_5^- \leftrightarrow HO_2^\bullet + O_3^{\bullet -}$	$k_5 > 10^7\ s^{-1}$	(5)	[117]
	$k_{-5} \sim 5\cdot10^9\ M^{-1}s^{-1}$		
$HO_5^- \rightarrow 2O_2 + OH^-$	$k_6 \sim k_5$	(6)	[117]
$HO_2^\bullet \leftrightarrow O_2^{\bullet -} + H^+$	$k_7 = 3.2\cdot10^5\ s^{-1}$	(7)	[111]
	$k_{-7} = 2.0\cdot10^{10}\ M^{-1}s^{-1}$		
$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2$	$k_8 = 1.6\cdot10^9\ M^{-1}s^{-1}$	(8)	[114]
$O_3^{\bullet -} \leftrightarrow O^{\bullet -} + O_2$	$k_9 = 1.94\cdot10^3\ s^{-1}$	(9)	[117]
	$k_{-9} = 3.5\cdot10^9\ M^{-1}s^{-1}$		
$O^{\bullet -} + H_2O \leftrightarrow HO^\bullet + OH^-$	$k_{10} = 9.6\cdot10^7\ s^{-1}$	(10)	[116,118]
	$k_{-10} = 1.2\cdot10^{10}\ M^{-1}s^{-1}$		
$HO^\bullet + O_3 \rightarrow O_2 + HO_2^\bullet$	$k_{11} = 2.0\cdot10^9\ M^{-1}s^{-1}$	(11)	[112]

Although cycloaddition and electrophilic substitution reactions typically dominate in water and wastewater ozonation, electron transfer reactions usually take place in competition [107]. The standard redox potential of ozone is high (2.07 V), this indicating the potential of this species to get involved in electron transfer processes. Good examples of this type of reactions are some of those constituting the radical chain decomposition mechanism of ozone in pure water, first introduced by Joseph Weiss in 1934 [110] and periodically re-investigated and revised since then [111–117]. Currently, the most accepted version of the mechanism is the one formed by reactions (1-11) gathered in Table 6, where reactions (1-6) are the steps contributing to initiate the radical chain mechanism and reactions (7-11) represent how this proceeds.

It is important to note that, as a consequence of the radical chain O_3 decomposition mechanism, hydroxyl radicals (•OH) are generated. This is an extremely reactive transient species, and it reacts with many organic and inorganic chemical species present in water [119]. In fact, •OH is in general more reactive than ozone, as well as significantly less selective [107]. To get a general idea about that, the second-order rate constants of hydroxyl radical reactions with organic compounds typically range between 10^8 and 10^{10} $M^{-1}s^{-1}$ (*i.e.*, three orders of magnitude) [119], whereas rate constants of ozone reactions can vary up to more than ten orders of magnitude (0.1-10^{10} $M^{-1}s^{-1}$) [107], depending on the chemical nature of the target species.

Hydroxyl radicals can present three types of reactions: addition reactions, hydrogen abstraction reactions and electron transfer reactions [107,120]. The most common and fast (many of them usually close to be diffusion-controlled) are addition reactions, which readily take place to double bounds (especially C=C, C=N, S=O) and aromatic rings (Figure 9) [120].

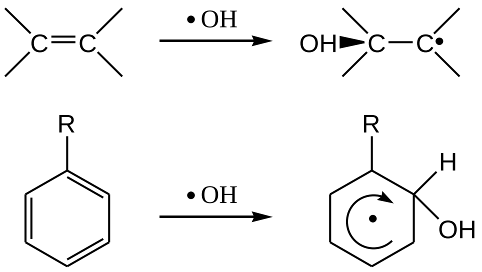


Figure 9. Examples of •OH addition reactions to double bounds and aromatic rings (early stages).

Hydrogen abstraction reactions also take place with frequency, especially when the first pathway is not possible [107]. These are usually slower than addition reactions and the only possible route for many saturated hydrocarbons (*i.e.*, only containing single bonds such as C-H, N-H and O-H bonds) [120]. The general scheme is represented by reaction (12).

$$^{\bullet}OH + R\text{-}H \rightarrow H_2O + R^{\bullet} \qquad (12)$$

Electron transfer reactions are rare with organic compounds and, contrarily to what is often thought, the high reduction potential of •OH (2.8 V) is not a measure of its high reactivity [107]. However, electron transfer reactions between hydroxyl radicals and some inorganic anions are possible, and indeed they are of great importance for ozone application in water and wastewater treatment, where several of these species are abundant [120]. They react with •OH without giving rise to other chain carriers such as the hydroperoxyl radical or the superoxide anion ($HO_2^{\bullet}$ and $O_2^{\bullet-}$, respectively), and therefore do not contribute to the radical chain propagation that eventually leads to further •OH generation (see Table 6). Inorganic compounds with these characteristics are known as •OH scavengers or radical chain inhibitors, as contribute to the termination of the ozone decomposition mechanism [121]. Some of the most important inhibition reactions are the ones involving carbonate and bicarbonate anions (Table 7) [121], although other species such as chloride or nitrite may also contribute [120].

Table 7. Main reactions involved in the inhibition of the radical chain ozone decomposition mechanism by carbonate and bicarbonate anions. Mechanistic and kinetic data is taken from [121].

Reaction	**Rate constants**	**Reaction No.**
$CO_3^{2-} + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + OH^-$	$k_{13} = 3.9 \cdot 10^8\ M^{-1}s^{-1}$	(13)
$HCO_3^- + {}^{\bullet}OH \rightarrow HCO_3^{\bullet} + OH^-$	$k_{14} = 8.5 \cdot 10^6\ M^{-1}s^{-1}$	(14)
$HCO_3^{\bullet} \leftrightarrow CO_3^{\bullet-} + H^+$	$K_{15} = 10^{-8}\ M\ ^*$	(15)
$CO_3^{\bullet-} + CO_3^{\bullet-} \rightarrow CO_2 + CO_4^{2-}$	$k_{16} = 2 \cdot 10^7\ M^{-1}s^{-1}$	(16)
$H_2CO_3 \leftrightarrow HCO_3^- + H^+$	$K_{17} = 4.5 \cdot 10^{-8}\ M\ ^*$	(17)
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	$K_{18} = 4.4 \cdot 10^{-11}\ M\ ^*$	(18)

* Equilibrium constants, which are equal to the quotient between rate constants of forward and backward reactions.

The main properties of hydroxyl radical, that is, higher reactivity and lower selectivity than ozone, make its production of great interest in ozone application to water and wastewater treatment, especially if the ultimate objective of the process is removing organic micropollutants. However, the ozone decomposition initiated by OH^- is not at all the main source of •OH production. Reaction between O_3 and OH^- is very slow (Table 6), and it only can play a significant role at very high pH conditions, for which OH^- presence in water is large. In fact, other reactions between ozone and different water constituents also producing •OH are much faster than this one at the typical pH range of water and wastewater (*i.e.*, up to 8) [107]. That is the case, for instance, of ozone reactions with the dissolved organic matter (DOM) typically contained in water and wastewater matrices. Although these reactions may happen through a variety of mechanisms, it has been suggested that part of the electron-rich aromatic components of DOM undergo electron transfer with O_3 (Figure 10) [122,123]. One of the products of this side reaction is the ozonide anion ($O_3^{\bullet -}$), which upon further reaction gives rise to •OH generation (see Table 6).

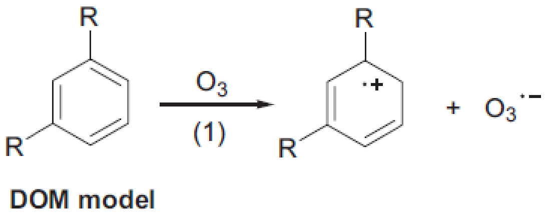


Figure 10. Electron transfer reactions between DOM (here represented by a generic aromatic compound) and ozone [107].

Hydroxylation of aromatic DOM moieties by electrophilic substitution (see Figure 8) can also lead to •OH generation [123], as phenolic moieties can also undergo electron transfer with O_3, giving rise to $O_3^{\bullet -}$ (Figure 10) [122]. Additionally, •OH can add to aromatic compounds of DOM (Figure 11). In the presence of an oxygen excess, which is the typical situation when ozone is injected in a given system, the resulting compound, a hydroxycyclohexadienyl radical, is in equilibrium with its corresponding peroxyl radical [122]. The latter then releases $HO_2^{\bullet}$, which as illustrated in Table 6 can undergo deprotonation and then react with O_3, ultimately leading to •OH production.

Although •OH is generated by DOM side reactions with ozone, and even if this generation is sustained by continuous reactions of both O_3 and •OH with primary (initial DOM) or newly generated electron-rich sites (products resulting from initial DOM components with O_3, such as phenols generated by hydrophilic substitution), only a fraction of the DOM initially present in water act as radical chain promoter (i.e., leads to radical species that ultimately give rise to •OH). The rest of it act as inhibitor, scavenging •OH or consuming O_3 without further •OH or chain carrier production [108,121].

Given the poor contribution of the ozone decomposition mechanism initiated by OH^- to $^{\bullet}OH$, and in view of the fact that DOM can lead to its generation but is also a known sink for radical species, it becomes clear that alternative strategies for promotion of •OH production during water treatment with ozone should be adopted if the indirect oxidation pathway (*i.e.*, oxidation through formed $^{\bullet}OH$) is wanted to be enhanced in a particular application. That, as already mentioned, can be beneficial if the objective of that application is micropollutants abatement from a given water matrix, as the less reactive and significantly more selective direct oxidation pathway (i.e., direct oxidation through O_3) often cannot be effective enough for organic compounds degradation [107].

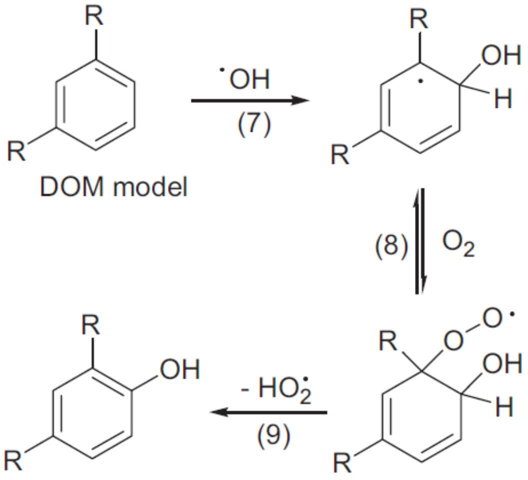


Figure 11. Hydroxyl radical addition to DOM (here represented by a generic aromatic compound), which in the presence of an O_2 excess gives rise to radical chain carriers and ultimately •OH [107].

1.3.2 Peroxone process

The combination of ozone with hydrogen peroxide (H_2O_2) for water treatment, also known as peroxone process, is the best-known of the existent ozone-based Advanced Oxidation Processes (AOPs) [107]. As any AOP, the basis and aim of this technology is the *in situ* generation of hydroxyl radicals, with the final purpose of using this oxidizing agent for the chemical destruction of pollutants that are present in water [117]. The process is based on the fast reaction of ozone with the deprotonated form of hydrogen peroxide (HO_2^-) [111,117], which is typically in equilibrium [Table 8, reaction (19)]. H_2O_2 reaction with ozone, on the other hand, is very slow ($k < 0.01$ $M^{-1}s^{-1}$ [111]). The fundamental reaction of peroxone process (*i.e.*, O_3-HO_2^- reaction) is, in fact, part of the radical chain mechanism of ozone decomposition described in section 1.3.1 [reaction (4) in Table 6]. In that system, however, HO_2^- is just a non-radical intermediate whose formation is kinetically disfavored [see rate constants of reactions (2) and (3) in Table 6]. Thus, in single ozonation this pathway should not contribute significantly to •OH production. When combining ozone with H_2O_2, however, a larger presence of HO_2^- in the medium allows the activation of this chemical route, which overall results in an enhanced generation of hydroxyl radicals [107].

Another particularity of the peroxone process compared to single ozonation is the fact that H_2O_2 may react with carbonate radicals formed upon reaction between •OH and carbonate anions (see reactions in Table 8), giving rise to $HO_2^{\bullet}$ [reaction (20)]. This has important and potentially advantageous implications for •OH production in the peroxone system, since carbonate/bicarbonate play the role of a promoter for O_3 decomposition in the presence of H_2O_2 [121]. The opposite happens in conventional ozonation, where –as already mentioned– CO_3^{2-}/HCO_3^- act as radical chain inhibitors.

Table 8. Characteristic reactions of the peroxone (O_3/H_2O_2) process (in addition to those already presented in Tables 6 and 7). Mechanistic and kinetic data is taken from [121].

Reaction	**Rate constants**	**Reaction No.**
$H_2O_2 \leftrightarrow HO_2^- + H^+$	$K_{19} = 2.5\cdot10^{-12}$ M *	(19)
$H_2O_2 + CO_3^{\bullet-} \rightarrow HCO_3^- + HO_2^{\bullet}$	$k_{20} = 4.3\cdot10^{5}$ $M^{-1}s^{-1}$	(20)
$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O$	$k_{21} = 2.7\cdot10^{7}$ $M^{-1}s^{-1}$	(21)

* Equilibrium constant, which is equal to the quotient between rate constants of forward and backward reactions.

Finally, it is worth to mention here that under certain circumstances, increasing H_2O_2 concentration with the aim of accelerating the process may not result in an advantage, since •OH reacts with H_2O_2 considerably fast [reaction (21)]. Thus, an excess of hydrogen peroxide could also lead to a reduction of the available amount of hydroxyl radicals in the reaction medium [107,108].

1.3.3 Other ozone-based oxidation processes

In addition to H_2O_2, and always with the aim of enhancing •OH production, ozone can be combined with homogeneous and heterogeneous catalysts, as well as with UV irradiation.

Regarding catalytic ozonation, both homogeneous and heterogeneous processes have been widely studied for years. From metals in solution (homogeneous process) to metal oxides, metal on supports, minerals containing metals and even activated carbon (heterogeneous processes), numerous works have described the potential benefits associated to the addition of catalysts to enhance the transformation of ozone to hydroxyl radicals [124–129]. Although some of the studied systems have proven useful on that purpose, the potential gain in efficiency is impaired by several problems related to catalysts. In homogeneous systems, the use of transition metals in water treatment would require their removal from treated water, which results quite impractical. In the case of heterogeneous systems, on the other hand, the optimal concentrations of catalysts are typically large (in the g L^{-1} range) [104,126,128]. That results in problems related to process design. Moreover, other issues such as catalyst separation, fouling and deactivation, the release of toxic compounds into water and synthesis and/or preparation costs must always be considered for these processes [104,126]. Such a collection of potential drawbacks probably constitutes the reason for which catalytic ozonation has remained at laboratory level during all these years, with scarce presence in real-world applications [126].

Concerning the combination of ozone with UV light, and although there are laboratory studies dealing with its potential application for enhanced •OH production, this process has not so far gained much practical application [107]. However, a recent comparative screening of electric expenses for different AOPs has revealed similar energy demands for O_3/H_2O_2 and O_3/UV processes when these are applied for the elimination of ozone-resistant micropollutants from water and wastewater [105].

In addition to the intrinsic disadvantages of other ozone-based AOPs different than O_3/H_2O_2, there is a fact that is decisive when choosing the best process considering a tradeoff between efficiency and feasibility (in terms of technical maturity and low energy demand). The H_2O_2-induced transformation of ozone to hydroxyl radicals presents a yield about 50%, that is, two O_3 molecules are approximately consumed to generate one •OH [130]. That only leaves a 2-fold margin improvement for a process with an •OH yield of 100%. Therefore, it is currently accepted that the peroxone process is the best option among ozone-based AOPs, and one of the best AOPs in terms of feasibility and effectiveness nowadays, together with the UV/H_2O_2 process [105,107,131]. Because of this, an important part of the current research effort on ozone-based treatments is being focused in the intensification of the peroxone process. Interesting options have lately emerged in that sense, such as the electrochemical production of H_2O_2 in the so-called electro-peroxone process, which avoids the transport and storage of chemicals and can be applied at various scales [104,131].

1.4 Ozone application for micropollutants abatement from wastewater effluents: state of the art

Although ozonation has proven effective for micropollutants oxidation, there is still a limited number of WWTPs in which additional ozone-based treatment steps are implemented with that purpose [107]. Traditionally, wastewater treatment with ozone –which is nowadays recognized as one of the best chemical disinfectants [132]– has mainly been installed for disinfection in regions of the world where disinfection of wastewater effluents is mandatory (*e.g.*, some states in the USA) [107]. During the last years, however, and in view of the growing importance of aquatic ecosystems protection and water reuse, the authorities of some countries have decided to upgrade their WWTPs with additional polishing steps, including ozonation, with the aim of reducing the amount of micropollutants discharged into the water bodies. One of the most representative examples of this approach is Switzerland, where to that purpose *ca.* 15% of the existing WWTPs are being improved either with ozonation or activated carbon [104,133]. In other European countries such as France or Germany, similar practices are currently under evaluation.

Regarding ozone use in wastewater reclamation schemes, this technology can be employed after activated sludge when reuse is intended for agricultural applications [107], or as part of a multibarrier advanced treatment in the case of direct potable reuse [104]. Good examples of the latter are found in California, where a rigorous framework of advanced treatment systems has been recently implemented to fulfill the criteria for direct water reuse, including disinfection and micropollutants abatement [134]. In all these treatment trains, ozonation is often the key disinfection/oxidation step.

There are some essential aspects to consider in ozone application for micropollutants removal from wastewater, which are key in order to assess the feasibility of the treatment [135]. These are briefly reviewed below.

1.4.1 Reaction kinetics

The efficiency of micropollutants oxidation during ozonation directly depends on the kinetics of reactions between these compounds and the main oxidants involved in the process, that is, ozone and hydroxyl radicals [104,133].

Abatement of ozone-recalcitrant micropollutants during ozonation

As above discussed, most organic micropollutants present high reactivity with hydroxyl radical. In ozone reactions, however, and because of the selective character of this oxidant, kinetics largely depends on the structure of the target chemicals and therefore rate constants may vary several orders of magnitude between different compounds. Being so, micropollutants can be grouped according to their respective reactivity with O_3 and $^{\bullet}OH$. Lee and coworkers [136], for instance, proposed the classification presented in Table 9. According to it, MPs belonging to group I are the most reactive compounds (and thus, more prone to undergo oxidation) during ozonation, whereas MPs in group V would be the most resistant to oxidative treatment. Micropollutants with rate constants for reactions with ozone lower than 10 $M^{-1}s^{-1}$ are often known as ozone-recalcitrant, ozone-refractory or ozone-resistant compounds [107,136].

Table 9. Micropollutants classification according to their reactivity with involved oxidants during ozonation. k_{O3} and $k_{\bullet OH}$ stand for the second-order rate constants of MPs reactions with ozone and hydroxyl radicals, respectively. Adapted from [136].

Group of MPs	**Reactivity**	**k_{O3} [$M^{-1}s^{-1}$]**	**$k_{\bullet OH}$ [$M^{-1}s^{-1}$]**
I	High with both O_3 and $^{\bullet}OH$	$> 1\cdot10^5$	$> 5\cdot10^9$
II	Moderate with O_3 and high with $^{\bullet}OH$	$10\text{-}1\cdot10^5$	$> 5\cdot10^9$
III	Low with O_3 and high with $^{\bullet}OH$	< 10	$> 5\cdot10^9$
IV	Low with O_3 and moderate with $^{\bullet}OH$	< 10	$1\cdot10^9\text{-}5\cdot10^9$
V	Low with both O_3 and $^{\bullet}OH$	< 10	$< 1\cdot10^9$

In full-scale applications of wastewater ozonation, it appears to be that the abatement of ozone-resistant MPs (groups III, IV and V according to the classification shown in Table 9) is not considered nowadays as a primary objective. The Swiss Federal Office for the Environment (FOEN), for example, established a list of 12 indicator substances that must be abated by at least 80% in average during upgraded wastewater treatment [137]. However, only substances with high and moderate reactivity with ozone (groups I and II) are included in this list. These compounds may present from acceptable (50-80%) to good (> 80%) efficiencies for ozone doses in wastewater treatment of about 0.5 mg of ozone per mg of dissolved organic carbon [0.5 mg O_3 mg C^{-1}]) [138], which allow compliance with the Swiss regulation. On the contrary, ozone-resistant MPs are in general moderate- or poorly abated when applying practical ozone doses (in general up to about 1.0 mg O_3 mg C^{-1}, although higher doses are usually tested [139]), as already demonstrated in several related studies [136,138,140,141].

Under the low ozone dosing conditions typically applied or considered practical for wastewater ozonation, ozone is readily consumed by the water constituents (mainly DOM or EfOM [*i.e.*, Effluent Organic Matter]) in a process stage often called primary ozonation or instantaneous ozone demand (IOD) stage [108,142,143]. Hydroxyl radicals formed through ozone reactions are strongly scavenged by water constituents, resulting this in a poor availability of this oxidant in the reaction medium [107,120]. After IOD completion, a secondary ozonation stage characterized by a slower ozone consumption (*i.e.*, higher ozone stability) and significantly lower •OH scavenging rate would start [108,143]. As mentioned, however, wastewater ozonation typically employ ozone dosages below IOD fulfillment.

The application of peroxone (O_3/H_2O_2) process, which as an AOP should enhance the removal of ozone-recalcitrant compounds through intensification of hydroxyl radical oxidation, neither appear to contribute significantly to that purpose [136,144,145]. The observed low effectivity could be related to the fact that, under the typically applied treatment conditions (*i.e.*, low ozone doses), the ozone decomposition process is strongly controlled by reactions with DOM [107]. Thus, hydrogen peroxide or –more precisely– its anion HO_2^- cannot compete in order to play an important role in the initiation step of the radical-chain O_3 decomposition mechanism (see section 1.3.2). In addition to increase the ozone dose in order to test if a more significant effect is observed on O_3-recalcitrant MPs removal, some optimization of the peroxone process –especially concerning the approach employed for oxidants (*i.e.*, O_3 and H_2O_2) dosing– is still to be fully explored.

Obtaining high quality reclaimed water may be imperative in a near future. In such situations, making efforts to further remove or at least control the fate of ozone-resistant micropollutants during ozonation and ozone-based AOPs application to wastewater effluents should become a necessary task, especially if some of these substances could pose risks to humans and the environment.

Prediction and control of micropollutants abatement during wastewater ozonation

According to chemical reaction kinetics, which in the case of ozone and hydroxyl radical reactions with micropollutants are considered to follow second-order laws (first order with respect to each reactant), the removal of a MP during ozonation can be described by Eq. (22) [136].

$$-\ln\left(\frac{[\mathrm{MP}]}{[\mathrm{MP}]_0}\right) = k_{\mathrm{O3}} \cdot \int [\mathrm{O_3}]\mathrm{d}t + k_{\bullet\mathrm{OH}} \cdot \int [\bullet\ \mathrm{OH}]\mathrm{d}t \qquad (22)$$

Predictions on MP removal could be thus performed as long as kinetic constants (*i.e.*, k_{O3} and $k_{\bullet\mathrm{OH}}$) and oxidant time-integrated concentrations –better known as oxidant exposures (*i.e.*, $\int[\mathrm{O_3}]\mathrm{d}t$ and $\int[\bullet\mathrm{OH}]\mathrm{d}t$)– are known. In the case of ozone-resistant MPs, the term in Eq. (22) describing ozone oxidation is much smaller than the term accounting for hydroxyl radical kinetics, as degradation process is controlled by the latter [136]. In the kinetic modelling of such compounds oxidation, therefore, Eq. (23) can be used instead.

$$-\ln\left(\frac{[\mathrm{MP}]}{[\mathrm{MP}]_0}\right) = k_{\bullet\mathrm{OH}} \cdot \int [\bullet\ \mathrm{OH}]\mathrm{d}t \qquad (23)$$

There is already a large database of second-order rate constants for O_3 [107] and •OH [146] reactions with organic micropollutants. Unknown constants can be determined experimentally [107], and semi-empirical prediction methods based on quantitative structure-activity relationships or quantum chemical calculations can alternatively be used for an estimation of these parameters [147–149].

Regarding oxidant exposures, these can be experimentally determined for different wastewater sources by means of batch ozonation experiments in which the residual concentration of both ozone and a •OH probe (*i.e.*, a compound only reacting with hydroxyl radicals) are monitored over time. By following this approach, Elovitz and von Gunten observed a couple of decades ago how for a given water matrix, the $\int[\bullet\mathrm{OH}]\mathrm{d}t/\int[\mathrm{O_3}]\mathrm{d}t$ ratio was constant over ozonation time [150]. This relationship was defined as the R_{ct} concept, and together with oxidant exposures determination, it was soon found potentially useful for performance characterization and kinetic modelling of ozone applications [151–154]. However, the whole methodology presents some drawbacks, especially when it is applied to wastewater ozonation, where a fast ozone consumption during the initial ozonation stage is typically observed (*i.e.*, the IOD stage discussed above). In first place, $\int[\mathrm{O_3}]\mathrm{d}t$ can be accurately determined by conventional methods only after some ozonation time, when ozone consumption becomes slower (*i.e.*, after IOD completion) [155,156]. Thus, R_{ct} concept cannot be neither determined for the entire ozonation time, but only for secondary ozonation stage. In addition, oxidant exposures and by consequence the R_{ct} concept strongly depend on significant seasonal and operational variations, such as temperature, concentration of organic and inorganic species in the water matrix and applied ozone dose [157,158]. Furthermore, comparing R_{ct} values between different wastewaters, although useful for other purposes, is not really meaningful in terms of oxidation efficiency, as both ozone and hydroxyl radical exposure variations may simultaneously affect the R_{ct} value [150].

In a related line of work, Kwon and coworkers recently proposed the $R_{\mathrm{OH,O3}}$ concept [159], a novel kinetic parameter that represents the exposure to •OH produced by $\mathrm{O_3}$ consumption [Eq. (24)]. Because of its features, the $R_{\mathrm{OH,O3}}$ parameter has potential as a tool for performance characterization, in terms of oxidation efficiency, of ozone-based oxidation processes. The $R_{\mathrm{OH,\,O3}}$ value does not depend on the ozone exposure but on the consumed ozone dose, an easily determinable parameter during the whole ozonation time. Moreover, it appears to be less affected by seasonal and operational variations than R_{ct}. The $R_{\mathrm{OH,O3}}$ concept, furthermore, has proven useful in the kinetic modelling of ozone-recalcitrant MPs abatement during ozonation [159].

$$R_{\mathrm{OH,O3}} = \frac{\int[\bullet\, OH]\mathrm{d}t}{\text{Consumed ozone}} \tag{24}$$

The use of the $R_{\mathrm{OH,O3}}$ parameter has been tested so far in synthetic and natural water ozonation. Thus, it is also required to explore its potential in wastewater ozonation, where ozone is highly unstable at the beginning of the process. Kwon and colleagues performed the whole study by means of batch ozonation studies, and therefore they could not obtain data for ozone or •OH probe depletion during the primary ozonation stage due to experimental shortcomings. They solved the problem by applying subsequent corrections based on mechanistic interpretations of ozone consumption, finally allowing an accurate prediction of MPs abatement [159]. However, it remains to be explored if this approach can be further improved to allow the description and kinetic modelling of the whole ozonation process. If possible, this would trigger its use in wastewater ozonation even for real-time control purposes.

Alternative to the use of models based on kinetic parameters for the prediction and control of micropollutants abatement during ozonation, an approach that is gaining increasing attention is the use of water quality parameters as surrogates or proxies. Some studies have already shown that decreases in ultraviolet absorbance (UVA) and total fluorescence (TF) of wastewater matrices during ozonation could be potentially correlated to the abatement of micropollutants [160–162]. The use of other potential surrogates, such as nitrate (NO_3^-) or the organic matter electron donating capacity (EDC), have been recently tested with similar purposes [163,164]. Because of the simplicity of its measurement, which could be easily implemented even for real-time control systems, the use of UVA monitoring for MPs abatement prediction during ozonation appears to be the most practical approach.

Empirical models resulting from studies using surrogates to assess MPs removal prediction, including UVA, do not always present satisfactory correlations, making them only useful for rough estimations. This approach, however, still appears to have a certain unexplored potential. For instance, the use of surrogates for potential online estimation of oxidant exposure, instead of MPs abatement, has not been studied yet.

1.4.2 Transformation products and their ecotoxicological effects

Ozonation rarely leads to micropollutants mineralization (*i.e.*, total transformation to CO_2 and H_2O, mostly achieved for AOPs in which •OH is massively produced). Instead, transformation products (TPs) are typically formed [107]. A combination of advanced analytical techniques and the knowledge of mechanisms of ozone and hydroxyl radical reactions with organic micropollutants (see section 1.3.1) allow the elucidation of these products [107,133,146]. In addition of knowing which products are formed during wastewater ozonation, the potential risks –to humans and the environment– associated to their presence in water matrices should be also kept in mind and tested, when possible, by means of bioassays [133]. Although the biological effect of several classes of compounds in general disappear by slight modifications of the chemical structure of the parent compound during ozonation, TPs more toxic than parent MPs may be formed [104,107]. Protocols comprising a wide range of specific and unspecific toxicity bioassays have been developed over the last years [135]. Experimentally studying the products obtained for the vast and increasing variety of existent MPs during ozonation, as well as their potential effects over living species, would be an extremely costly and time-consuming task [104]. Computer-aided methods based on the existing knowledge for a number of model compounds are nowadays being developed and continuously improved for initial screening purposes [165–167].

1.4.3 Formation of oxidation by-products

Another important aspect that requires proper consideration is the formation of oxidation by-products as a consequence of ozone and hydroxyl radical reactions with regular wastewater constituents. A case in point is the generation of bromate –a carcinogenic product– from bromide [107,146]. Even though the process is still not fully understood due to its highly complicated chemistry, efficient strategies for its mitigation during wastewater ozonation – such as the use of the O_3/H_2O_2 combination (*i.e.*, peroxone process) – are nowadays fairly well known [165]. The generation of oxygen-rich by-products (*e.g.*, aldehydes, ketones and carboxylic acids) from DOM transformations during ozonation also needs to be carefully considered [168,169]. Although in general less toxic than MPs or their TPs, these products are formed in total concentrations that significantly surpass the sum of the concentration of micropollutants detected after ozonation [104]. Being so, they may contribute more to the negative biological effects of the treated effluent than MPs and their TPs. Moreover, residual DOM and its oxidation products may trigger some technical and additional environmental problems if further treatment steps are planned next, such as membrane fouling, saturation in adsorption systems or formation of toxic disinfection by-products [170]. In addition, these compound can cause bacterial growth in distribution systems if the treated effluent is intended for water reuse purposes, as well as to contribute to eutrophication in receiving water bodies [170], regardless if the effluent is discharged or reused in environmental applications (*e.g.*, aquifer recharge).

There are several studies assessing the formation of DOM oxidation by-products during oxidative water and wastewater treatment [171–173], and potential strategies for the mitigation of the derived negative impacts (*i.e.*, biological post-treatments) have been already proposed [138,174]. However, the knowledge regarding the fate of the different DOM (or dissolved EfOM) fractions during wastewater ozonation is still limited.

2 Objectives, justification and thesis structure

2.1 Objectives

Although ozonation is a mature and suitable technology for enhanced wastewater treatment and reclamation, there are still some knowledge gaps regarding micropollutants (MPs) abatement process that require further research on this area. For instance, little is known about the degradation by ozonation of several MPs categorized as priority or emerging concern substances in the latest European regulations in the field of water policy. A great percentage of these compounds are pesticides belonging to different chemical families. The abatement of ozone-resistant chemicals during ozonation is rarely discussed in literature, and the same happens with the fate of the effluent organic matter (EfOM) along this process. Moreover, exploring strategies for further promoting hydroxyl radical oxidation of these compounds together with their monitoring along the ozonation process is needed, for a more efficient application and control of MPs fate.

The work of this thesis is focused on the above mentioned research needs, with the following specific objectives:

1. Study of kinetic, mechanistic and toxicological aspects of especially concerning micropollutants degradation during ozonation. Concretely,
    - Determining the second-order rate constants of reactions between three selected pesticides, reported to be emerging concern or priority MPs, and both ozone and hydroxyl radicals.
    - Studying the generation of transformation products and proposing degradation pathways for all compounds.
    - Assessing the potential ecotoxicological effects of formed transformation products.

2. Exploring the abatement of ozone-recalcitrant chemicals from six different wastewater treatment plant effluents during ozonation, including the study of potential modelling strategies for this process. This included,
    - Study of extended ozone doses for the effective abatement of ozone-recalcitrant compounds.

- Testing the R_{OHO3} concept as potential tool for performance characterization and kinetic modelling of ozone-resistant MPs degradation during wastewater ozonation.
- Proposal of surrogate monitoring strategies for prediction and monitoring of ozone-refractory micropollutants during ozonation.

3. Assessment of effluent organic matter changes during ozonation applied for micropollutants abatement, including ozone-refractory compounds. Particularly,

- Studying organic matter transformation through analysis of general effluent quality parameters.
- Examining changes experimented by the different organic fractions forming part of EfOM along ozonation, and comparing these with variations observed in general parameters.
- Studying relationships between EfOM changes, typical ozonation parameters and effluent quality properties that could be useful for a first assessment or estimation of the fate of organic matter during ozonation.

4. Application, intensification and modelling of peroxone (O_3/H_2O_2) process for enhanced oxidation of ozone-refractory micropollutants in wastewater effluents. Concretely,

- Exploring novel strategies for hydrogen peroxide dosing during this process application, particularly the addition of this reagent simultaneously to ozone dosing. Process modelling through R_{OHO3} concept application.
- Comparison in terms of oxidation efficiency between continuous and initial H_2O_2 dosing strategy.
- Testing prediction and monitoring strategies for ozone-refractory MPs abatement during this process application based on the use of reaction kinetics, R_{OHO3} concept and effluent quality parameters.

2.2 Justification and thesis structure

The general objective of this thesis was contributing to the existing knowledge regarding performance characterization and kinetic modelling of ozone-based processes applied to micropollutants removal from aqueous matrices. Under this framework, the specific objectives above detailed were proposed, this leading to the separation of the thesis results in various sections. The completion of each specific objective derived in the publications indicated for each section and presented in Appendices I-VI.

Section 4.1: Kinetic, mechanistic and toxicological studies of selected priority/emerging concern pesticides degradation during ozonation (Appendices I-III). Three pesticides belonging to three different chemical classes, namely methiocarb (carbamates), acetamiprid (neonicotinoids) and dichlorvos (organophosphorus), were selected for this part of the work, considering the special concern posed by this family of micropollutants. Derived results provided fundamental information regarding the removal efficiency of these compounds in existing or newly planned ozone-based treatments, including the potential consequences of their respective oxidations in terms of transformation products and associated toxicity. At the same time, kinetic data (*i.e.*, rate constants of reactions of selected compounds with ozone and hydroxyl radicals) served to model abatement of micropollutants in ozone-based applications. Finally, kinetic, mechanistic and ecotoxicological data contributed to enrich the existing databases and computer-based platforms employing quantitative structure-activity relationships or quantum chemical calculations for *in silico* estimation of these properties for a variety of micropollutants.

The following three publications, included as Appendices I-III in section 4.1, were derived from results obtained in this part of the thesis:

Cruz-Alcalde, A., Sans, C., Esplugas, S. (2017). Exploring ozonation as treatment alternative for methiocarb and formed transformation products abatement, *Chemosphere* 186, 725-732.

Cruz-Alcalde, A., Sans, C., Esplugas, S. (2017). Priority pesticides abatement by advanced water technologies: The case of acetamiprid removal by ozonation, *Science of the Total Environment* 599-600, 1454-1461.

Cruz-Alcalde, A., Sans, C., Esplugas, S. (2018). Priority pesticide dichlorvos removal from water by ozonation process: Reactivity, transformation products and associated toxicity, *Separation and Purification Technology* 192, 123-129.

Section 4.2.1: Abatement of ozone-recalcitrant species, kinetic modelling and potential control strategies (Appendix IV). In this part of the thesis an assessment of ozone-refractory compounds fate during wastewater ozonation was performed through experiments in six wastewater effluents showing a broad range of water qualities. These were spiked with some ozone-resistant micropollutants as model compounds, including ACMP as •OH probe. Modelling and online monitoring strategies involving kinetic concepts and effluent quality parameters were tested.

The following publication, included as Appendix IV in section 4.2, was derived from results obtained in this part of the thesis:

Cruz-Alcalde, A., Esplugas, S., Sans, C. (2019). Abatement of ozone-recalcitrant micropollutants during municipal wastewater ozonation: Kinetic modelling and surrogate-based control strategies, *Chemical Engineering Journal,* in press. DOI: 10.1016/j.cej.2018.10.206

Section 4.2.2: Assessment of EfOM changes taking place through ozone application for micropollutants abatement, including ozone-refractory compounds (Appendix V). The assessment of EfOM evolution during wastewater ozonation was carried out in this part of the thesis, taking as reference the treatment conditions required for the removal of ozone-refractory compounds and employing the same effluent samples used to perform the previous part (Appendix IV). The study was carried out through analyses of general quality parameters related to EfOM content and by means of advanced chromatographic techniques such as SEC-OCD, which allowed the characterization of EfOM components through their classification into different fractions.

The following publication, included as Appendix V in section 4.2, was derived from results obtained in this part of the thesis:

Cruz-Alcalde, A., Esplugas, S., Sans, C (2019). New insights on the fate of EfOM during ozone application for effective abatement of micropollutants in wastewater effluents, submitted to *Journal of Hazardous Materials*.

Section 4.3: Application, intensification and modelling of peroxone process for enhanced oxidation of ozone-refractory micropollutants in wastewater effluents (Appendix VI). The combination of ozone with hydrogen peroxide (peroxone process) was tested as a potential method for enhancing the removal of ozone-resistant micropollutants during ozone application to wastewater effluents. Some alternative strategies related to oxidants (O_3 and H_2O_2) dosing during the treatment were tested and compared. The work was performed through ozonation studies employing three different wastewater effluents spiked again with model micropollutants. Similarly to the work performed in single ozonation studies (Appendix IV), some modelling strategies for micropollutants abatement in improved peroxone process were investigated.

The following publication, included as Appendix VI in section 4.3, was derived from results obtained in this part of the thesis:

Cruz-Alcalde, A., Esplugas, S., Sans, C (2019). Continuous H_2O_2 addition in peroxone process: performance improvement and modelling in wastewater effluents, submitted to *Chemical Engineering Journal* and currently under 2nd review.

3 Materials and methods

3.1 Chemicals and reagents

3.1.1 Priority pesticides, model micropollutants and reference compounds

Relevant data of priority pesticides (MC, ACMP, and DDVP), model micropollutants (ATZ and IBU) and reference compounds (rest of them) employed in the research presented in this thesis are gathered in Table 10. All of them were analytical grade standards acquired from Sigma-Aldrich (Germany).

Table 10. Main data of employed priority pesticides, model micropollutants and reference compounds.

Compound	Abbreviation	Chemical formula	Molecular Weight	CAS Number
Acetamiprid	(ACMP)	$C_{10}H_{11}ClN_4$	222.676	135410-20-7
Atrazine	(ATZ)	$C_8H_{14}ClN_5$	215.685	1912-24-9
p-Benzoquinone	(pBZQ)	$C_6H_4O_2$	108.096	106-51-4
p-Chlorobenzoic acid	(pCBA)	$C_7H_5ClO_2$	156.565	74-11-3
Dichlorvos	(DDVP)	$C_4H_7Cl_2O_4P$	220.980	62-73-7
Ibuprofen	(IBU)	$C_{13}H_{18}O_2$	206.285	15687-27-1
Methiocarb	(MC)	$C_{11}H_{15}NO_2S$	225.306	2032-65-7
Metoprolol	(MPL)	$C_{15}H_{25}NO_3$	267.369	51384-51-1
Phenol	(PH)	C_6H_6O	94.113	108-95-2
Sulfamethoxazole	(SMX)	$C_{10}H_{11}N_3O_3S$	253.276	723-46-6

3.1.2 Rest of chemicals and reagents

Mercuric sulfate ($HgSO_4$), potassium iodide (KI), sodium dihydrogen phosphate (NaH_2PO_4), sodium hydrogen phosphate (Na_2HPO_4), sodium hydroxide (NaOH), hydrochloric acid solution (HCl, 37% w/w), hydrogen peroxide solution (30% w/v), phosphoric acid solution (H_3PO_4, 85% w/w), potassium dichromate solution ($K_2Cr_2O_7$, 0.04 M with 80 g L^{-1} of $HgSO_4$), silver sulfate solution (Ag_2SO_4, 10 g L^{-1} in H_2SO_4), *tert*-Butanol (tBuOH) and HPLC grade acetonitrile (ACN) were acquired from Panreac (Spain). Ammonium metavanadate (NH_4VO_3) and potassium indigotrisulfonate ($C_{16}H_7K_3N_2O_{11}S_3$, ≥ 60%) were purchased from Sigma-Aldrich (Germany). Unless otherwise specified, the above reagents were analytical grade. Ultrapure water (TOC < 2 ppb; resistivity: 18.2 MΩ cm) was produced by a Milli-Q filtration system (Millipore, USA). Pure oxygen (≥ 99.999%) was supplied by Abelló Linde (Spain). Finally, all the reagents employed during toxicity bioassays (Microtox® Acute Reagent, Reconstitution Solution, Osmotic Adjustment Solution and Diluent) were purchased from Modern Water (UK).

3.2 Wastewater samples

Wastewater effluents from five WWTPs in the province of Barcelona (Spain) were employed in this thesis (see Figure 12).

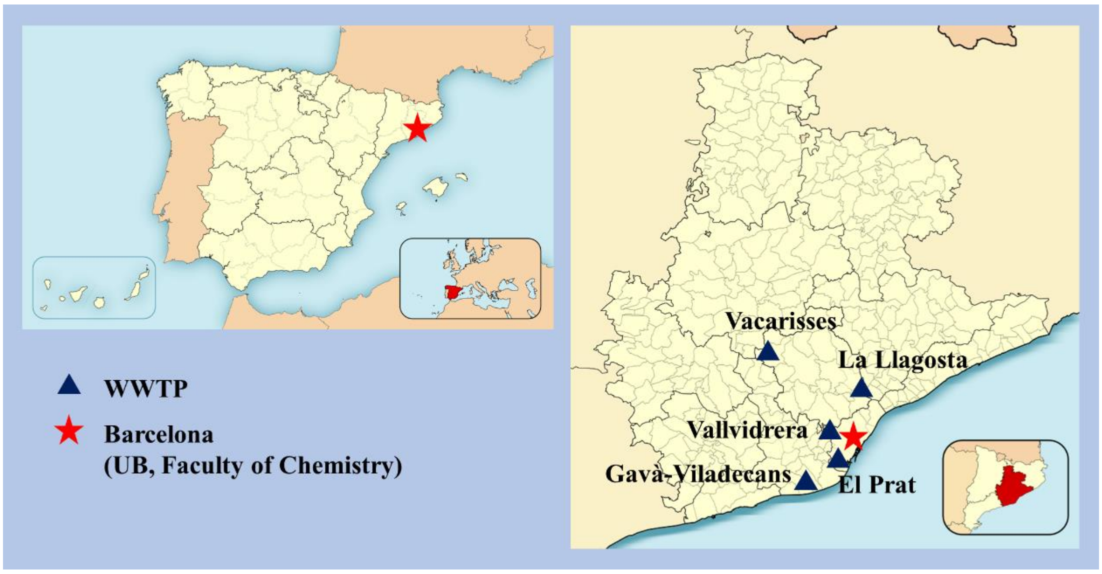


Figure 12. Location of WWTPs in the province of Barcelona from where effluent samples were collected.

All these plants employ similar physicochemical processes in order to remove large and suspended solids from the raw wastewater influent, in first place, and then different secondary or biological treatments for the removal of biodegradable organic matter. The WWTP located in La Llagosta [358333 population equivalent (PE); design flow (DF): 43000 m^3 d^{-1}] employs conventional activated sludge (CAS, see Figure 13) technology in the secondary treatment, without removal of nitrogen or phosphorus. Effluent sample C-LLA (or C3) was collected there. Two different treatment lines are implemented in the WWTP of El Prat de Llobregat (2275000 PE; DF: 420000 m^3 d^{-1}). However, only effluent sample from the line employing CAS technology with nutrient elimination (C-PRA or C1) as biological treatment was used in this thesis. Similarly, two different treatment lines are operated in the plant of Gavà-Viladecans (384000 PE; DF: 64000 m^3 d^{-1}). In this case, however, effluent samples from both systems were collected for experimentation. One of the lines employs a modified (capacity augmented) CAS system through integrated fixed-film activated sludge (IFAS) technology. Effluent samples C-GAV (or C2) and CAS-3 came from this system. The other line treats wastewater through a secondary process that consists of a membrane bioreactor (MBR, see Figure 13) system, a combination of CAS process with ultrafiltration membrane technology. Nitrogen and phosphorus are removed in both treatment lines. Effluent samples M-GAV (or M3) and MBR-2 were collected from this process. The biological process in the WWTPs of Vacarisses (5280 PE; DF: 1320 m^3 d^{-1}) and Vallvidrera (5500 PE; DF: 1100 m^3 d^{-1}) consist both of MBR processes. Effluents M-VAC (or M1) and MBR-1 were collected from Vacarisses, whereas effluent M-VAL (or M2) came from Vallvidrera.

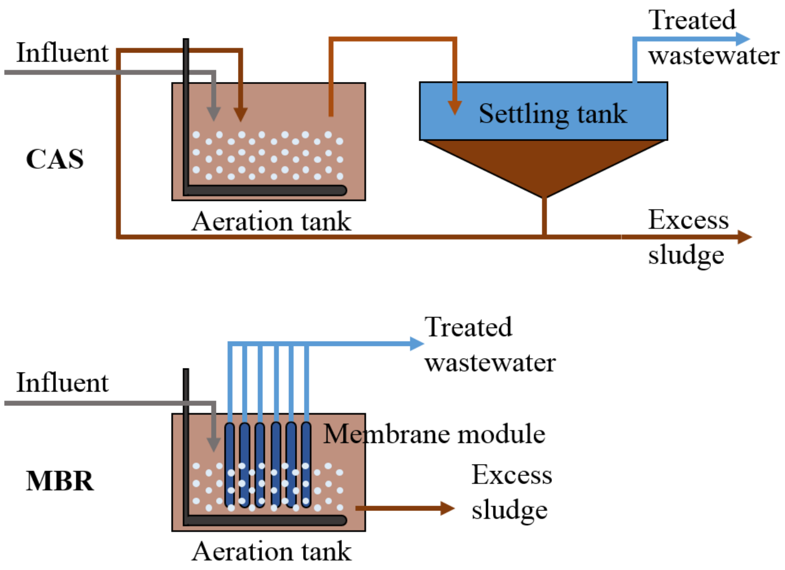


Figure 13. Scheme of the aerobic biological stage of wastewater treatment in conventional activated sludge (CAS) and membrane bioreactor (MBR) systems. In MBR technology, a secondary clarifier (settling tank) is not necessary to separate clean effluent from biomass and other suspended solids, as these are retained by the membrane.

Different sampling campaigns were carried out between 2017 and 2018, with the aim of having fresh effluent available to carry out experiments and minimize sample degradation. Effluents M-VAC (M1), M-VAL (M2), M-GAV (M3), C-PRA (C1), C-GAV (C2) and

C-LLA (C3) were employed for single ozonation studies (*i.e.*, publications presented in Appendices IV and V, the first nomenclature is the one employed in Appendix IV, while the one in brackets was used in Appendix V), whereas effluents MBR-1, MBR-2 and CAS-3 were used in the work testing the peroxone process (publication presented in Appendix VI). A summary of their main quality parameters are gathered in Table 11.

The raw CAS effluents [*i.e.*, C-PRA (C1), C-GAV (C2), C-LLA (C3) and CAS-3] were filtered with conventional filter paper to remove the largest solid particles. Effluent samples coming from MBR systems (*i.e.*, M-VAC (M1), M-VAL (M2), M-GAV (M3), MBR-1 and MBR-2) were used as collected. All samples were stored at 4ºC prior to be used.

Table 11. Main quality parameters of employed wastewater effluents. All measurements were performed in triplicate, with standard deviations lower than 5% in all cases. Some samples were employed in the studies presented in both Appendices IV and V, using two different nomenclatures in their designation. In this table, both are indicated. The first one corresponds to that used in Appendix IV, while the one in brackets is that employed in the work presented in Appendix V.

Sample ID	**pH**	**TOC [mg C L^{-1}]**	**DOC [mg C L^{-1}]**	**UV$_{254}$ [cm^{-1}]**	**Alkalinity [mg CaCO$_3$ L^{-1}]**	**NO$_2^-$ [mg N L^{-1}]**
M-VAC (M1)	7.9	6.7	6.6	0.179	330	0.85
M-VAL (M2)	7.4	10.5	10.3	0.163	178	0.03
M-GAV (M3)	7.7	12.4	12.1	0.149	200	0.12
C-PRA (C1)	7.5	14.0	13.6	0.229	264	0.09
C-GAV (C2)	7.8	42.1	27.6	0.672	517	0.09
C-LLA (C3)	7.7	25.6	21.3	0.664	419	0.03
MBR-1	7.8	7.2	7.1	0.090	448	0.03
MBR-2	7.7	13.6	13.3	0.174	208	0.19
CAS-3	7.8	51.1	21.7	0.503	569	0.16

3.3 Ozonation experiments

Batch ozonation is probably the most accurate method for exact ozone dosing. If high doses of this oxidant are wanted to be applied, however, this approach becomes limited by the maximum concentration that can be achieved in the ozone stock solution. If this is not large enough, the sample dilution after O_3 addition may be excessive. To avoid this situation, ozone is applied to the system by means of a gas-liquid contactor.

In this thesis, ozonation experiments were performed by following two different procedures. For kinetic, mechanistic and toxicological studies of priority pesticides (MC, ACMP and DDVP) performed in synthetic water (*i.e.*, studies conducting to the journal publications gathered in Appendices I-III), batch ozonation assays were carried out. In studies employing actual wastewater effluent samples (*i.e.*, studies leading to the journal publications presented in Appendices IV-VI), experiments were conducted in semi-batch mode.

3.3.1 Control experiments

Control experiments consisting of hydrolysis, photolysis and adsorption tests were carried out prior to ozonation assays in order to check if other mechanisms different than ozone and hydroxyl radical oxidation could contribute to pesticides degradation during ozonation experiments.

Solutions containing the target pesticides (4-20 µM) were placed into 250 mL stirred beakers. For hydrolysis assays, the medium pH was adjusted at the desired value (generally 7) by means of phosphate buffers (1 mM) and/or a few drops of concentrated H_3PO_4 or NaOH. The beaker was closed and covered with aluminum foil to avoid light exposure. Samples were taken at 1, 2, 5, 12 and 24 h for pesticides residuals analyses. Photolysis at lab conditions followed the same procedure, but it was tested in unbuffered ultrapure water (pH ~ 5.5) and without covering or closing the beaker containing the pesticide solution. Finally, adsorption tests were performed with unbuffered ultrapure water and in a covered and closed beaker. In this case, however, the pesticides were kept in contact during the assays with some materials commonly employed in the laboratory (i.e., plastic tubing, filters…) in order to check their potential adsorption onto these non-polar surfaces.

3.3.2 Batch ozonation

Since a greater control of reaction conditions can be achieved by means of this methodology, batch ozonation experiments were useful to determine the absolute (second-order) rate constants for reactions between pesticides (MC, ACMP and DDVP) and both, ozone and hydroxyl radicals. Moreover, this approach was also employed to elucidate the degradation pathways of these compounds and to assess the acute toxicity of unreacted and oxidized samples containing the parent compound and/or transformation products.

Ozonation experiments in batch mode were performed by mixing aqueous ozone stock solutions with aqueous solutions of the target pesticides. Ozone stock solutions (~ 10-14 mg L^{-1}) were prepared in a 1000 mL reactor by continuously bubbling a gaseous oxygen/ozone mixture (C_{O3} ~ 48 mg L^{-1}) into ultrapure water at a rate of 40 L/h. The water temperature was kept at 5-10 ºC by means of a KISS K6 thermostatic bath (Huber, Germany). Ozone was produced by a 301.19 lab-scale ozone generator (Sander, Germany), which was fed with a dry pure oxygen stream (2 bar). The generator was also cooled through a 280 Minichiller circulator, also supplied by Huber. The O_3 concentration in aqueous phase was continuously monitored by means of a Q45H/64 ozone probe (Analytical technology, USA). All kinetic and degradation experiments were performed in triplicate, at a temperature of 20 ± 2 ºC.

Rate constants of ozone reactions with selected pesticides

The second-order rate constants for the reactions of MC and DDVP with O_3 were determined by competition kinetics, employing SMX and MPL as reference compounds, respectively. In short, a target micropollutant M and a reference compound R react with ozone [reactions (25) and (26)]. The respective second-order rate constants were $k_{M,O3}$ and $k_{R,O3}$. The method required that $k_{R,O3}$ was already known, which implied its previous determination by means of a reliable method [107]. In this case, values of rate constants required for kinetic determinations were taken from previous literature (Table 12).

$$M + O_3 \rightarrow \text{Oxidation products of M} \qquad (25)$$

$$R + O_3 \rightarrow \text{Oxidation products of R} \qquad (26)$$

The relative degradations as a function of the ozone concentration, which were determined experimentally, were given by equation (27).

$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right)=\frac{k_{\mathrm{M,O3}}}{k_{\mathrm{R,O3}}}\cdot\ln\left(\frac{[\mathrm{R}]}{[\mathrm{R}]_0}\right) \tag{27}$$

The medium pH was kept at a constant value of 7 by means of a $H_2PO_4^-/HPO_4^{2-}$ buffer (1 mM), and tBuOH (100 mM) was added as •OH scavenger. Varying volumes of ozone stock solutions and solutions containing the target pesticides and reference compounds (4-20 µM) were mixed to reach different ozone doses, which were between 5 and 50 µM. Vials were then capped and placed in an orbital shaker until ozone was completely consumed, which in general occurred within 2 h. Then, the residual concentrations of target and reference chemicals were determined.

Since acetamiprid was found to barely react with ozone during preliminary experiments, a different protocol than competition kinetics was adopted in order to determine the second-order rate constant of the ACMP-O_3 reaction. In that case, the reactor was a 250 mL glass bottle and experiments were performed at pH 2 to avoid the presence of hydroxyl radicals. ACMP and O_3 stock solutions were mixed to reach initial reactants concentrations of 4 and 200 µM, respectively. The medium was stirred for 10 s to achieve homogeneous conditions. 0.5 mL aliquots were withdrawn at selected reaction times and quenched by 2.5 mL of an indigo solution. Then, the residual concentrations of ACMP and O_3 were determined and the rate constant could be calculated according to equation (28). The time-integrated ozone concentration was determined by means of the trapezoidal method of numerical integration.

$$-\ln\left(\frac{[\mathrm{ACMP}]}{[\mathrm{ACMP}]_0}\right)=k_{\mathrm{ACMP,O3}}\cdot\int[O_3]\mathrm{d}t \tag{28}$$

Rate constants of hydroxyl radical reactions with selected pesticides

The second-order rate constants for the reactions of MC, ACMP and DDVP with •OH were also determined by competition kinetics, following a similar procedure than the one described above for O_3-pesticides reactions. This time, however, tBuOH was not employed. For ACMP reaction kinetics with $^{\bullet}$OH, pCBA was employed as reference compound. Ozone oxidation of pCBA could be neglected due to its low reactivity with this oxidant, compared to that with hydroxyl radicals (see Table 12). On the other hand, in the case of MC and DDVP determinations, two reference compounds (for MC: SMX and PH; for DDVP: MPL and pBZQ) were employed instead of one, as both ozone and hydroxyl radical reactions contributed to pesticides degradation. In these cases, the rate constant $k_{\mathrm{M,\bullet OH}}$ was determined by solving the system formed by equations (29) and (30), provided that the rest of kinetic constants were known (R and S represent two generic reference compounds). R_{ct}, which is defined as the constant relationship between hydroxyl radical and ozone concentrations (see section 1.4.1), also became determined by means of this procedure.

$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = \frac{(k_{\mathrm{M,O3}} + k_{\mathrm{M,\bullet OH}} \cdot R_{\mathrm{ct}})}{(k_{\mathrm{R,O3}} + k_{\mathrm{R,\bullet OH}} \cdot R_{\mathrm{ct}})} \cdot \ln\left(\frac{[\mathrm{R}]}{[\mathrm{R}]_0}\right) \tag{29}$$

$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = \frac{(k_{\mathrm{M,O3}} + k_{\mathrm{M,\bullet OH}} \cdot R_{\mathrm{ct}})}{(k_{\mathrm{S,O3}} + k_{\mathrm{S,\bullet OH}} \cdot R_{\mathrm{ct}})} \cdot \ln\left(\frac{[\mathrm{S}]}{[\mathrm{S}]_0}\right) \tag{30}$$

Table 12. Kinetic data of reactions involved in competition kinetics experiments. Data of rate constants in the case of dissociating compounds are given for pH 7, that is, conditions under which assays were carried out.

Reaction	***k* [$M^{-1}s^{-1}$]**	**Reference**
SMX + O_3 → products	$2.0 \cdot 10^6$	[175]
SMX + $^\bullet OH$ → products	$5.5 \cdot 10^9$	[176]
PH + O_3 → products	$1.8 \cdot 10^6$	[177]
PH + $^\bullet OH$ → products	$5.5 \cdot 10^9$	[119]
pCBA + O_3 → products	< 0.15	[178]
pCBA + $^\bullet OH$ → products	$5.0 \cdot 10^9$	[119]
MPL + O_3 → products	$2.0 \cdot 10^3$	[179]
MPL + $^\bullet OH$ → products	$7.3 \cdot 10^9$	[179]
pBZQ + O_3 → products	$2.5 \cdot 10^3$	[180]
pBZQ + $^\bullet OH$ → products	$1.2 \cdot 10^9$	[119]

Additional degradation experiments

Additional degradation experiments were carried out with the following purposes: 1) demonstrating the relative contribution of each oxidant (*i.e.*, ozone and hydroxyl radicals) to the overall pesticides degradation; 2) elucidating the degradation pathways followed by pesticides during ozonation process; and 3) assessing the ecotoxicity of both parent compounds and degradation products. Experiments with and without the presence of tBuOH (25 mM) were performed. The medium pH was kept at a constant value of 7 by means of a $H_2PO_4^-/HPO_4^{2-}$ buffer (1 mM). Varying volumes of ozone stock solutions and solutions containing the target pesticides (4-20 µM) were mixed to reach different ozone doses, which were between 5 and 175 µM. Samples were withdrawn after total O_3 consumption. Once the residual concentrations of pesticides were determined, samples were frozen and later employed for TPs and toxicity determinations.

3.3.3 Semi-batch ozonation

To achieve higher ozone doses in actual wastewater samples while avoiding sample dilution, ozonation in semi-batch mode was selected as work methodology in this part of the research. A semi-batch ozonation setup (Figure 14) was especially designed and built on this purpose over the period between September 2016 and July 2017, simultaneously to the performance of the first part of the thesis experimental work (*i.e.*, batch ozonation studies).

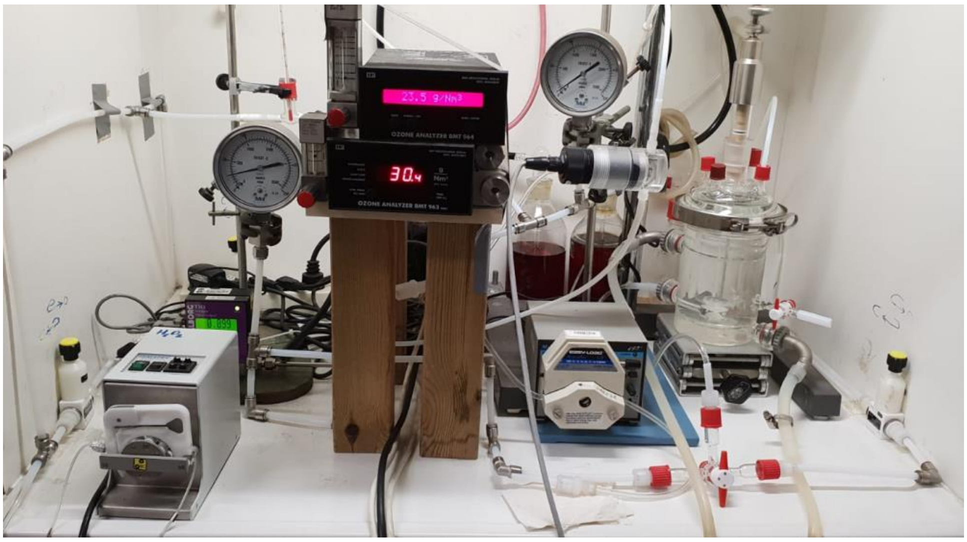


Figure 14. Picture of the lab-scale, semi-batch ozonation setup.

Wastewater ozonation experiments in semi-batch mode were performed in a tailor-made, 750 mL jacketed glass reactor (approx. vessel dimensions: 15x8 cm), which was ordered to Verres Vagner (France). Ozone was again produced from dry pure oxygen and injected at the bottom of the reactor through a fritted glass diffuser (pore size: 150-250 µm), also fabricated by Verres Vagner. The reactor was equipped with a mechanical mixing system that ensured medium homogeneity and a proper contact between liquid and gas phases. This system consisted of a stainless steel drive shaft with ball bearings, rotor and lower bearing made of PTFE and a conductor made of glass, all supplied by Bola (Germany). The 6-bladed propeller stirrer, which was also made of glass and supplied by Verres Vagner, was placed at a distance of 5 mm from the gas diffuser. The stirring velocity, achieved through a RSLab-13 overhead stirrer (RSLab, UK), was kept at 300 rpm.

Experiments were performed at 20 ± 1 ºC by employing a KISS K6 thermostatic bath (Huber, Germany). No adjustment of the medium pH was performed. The gas flow rate and the inlet ozone concentration were maintained at 0.1 NL min^{-1} and 30 mg NL^{-1}, respectively. The gas flow rate was continuously measured by means of a GMF17 TIO gas totalizer and flow meter (Aalborg, USA). Inlet and outlet gas-phase ozone concentrations were monitored by two BMT 964 ozone analyzers (BMT Messtechnik, Germany), placed up and downstream the reactor, respectively. The ozone concentration in the aqueous phase was continuously measured by means of a Q45H/64 dissolved O_3 probe (Analytical Technology, USA), which was connected to a liquid recirculation stream (flow rate of 200 mL min^{-1}) propelled by a Masterflex L/S compact pump (Cole Parmer, USA). Ozone concentration data measured in both gas and liquid phases was registered every 10 s by means of a DaqPRO® 5300 portable data logger (Fourtec, USA). A detailed scheme of the ozonation setup is shown in Figure 15.

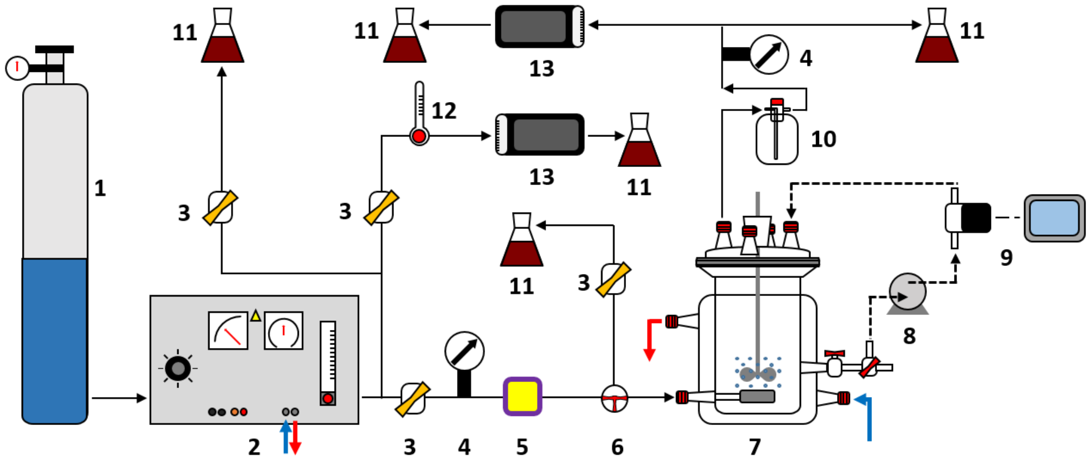


Figure 15. Scheme of the lab-scale, semi-batch ozonation setup. 1. Oxygen bottle; 2. Ozone generator; 3. Regulating valve; 4. Manometer; 5. Gas flow-meter; 6. Three-way valve; 7. Reactor; 8. Pump; 9. Dissolved ozone measuring system; 10. Foam trap; 11. KI solution for O_3 quenching; 12. Thermometer; 13. Ozone analyzer (gas-phase). Continuous and dashed lines indicate gas and liquid streams, respectively. Red and blue arrows in the ozone generator and reactor indicate the cooling water circuit.

Ozone consumption was determined as the Transferred Ozone Dose (TOD), which is defined through Eq. (31) and represents the transferred ozone to the liquid phase per unit of volume and time. *F* and *V* are the gas flow rate and the liquid volume, respectively, *t* is the ozonation time and $[O_3]_{in}$ and $[O_3]_{out}$ represent the ozone concentrations measured at the inlet and outlet gas streams, respectively. The trapezoidal method of numerical integration with a step size of 10 s was implemented for TOD calculation.

$$\mathrm{TOD} = \int \frac{F}{V} \cdot \left([\mathrm{O_3}]_{\mathrm{in}} - [\mathrm{O_3}]_{\mathrm{out}}\right)\mathrm{d}t \tag{31}$$

For a more accurate estimation of ozone consumption during experiments, TOD corrections were applied taking into account the reactor headspace and the dead volume existent between the liquid-gas interface and the outlet ozone analyzer. The headspace was modelled as a continuous stirred-tank reactor (CSTR) to account for ozone dilution in the gas phase, whereas the gas stream circulating from the reactor outlet to the O_3 analyzer was considered to follow a plug-flow model.

The IOD values for tested effluents were estimated as the minimum TOD required for ozone detection in the aqueous phase, according to the methodology firstly proposed by Roustan et al. [142] for continuous bubble columns and here adapted for a semi-batch ozone contactor. This and other important parameters related to ozone mass transfer from gas to liquid phase, such as the volumetric mass transfer coefficient (k_La), the mass transfer efficiency (η_{tr}) or the first-order O_3 decay constant (k_d) were also determined in semi-batch ozonation experiments (for wastewater effluents used in Appendices IV and V). They provided information about effluent quality and its relationship with the gas-liquid ozone transfer, a critical process in wastewater ozonation. Detailed information about these parameters and their estimation procedures can be found in the Supplementary Information of the publication presented in Appendix IV.

In a typical experiment, a wastewater effluent sample was first spiked with low concentrations (≤ 100 µg L^{-1}) of one or more model compounds. In general, ACMP (100 µg L^{-1}) was employed as •OH probe, whereas ibuprofen (IBU) and atrazine (ATZ) (25-50 µg L^{-1}) were mainly used to validate kinetic models for ozone-refractory MPs abatement prediction. Finally, methiocarb (MC) and dichlorvos (DDVP) (50 µg L^{-1}) were used in some experiments as model ozone-reactive MPs. After MPs spiking, the resulting solution was placed in the reactor vessel and ozonized for 30-60 min under the operational conditions described above. Samples were taken at known time intervals and kept at room conditions until complete consumption of dissolved ozone was achieved. Then, analyses were conducted. Parameters such as the residual concentration of micropollutants, UV absorbance, TOC (or DOC) and COD were typically determined. Others, such as the type and concentration of EfOM fractions were only analyzed when required (see Appendix V).

In peroxone experiments, that is experiments employing hydrogen peroxide combined with ozone (see Appendix VI), the addition of H_2O_2 was performed by two different methods: a) total initial spiking; or b) continuous dosing by means of a metering pump. In the latter case, an Ismatec 829 pump (Cole-Parmer, USA) supplied the ozone contactor with H_2O_2 from a reservoir tank containing a dilution of the commercial solution. The pump flow-rate was set at the lowest possible value (0.33 mL min^{-1}) to minimize the medium dilution. The transferred ozone dose per unit time (TOD/*t*, mg O_3 L^{-1} min^{-1}) was employed as reference parameter for H_2O_2 addition, with the aim of applying H_2O_2/O_3 molar ratios of 0.25, 0.5 and 1 when working in continuous dosing mode. As ozonation typically exhibits a two-stage behavior regarding ozone transfer to the liquid phase (see section 1.4.1 and ref. [143]), two TOD/*t* values previously determined in single ozonation assays were required to calculate the H_2O_2 flow necessary to meet the working oxidant ratios. Being so, hydrogen peroxide addition initially started from a reservoir tank containing a more concentrated H_2O_2 solution (tank 1), since the ozone mass transfer in this stage was faster (*i.e.*, higher TOD/*t*). After IOD completion, the secondary ozonation regime started. In this stage, characterized by a slower ozone consumption (*i.e.*, lower TOD/*t*), H_2O_2 was dosed from a reservoir containing a less concentrated dilution (tank 2). For details regarding dosing conditions in peroxone experiments, the reader is referred to Appendix VI.

3.4 Analyses

3.4.1 Micropollutants residual concentrations

The concentrations of micropollutants during oxidation experiments were determined by High Performance Liquid Chromatography with ultraviolet detection (HPLC-UV). A 1260

Infinity HPLC (Agilent Technologies, USA) equipped with a Diode Array Detector (DAD) was used on that purpose. The employed column was a Mediterranea Sea 18 (250 mm x 4.6 mm, 5 µm size packaging) supplied by Teknokroma (Spain). Mixtures of acetonitrile (ACN) and ultrapure water (pH 3, acidified with H_3PO_4) at varying proportions were employed as mobile phase. The flow rate was generally set around 1 mL min^{-1}, although it was modified as appropriate. The sample (previously filtered through 0.45 µm PTFE membranes) injection volume ranged from 20-100 µL, depending on the compound of interest and the range of concentrations to determine. The wavelengths of detection were selected according to the UV absorption properties of the different analytes that were quantified, but always in the range between 205 and 270 nm. Details of HPLC conditions regarding mobile phases, injection volumes and detection wavelengths can be found in Appendices I-VI.

3.4.2 Oxidation intermediates

Degradation intermediates of the studied pesticides were elucidated by HPLC-UV combined with Mass Spectrometry (MS). These analyses were performed in collaboration with the Molecular Characterization Mass Spectrometry Unit of the Scientific and Technological Centers of the University of Barcelona. An Agilent G1969A Electrospray-Ionization-Time-of-Flight (ESI-TOF) MS system was coupled in series to a 1100 HPLC system equipped with a DAD, also supplied by Agilent. The MS settings were as follows: sample inlet flow: 0.3 mL min^{-1}; capillary voltage, 4000 V; fragmentor voltage, 175 V; drying gas temperature, 325 ºC; drying gas flow, 10 L min^{-1}; nebulizer pressure, 30 psig; data acquisition, 25-1000 m/z. Both negative and positive ESI modes were preliminary tested during the identification of all three pesticides (MC, ACMP and DDVP) degradation intermediates. However, positive ionization allowed a better detection of MC and ACMP intermediates, whereas negative ESI mode worked better in the case of DDVP degradation products.

3.4.3 Total Organic Carbon

The Total Organic Carbon (TOC) content was determined by means of a 5055 TOC-VCSN analyzer equipped with an ASI-V autosampler, all by Shimadzu (Japan), and according to the Standard Methods 5310 B procedure [181]. The analysis consists of three steps:

a) removal of inorganic carbon by sample acidification (HCl, 2 M) and subsequent air bubbling, b) catalytic combustion of the sample at 680 ºC and c) quantification of CO_2. Dissolved Organic Carbon (DOC) can also be measured through this procedure, previous filtration of the sample through 0.45 µm syringe filters.

3.4.4 Chemical Oxygen Demand

The Chemical Oxygen Demand (COD) gives a global measurement of the organic load in a water sample. This analysis determines the equivalent amount of oxygen necessary to oxidize organic species contained in a water sample by means of strong oxidizing agents. Tests were carried out by following the Standard Methods 5220 D procedure [181]. 2.5 mL of the sample were digested at 150 ºC during 2 h with 1.5 mL of potassium dichromate ($K_2Cr_2O_7$, 4 mM) and 3.5 mL of silver sulfate solution (Ag_2SO_4, 10 g L^{-1}) in sulfuric acid (H_2SO_4). Mercuric sulfate ($HgSO_4$, 25 g L^{-1}) was also present in the medium in order to avoid potential interferences caused by chloride anion. During the oxidation reaction, Cr^{6+} is reduced to Cr^{3+}. The Cr^{6+} disappearance, which is proportional to the extent of the oxidation reaction, was quantified by measuring the absorbance of the solution at 420 nm (low COD protocol) with an Odyssey DR2500 UV-Vis spectrophotometer (Hach, USA). Tubes employed for sample digestion (round bottom, 16 mm diameter) were also employed as cuvettes for colorimetric measurements.

3.4.5 Ultraviolet Absorbance

All dissolved organic matters (*e.g.*, EfOM in the case of wastewater effluents) have in common that they exhibit strong UVA (Figure 16). This fact makes this parameter useful to characterize water and wastewater samples.

Particularly, UVA measured at a wavelength of 254 nm (*i.e.*, UVA_{254}) has been traditionally considered a good indicator of the level of aromatic moieties in aqueous matrices. For a better characterization of EfOMs, UVA_{254} is typically normalized to the concentration of organic matter of the sample (*e.g.*, UVA_{254}/DOC, also known as specific UV absorbance or SUVA). Since UV active moieties of EfOM have a certain reactivity with ozone, this parameter can be of interest when applying ozonation process for water and wastewater treatment. Further details regarding the relevance of UVA for water and wastewater ozonation can be found in the book *Chemistry of Ozone in Water and Wastewater Treatment* by von Sonntag and von Gunten [107]. UVA was determined by means of a DR6000 UV-Vis spectrophotometer (Hach, USA). Measurements at 254 nm or wavelength scans (200-400 nm) were typically performed. 1x1 cm quartz cuvettes were in all cases employed.

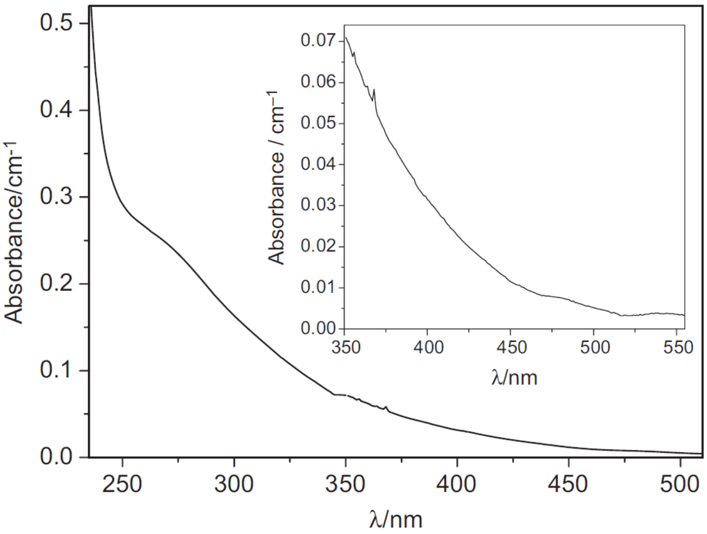


Figure 16. UV-Vis spectrum of a typical wastewater (effluent of the municipal WWTP in Neuss, Germany) [107].

3.4.6 Turbidity

Turbidity in water is caused by suspended and colloidal matter. In wastewater effluent samples, the measurement of this parameter together with other physicochemical parameters such as TOC and DOC may provide additional data regarding the physical state (dissolved, colloidal or suspended) of EfOM. Turbidity was determined by means of a Hach 2100P portable turbidimeter, through a protocol that is based on the Standard Methods 2130 B procedure [181].

3.4.7 Assessment of Effluent Organic Matter fractions

Typical physicochemical parameters employed for EfOM characterization, such as TOC, DOC, COD, UVA do not always provide enough information regarding the chemical nature of wastewater organic constituents. Under some circumstances, especially for wastewater reuse applications, it may be convenient to know the type and concentration of the different fractions of organic matter that is present in wastewater effluents, and how this composition may vary after applying subsequent treatment steps (*e.g.*, ozonation). Quantitative information regarding dissolved EfOM fractions can be obtained by means of Size Exclusion Chromatography combined with Organic Carbon Detection (SEC-OCD). This technique, which also employs UV and Organic Nitrogen Detection (OND), allows the identification and quantification of the organic fractions gathered in Table 13 [182,183].

Table 13. Characteristics of dissolved EfOM fractions [182].

Dissolved EfOM fraction	**Molecular Weight**	**Description**
Biopolymers (BP)	> 50000-2000000	Hydrophilic. Associated to amino acids and proteins. Not UV-absorbing.
Humic substances (HS)	100-100000	Mix of humins (non-soluble) and humic/fulvic acids, in varying concentrations.
Building Blocks (BB)	350-500	Degradation products of HS and precursors of LMWA.
Low Molecular Weight Acids (LMWA)	< 350	Final degradation products of organics. Also released by algae and bacteria.
Low Molecular Weight Neutrals and Amphiphilics (LMWN)	<350	Short-chained, slightly hydrophobic products, such as alcohols, aldehydes, ketones and amino acids.

SEC-OCD determinations were performed in collaboration of the R&D Department of ACCIONA Agua, a Spanish company dedicated to the development and management of water services. As recommended, samples were filtered through 0.45 µm PTFE membranes and preserved at 4 ºC and dark conditions until analyses were performed.

3.4.8 Nitrite content

Nitrite (NO_2^-) concentration is an important parameter that should be always considered in wastewater ozonation. Ozone rapidly reacts with nitrite (k_{O3} with nitrite: $3.8\cdot10^5$ $M^{-1}s^{-1}$), yielding nitrate (NO_3^-) and singlet oxygen ($^1O_2$) as main products [reaction (32)].

$$NO_2^- + O_3 \rightarrow NO_3^- + {}^1O_2 \tag{32}$$

In addition to this reaction, •OH is also formed, but the yield is only near 4% [184]. By a simple calculation, therefore, it can be deducted that each mg of nitrogen in the form of nitrite (NO_2^- expressed as mg N L^{-1}) consumes 3.43 mg of ozone without generating hydroxyl radicals. This effect can be critical in wastewater ozonation, where nitrite formed during partial nitrification of ammonia can be present.

Nitrite content in wastewater effluents samples was determined by Ion-Exchange Chromatography (IEC). An HPLC system consisting of a 515 pump (Waters, USA), a 465 autosampler and a 332 UV detector (Kontron, Germany) was employed in this analysis. The column was a IC-Pak Anion (150 mm x 4.6 mm, 10 µm size packaging), also supplied by Waters. The mobile phase consisted of a borate-gluconate buffer, and the flow was maintained at 2 mL min^{-1}. The injection volume was 200 µL, and the detection was carried out at 214 nm.

3.4.9 Alkalinity

Alkalinity of a water is a measure of its capacity for neutralizing acids. In wastewater, this buffering capacity is mainly attributed to the bicarbonate (HCO_3^-) and carbonate content (CO_3^{2-}), although other species such as hydroxide, phosphate, ammonia and sulfate can also contribute to this property. The alkalinity was measured through an automatic titration system (pH Burette 24) combined with a Basic 20 pH meter, all supplied by CRISON (Spain). Samples were titrated with hydrochloric acid (HCl, 0.1 M), and the selected end-point was pH 4.3.

3.4.10 Dissolved ozone concentration

The residual concentration of ozone (O_3) in batch ozonation experiments was determined by the indigo method, first described by Bader and Hoigné in 1981 [185] and included as 4500-O_3 B procedure in the Standard Methods [181]. The principle of this method is that ozone rapidly decolorizes indigo dye in acidic solution, being the decrease in absorbance linear with increasing concentration of the oxidant. 0.5 mL of the sample was added to 2.5 mL of indigo reagent II solution (potassium indigo trisulfonate [$C_{16}H_7N_2O_{11}S_3K_3$], 77 mg L^{-1}; sodium dihydrogen phosphate [NaH_2PO_4], 10 g L^{-1}; concentrated phosphoric acid [H_3PO_4, 85% w/w] 7.1 mL in 1 L). The absorbance at 600 nm was immediately measured by means of a DR6000 UV-Vis spectrophotometer (Hach, USA). The concentration of ozone was determined from the difference between the absorbance measured in sample and blank (prepared with ultrapure water). 1x1 cm quartz cuvettes were employed.

Regular calibrations of the O_3 probe employed in semi-batch ozonation experiments were also carried out employing the indigo method as reference, as recommended by the manufacturer.

3.4.11 Hydrogen peroxide concentration

H_2O_2 concentration was determined by means of the metavanadate spectrophotometric procedure [186]. 1.5 mL of the sample were mixed with 1.5 mL of an ammonium metavanadate solution (5.14 g L^{-1}) prepared in acidic medium (19.2 mL H_2SO_4 L^{-1}). Under these conditions, the metavanadate (VO_3^-) anion reacts with H_2O_2 forming the species VO_2^{3+}, which presents an orange-coloration. The generation of this species, proportional to H_2O_2 concentration, was measured at 450 nm by means of a DR3900 UV-Vis spectrophotometer (Hach, USA). 13 mm diameter (flat bottom) test tubes were employed as cuvettes.

3.4.12 Acute toxicity: Microtox® bioassay

Acute ecotoxicity of pesticides and their respective degradation products was assessed by means of the Microtox® toxicity test, which employs bioluminescent bacteria *Vibrio fischeri*, a marine organism. When exposed to a toxic substance, bacteria respiration is disrupted, inhibiting the metabolic pathway that converts chemical energy into visible light. Response to toxicity is therefore measured as a change in luminescence. The tests were conducted by strictly following the protocol recommended by the manufacturer (Modern Water, UK). After reconstitution of a freeze-dried culture of *Vibrio fischeri* (Microtox® Acute Reagent) in 1 mL of the Microtox® Reconstitution Solution (especially prepared ultrapure water), 10 µL of this reagent were mixed with 0.5 mL of the Microtox® Diluent (especially prepared ultrapure water containing 2% NaCl). After waiting 15 min for the stabilization of bacteria light emission, luminescence was recorded by means of a Microtox® M500 analyzer, a temperature-controlled photometer. Then, bacterial dilutions and the sample (adjusted with the Microtox® Osmotic Adjustment Solution, which is a 22% NaCl solution in ultrapure water) were mixed to finally prepare 45, 22.5, 11.25 and 5.6% serial dilutions. After 15 min of contact, luminescence of all dilutions was recorded. Results were expressed as $1/EC_{50}$, where EC_{50} is the sample dilution causing a 50% reduction in light emission after 15 min of contact. A scheme of the protocol employed in this bioassay is shown in Figure 17.

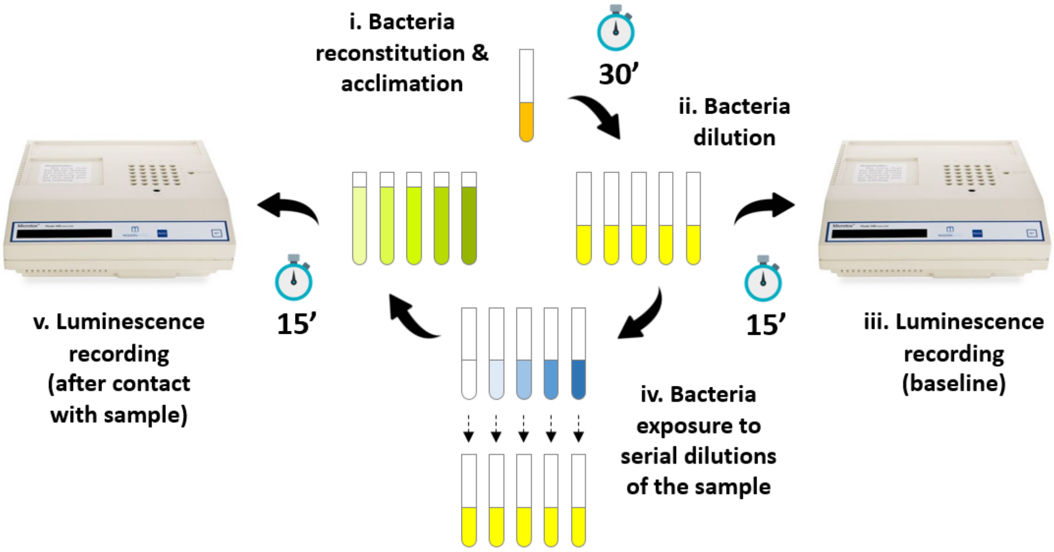


Figure 17. Microtox® tests. Scheme of procedure.

4 Results and discussion

A summary of most relevant findings of this thesis are presented in the following sections. First, the results of kinetic, mechanistic and ecotoxicological studies of selected pesticides oxidation during ozonation (corresponding to publications in Appendices I, II and III) are presented. Then, the main findings of ozone application to municipal wastewater effluents are discussed. This second part starts with the results obtained in the study dealing with the effective abatement and control of ozone-recalcitrant MPs during ozone application (Appendix IV), including kinetic modelling and surrogate control strategies, and ends with the presentation of results about the fate of dissolved EfOM fractions during the treatment (Appendix VI). Finally, results obtained in the study dealing with the combination of ozone and hydrogen peroxide (*i.e.*, peroxone process) for enhanced micropollutants oxidation in wastewater effluents are presented (Appendix VI). The latter includes potential strategies for performance improvement and kinetic modelling of the process.

4.1 Kinetic, mechanistic and toxicological studies of selected priority/emerging concern pesticides degradation during ozonation (Appendices I-III)

4.1.1 Reaction kinetics

Kinetic studies performed according to the methods detailed in section 3.3.2, allowed the determination of the second-order rate constants of ozone and hydroxyl radical reactions with MC, ACMP and DDVP. Obtained values are presented in Table 14.

The rate of reaction between MC and ozone was determined to be considerable high, which is attributable to the thioether or sulfide moiety that is present in the carbamate molecule. Sulfides, with sulfur atom in its lowest oxidation state, can undergo fast O-transfer reactions with ozone [107]. On its part, ACMP reaction with ozone was determined to occur very slowly. According to the classification by ozone reactivity proposed by Lee and coworkers [136], this pesticide would be considered ozone-refractory. The pyridine group is quite unreactive to ozone, and the terminal cyano moiety, with strong electron withdrawing properties, probably contributes to hinder ozone oxidation in other site of the molecule.

Regarding DDVP reaction with ozone, a moderate rate constant value was obtained. Organic phosphates are typically ozone-refractory compounds [107,122], although the double bound in the dichlorovinyl moiety can probably undergo cycloaddition reactions [107].

Table 14. Rate constants of ozone and hydroxyl radical reactions with studied pesticides. Categorization into high, moderate or low reactivity groups is based on the classification established by Lee et al. [136]. For O_3 reactions: $k < 10$ $M^{-1}s^{-1}$ (low); $10 < k < 10^5$ $M^{-1}s^{-1}$ (moderate); $k > 10^5$ $M^{-1}s^{-1}$ (high). For •OH reactions: $k < 1\cdot10^9$ $M^{-1}s^{-1}$ (low); $1\cdot10^9 < k < 5\cdot10^9$ $M^{-1}s^{-1}$ (moderate); $k > 5\cdot10^9$ $M^{-1}s^{-1}$ (high). Data compiled from publications presented in Appendices I-III.

Pesticide	**k_{O3} [$M^{-1}s^{-1}$]**	**O_3 reactivity**	**$k_{\bullet OH}$ [$M^{-1}s^{-1}$]**	**•OH reactivity**
MC	$1.7\cdot10^6$	High	$8.2\cdot10^9$	High
ACMP	0.25	Low	$2.1\cdot10^9$	Moderate
DDVP	590	Moderate	$2.2\cdot10^9$	Moderate

Concerning reactions with hydroxyl radical, the corresponding rate constants for all pesticides with this oxidant were determined to be in the 10^9 $M^{-1}s^{-1}$ order, which is typical for most organic micropollutants given the high reactivity and low selectivity of •OH. According to the classification by reactivity established by Lee et al. (see ref. [136] and/or Table 9 in section 1.4.1), MC rate constant values would be considered high, whereas those for ACMP and DDVP would be categorized as moderate.

4.1.2 Degradation mechanisms

HPLC-MS analyses of samples obtained in degradation experiments at different ozone doses allowed the identification of MC, ACMP and DDVP oxidation products (see Tables 2, 1 and 2 of Appendices I, II and III, respectively). According to this information and some knowledge on O_3 and •OH oxidation mechanisms with organic compounds, degradation mechanisms for all three pesticides were tentatively proposed to explain their degradation during ozone application.

Regarding MC (see proposed mechanisms in Figure 3 of Appendix I), detection of methiocarb sulfoxide (MCX), methiocarb sulfoxide phenol (MCXP) and methiocarb sulfone phenol (MCNP) led to the conclusion that the sulfur group in the parent compound molecule was firstly oxidized, leading to MC sulfoxidation followed by hydrolysis and subsequent sulfonation of the resulting phenol sulfoxide. Further oxidized TPs could not be detected, and different TPs for the two typical degradation pathways in ozonation, namely ozone and hydroxyl radical oxidation, could not be distinguished through experiments with and without the presence of tBuOH. However, obtained TPs could be followed through HPLC-UV at different ozone doses (see Figure 2 in Appendix I), revealing initial and simultaneous formation of MCX and MCXP followed by a signal decay after reaching a maximum. Gradual formation of MCNP was also observed after an initial lag phase. Thus, the mechanism proposed for MC degradation during ozonation was confirmed in view of these findings. Another interesting observation was that the system experimented less significant changes (at the same ozone doses) in experiments conducted in the presence of tBuOH. Oxidation by •OH, formed through ozone decomposition and suppressed in the presence of this scavenger, proved useful for a more effective degradation of both MC and TPs. This was especially relevant for TPs abatement, as sulfoxides and sulfones are significantly less reactive to ozone than sulfides (*i.e.*, the -S- moiety in the MC molecule) [107]. Thus, •OH could contribute to its effective degradation.

As ACMP showed a high resistance to ozone oxidation, the study of their degradation pathways focused on oxidation by hydroxyl radical. According to the identified structures, different possible pathways were proposed (see Figure 4 in Appendix II). The first tentative route would start with H-abstraction in the methylene group of the ACMP tertiary amine, ultimately yielding the identified compounds 6-chloronicotinic acid and *N'*-cyano acetamidine through a combination of •OH and O_2 oxidation with hydrolysis steps. *N'*-cyano acetamidine would be potentially preceded by formation of the corresponding *N'*-cyano-*N*-methyl acetamidine, a chemical species that was also identified through HPLC-MS. The initial ACMP oxidation by •OH could also occur by H-abstraction in the methyl group of its amine moiety. In that case, ACMP-N-desmethyl –which was also identified– would be formed as oxidation product.

Degradation of the pesticide DDVP could occur via hydroxyl radical –but also ozone– oxidation, as shown in the tentative mechanisms represented in Figure 4 of Appendix III. In the first case (•OH), various initial steps are possible, in the view of the identified TPs. Thus, oxidation could start by H-abstraction at one of the methyl groups bonded to DDVP phosphate group, or by •OH addition to the phosphorus atom in the same structure. In any of these two cases, desmethyl dichlorvos (*d*-DDVP) would be formed as transformation product, either by further •OH oxidation and formaldehyde release or by elimination of a methanolate from the resulting structures. Additionally, •OH could also attack the dichlorovinyl moiety of DDVP. In this case, the degradation route would ultimately yield dimethyl phosphate (DMP) and dichloroacetic acid (DCA) as products. The latter (DCA), could also be formed through hydrolysis and subsequent O_2 oxidation of the intermediate *d*-DDVP, formed in the firstly described pathway. According to the only TP identified in ozonation experiments in the presence of tBuOH, DMP, DDVP could first undergo a cycloaddition reaction with ozone, followed by decarbonation of the resulting molecule.

4.1.3 Ecotoxicological assessment

The potential, negative ecotoxicological effects of the studied pesticides and their respectively formed transformation products during ozonation were evaluated through bioassays employing the luminescent bacteria *Vibrio fischeri*.

Although the composition of tested (*i.e.*, oxidized) samples was unknown in all experiments with the exception of the initial model solutions, an interesting correlation was observed in MC degradation experiments between the observed toxicity and the corresponding HPLC-UV of the reaction intermediate MCX (see Figure 4 in Appendix I). According to previous studies, it appears to be that MCX is even more toxic than the parent compound MC [65–67], and that was probably the reason why toxicity increased during the process, reaching a maximum level at approximately the ozone dosage for which the maximum concentration of this compound was measured. Moreover, inhibition in bacteria light emission decreased when this chemical species started to be abated by the joint action of ozone and hydroxyl radicals. In experiments performed in the presence of tBuOH, toxicity levels reached higher levels in comparison to experiments without radical scavenger addition. The most effective abatement of MCX in the presence of •OH, compared to ozone, also led to a fastest toxicity reduction.

Ecotoxicity evaluation in the case of ACMP ozonation (see Figure 5 in Appendix II) also yielded interesting results, although in that case the observed rising in solution toxicity at intermediate ozone doses could not be attributed to any detected degradation compound. In fact, the identified TPs should apparently not be more toxic than the parent compound.

Synergistic effects between various TPs formed in the process, as well as the presence of non-detected TPs were proposed as possible explanation to the observed results.

Ozonation of DDVP also led to changes in the toxicity of the model solution, although the observed trend was different in experiments with or without addition of tBuOH. These results are represented in Figure 5 of Appendix III. In the first case, in which only ozone oxidation contributed to DDVP oxidation, solution toxicity initially decreased, and then started an increasing trend. Some explanations to these findings were proposed, namely synergy between detected TPs or additional toxicity exerted by non-detected intermediate species. Phosgene formation was described as part of the suggested DDVP degradation mechanism by ozone. However, this toxic species is known to rapidly hydrolyze in aqueous solution [187], and therefore its presence was dismissed as potential contributor to the observed increase in toxicity. Other possibilities could be the formation of aldehydes or peroxides typically formed through ozonation [107], although the presence of any of these species could not be confirmed. Finally, accumulation of the detected intermediate DMP, which is expected to react slowly with ozone, was also regarded as potential explanation for the observed results. In the case of DDVP oxidation by the joint action of ozone and hydroxyl radicals, a slightly, initial increase in the $1/EC_{50}$ value was observed, followed by a decreasing trend that was attributed to effective oxidation by •OH of all species potentially contributing to solution toxicity.

Appendix I

Exploring ozonation as treatment alternative for methiocarb and formed transformation products abatement

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Exploring ozonation as treatment alternative for methiocarb and formed transformation products abatement

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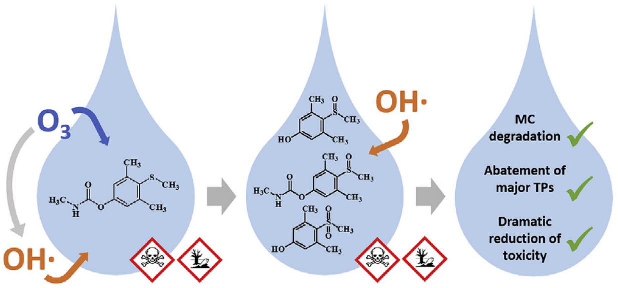
HIGHLIGHTS

- MC showed high reactivity with both molecular ozone and formed hydroxyl radicals.
- The generation of TPs equally or even more toxic than MC was observed.
- Changes in toxicity were associated to the concentration of a major TP, MCX.
- Ozone could only degrade MC, whereas hydroxyl radicals oxidized all species.
- Indirect reaction must be favored to ensure MC removal and toxicity abatement.

GRAPHICAL ABSTRACT



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ABSTRACT

Despite the high toxicity and resistance to conventional water treatments exhibited by methiocarb (MC), there are no reports regarding the degradation of this priority pesticide by means of alternative purification technologies. In this work, the removal of MC by means of ozonation was studied for the first time, employing a multi-reactor methodology and neutral pH conditions. The second-order rate constants of MC reaction with molecular ozone (O_3) and formed hydroxyl radicals (OH·) were determined to be $1.7 \cdot 10^6$ and $8.2 \cdot 10^9$ M^{-1} s^{-1}, respectively. During degradation experiments, direct ozone reaction was observed to effectively remove MC, but not its formed intermediates, whereas OH· could oxidize all species. The major identified TPs were methiocarb sulfoxide (MCX), methiocarb sulfoxide phenol (MCXP) and methiocarb sulfone phenol (MCNP), all of them formed through MC oxidation by O_3 or OH· in combination with hydrolysis. A toxicity assessment evidenced a strong dependence on MCX concentration, even at very low values. Despite the OH· capability to degrade MC and its main metabolites, the relative resistance of TPs towards ozone attack enlarged the oxidant dosage (2.5 mg O_3/mg DOC) necessary to achieve a relatively low toxicity of the medium. Even though ozonation could be a suitable technique for MC removal from water compartments, strategies aimed to further promote the indirect contribution of hydroxyl radicals during this process should be explored.

1. Introduction

Methiocarb (mesurol, 3,5-dimethyl-4-(methylthio)phenyl methylcarbamate) (MC) is one of the most common carbamate pesticides worldwide, employed in agriculture as insecticide, acaricide,

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molluscicide and bird repellent (Altinok et al., 2006; Blažková et al., 2009; Gitahi et al., 2002; Keum et al., 2000; Sinclair et al., 2006). This chemical has been detected in natural waters of several countries (APVMA, 2005; Barceló et al., 1996; Fytianos et al., 2006; García de Llasera and Bernal-González, 2001; Squillace et al., 2002) at concentration levels ranging from ng L^{-1} to μg L^{-1}. It also has been detected in wastewater effluents (Campo et al., 2013; Masiá et al., 2013), this last suggesting the resistance of MC to conventional wastewater treatments. Although the detected concentrations of this micropollutant in water compartments are generally low, it represents a serious threat to the aquatic and human life considering its high toxicity and that of some of its water metabolites (UNFAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization), 1999). For example, methiocarb sulfoxide (MCX), which is one of the typical MC natural transformation products (TPs), has been reported to be even more toxic than the parent compound (Marss, 1998), and is currently included on the Priority List of Transformation Products in Great British Drinking Water Supplies (Sinclair et al., 2006). Because of all these reasons, the World Health Organization has classified MC as a highly hazardous pesticide (World Health Organization, 2010). Furthermore, MC has been included in the recently launched 1st watch list of Decision (2015)/495/EU for European monitoring (The European Comission, 2015), among other micropollutants considered as priority substances.

Several studies regarding the fate of MC during conventional wastewater and simulated drinking water treatment have been reported during the last few years. For wastewater treatment, no concluding results have been obtained about MC fate. For example, higher concentrations were found in the effluents than in the influents in a Spanish sewage treatment plant, probably due to limitations in sampling procedure (Barbosa et al., 2016; Campo et al., 2013). Studies regarding the fate of MC in simulated drinking water treatment have demonstrated that reactions between this pesticide and most commonly used disinfectants (i.e.: free chlorine, ClO_2 and NH_2Cl), which also possess a certain oxidizing power, yield transformation products (TPs) more toxic and persistent than the parent compound, even though this one becomes degraded (Qiang et al., 2014; Tian et al., 2013, 2010). However, despite the safety concern regarding the presence of this pesticide and their TPs in the aqueous systems, no studies related to the removal of MC by advanced treatment options have been found in literature, as also stated in a recent review by Barbosa et al. (2016). A possible explanation for this lack of data could be related to the moderate-high hydrophobic character of MC (log Kow = 3.2 and water solubility 27 mg L^{-1}, at 20 °C (UNFAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization), 1999)), which could complicate the handling of MC during the experimental work due to its probable tendency of becoming adsorbed to other hydrophobic materials.

Ozonation for the abatement of micropollutants has been demonstrated to be an effective process (Dantas et al., 2008, 2007; Huber et al., 2003; Jin et al., 2012; Vel Leitner and Roshani, 2010), thus indicating the great potential of this advanced technology for that purpose. Ozone (O_3) is a strong oxidant that also undergoes self-decomposition in water to release hydroxyl radicals ($OH\cdot$), under neutral and alkaline conditions, with stronger oxidizing capability than O_3 (Gligorovski et al., 2015). Since this technology is increasingly employed in wastewater and drinking water treatment, detailed information about kinetics, intermediates generation and associated toxicity changes during the process is essential, even more with the detection of new micropollutants.

To the best of our knowledge, this is the first report on MC removal by means of ozonation. The study aimed to determine the kinetics of the process considering both, direct reaction with molecular ozone and indirect reaction through hydroxyl radicals. The possible reaction pathways of MC ozonation were also explored by means of its main formed intermediates elucidation and finally, the potential ecotoxicological effects of MC and its TPs during the process were assessed by means of bacteria luminescence inhibition assays.

2. Materials and methods

2.1. Chemicals and reagents

Methiocarb, sulfamethoxazole and phenol analytical standards were acquired from Sigma-Aldrich (Germany). NaH_2PO_4, Na_2HPO_4, H_3PO_4, *tert*-butanol and acetonitrile were purchased from Panreac (Spain), and were all analytical grade. Milli-Q water was produced by a filtration system (Millipore, USA). Finally, all the reagents employed during toxicity bioassays were purchased from Modern Water (UK).

As early commented, MC was suspected to be adsorbed to some non-polar materials, due to its hydrophobicity. In order to be sure about that, some preliminary experiments were performed. Results revealed important losses of MC when aqueous solutions of this chemical were put in contact with plastic elements (i.e. filters, tubing), whereas this was not observed when working with glassware. Therefore, glass was selected as material for handling MC solutions during experimentation.

2.2. Ozonation experiments

All ozonation experiments were carried out at 20 ± 2 °C and pH 7, in Milli-Q water. Preliminary hydrolysis tests at pH 7 were performed in order to determine the influence of this mechanism on the overall MC removal. Reaction solution did not show hydrolysis after a period of 2 h, which is exactly the time interval employed for ozonation experiments, including analysis. Due to the tendency of MC to become adsorbed onto many materials, as well as to the fast reaction kinetics also exhibited during the preceding assays, ozonation runs were carried out employing a multi-reactor methodology, successfully used in several works (Borowska et al., 2016; Ning et al., 2007). Detailed information of ozone stock solutions preparation can be found in the supplementary information (Text and Fig. S1). All ozonation experiments were done in triplicate.

Since preliminary experiments showed fast reaction rates ("k" values > 1000 M^{-1} s^{-1}), the extensively-employed competition kinetics method (Borowska et al., 2016; Buxton et al., 1988; Hoigné and Bader, 1983; Huber et al., 2003; Jin et al., 2012) must be used to determine the kinetic constants of the reaction between MC and both, molecular ozone and hydroxyl radicals.

For $k_{MC,O3}$ measurement, experiments were carried out in a series of 25 mL vials containing 20 μM of MC and 20 μM of sulfamethoxazole (SMX), the reference compound. The competitor was selected considering the high-reactivity of MC with molecular ozone. To avoid reactions involving hydroxyl radicals ($OH\cdot$), *tert*-butanol was employed as $OH\cdot$ scavenger (100 mM). Adequate quantities of a $H_2PO_4^-/HPO_4^{2-}$ buffer were also added in order to maintain the medium pH at a constant value of 7. Different doses (from 5 to 50 μM) of the ozone stock solution were injected to each vial as reactant. The mixtures were vigorously shaken for a few seconds, to completely mix the ozone in. Samples were withdrawn when the total consumption of ozone was achieved, and quickly analyzed. The residual concentrations of MC and SMX were determined by HPLC-DAD.

For $k_{MC,OH\bullet}$ determination, a similar procedure was followed. The multi-reactor system was used again, with initial concentrations of 20 μM for all compounds and without the presence of a radical scavenger. Two references were employed since two reactions (i.e. MC with both, O_3 and $OH\cdot$) took place at the same time and needed to be considered due to their expected important contribution to MC depletion. SMX and phenol (PH) were chosen as competitors, since both were expected to present similar overall reactivity than MC.

Two extra sets of experiments were performed in order to demonstrate the relative contribution of hydroxyl radicals on MC removal. For direct reaction with ozone, each one of the 25 mL reaction vials contained 20 μM of MC, 25 mM of *tert*-butanol and adequate quantities of the pH 7 phosphate buffer. For reaction involving molecular ozone and hydroxyl radicals, the same procedure was followed but no scavenger was added. For both experiments, a wider range of ozone doses were applied (from 5 to 140 μM) in order to achieve the complete depletion of the pesticide. Once analyzed, the samples withdrawn in these experiments were frozen and lately employed for TPs and toxicity determinations.

2.3. Analytical procedures

The concentrations of MC, SMX and PH were quantified by means of an HPLC equipped with a diode array detector (DAD), all supplied by Agilent (1260 Infinity). For MC, PH and SMX analysis, the column employed was a Teknokroma Mediterranea Sea18 (250 mm × 4.6 mm and 5 μm size packing). The chromatographic conditions for each compound separation and detection are summarized in Table S1 (supplementary information).

In order to elucidate the possible reaction pathways during MC ozonation, samples in which different ozone doses were applied were analyzed by LC-MS. An Agilent 1100 HPLC coupled with a G1969A LC/MSD-TOF mass spectrometer was employed. MS data were collected in full scan mode (25–1100 *m*/*z*), employing positive electrospray ionization. The separation conditions were the same ones employed for DAD quantification.

To assess the acute toxicity as a function of the applied ozone dose, Microtox® bioassays were performed. This method measures the inhibition of light emission of bioluminescent bacteria *Vibrio fischeri* caused by the presence of toxic compounds in the aqueous media. The results of this assay are usually expressed as $EC_{50,15min}$, which represents the percentage of sample dilution (v:v) that causes a 50% reduction in bacteria luminescence after a contact time of 15 min. All the tests were carried out in duplicate in a Microtox® M500 (Modern Water, UK) toxicity analyzer.

3. Results and discussion

3.1. Rate constant for the reaction between MC and O_3

The second-order rate constant for the reaction of MC with molecular ozone was calculated from Eq. (1), being this one obtained by dividing the kinetic equations corresponding to the direct reactions between MC and SMX with O_3, as described elsewhere (Dantas et al., 2008, 2007).

$$-ln\left(\frac{[MC]}{[MC]_0}\right) = \frac{k_{MC,O_3}}{k_{SMX,O_3}}\left(-ln\left(\frac{[SMX]}{[SMX]_0}\right)\right) \tag{1}$$

As shown in this expression, a linear dependence between the natural logarithm of the relative MC concentration and the natural logarithm of the relative SMX concentration is expected, with the ratio between the second-order kinetic constants of the target and the reference compound being the slope. For the three replicates that were performed, linear regression coefficients greater than 0.99 were obtained, together with a good agreement between the corresponding slope values (0.87 ± 0.01, see Fig. S2 of the supplementary information). Considering a value of $2.0\cdot10^6\ M^{-1}\ s^{-1}$ for $k_{SMX,O3}$ at pH 7 (Huber et al., 2003; Jin et al., 2012), the second-order rate constant for reaction between MC and molecular ozone, $k_{MC,O3}$, was determined to be $(1.7 \pm 0.1)\cdot10^6\ M^{-1}\ s^{-1}$. As suspected during preliminary experiments, the rate of the reaction between MC and O_3 is considerable fast. MC molecule contains a thioether moiety, which has been considered to be the main responsible for the fast kinetics (between $2.0\cdot10^5$ and $6.7\cdot10^5\ M^{-1}\ s^{-1}$) presented by other compounds containing this functional group in their corresponding reactions with molecular ozone (Dodd et al., 2006; Jeon et al., 2016). Since MC does not show basic or acidic properties in aqueous systems (UNFAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization), 1999), the reactivity of this compound with ozone is not expected to be dependent on the medium pH, as reported for many other dissociating chemicals (Borowska et al., 2016; Dantas et al., 2008, 2007; Hoigné and Bader, 1983).

3.2. Rate constant for the reaction between MC and OH·

For $k_{MC,OH\cdot}$ determination, a different protocol was employed: since no radical scavenger was added to the reaction medium, the contribution of molecular ozone and hydroxyl radicals to the overall MC depletion must be considered. Because of that, two reference compounds (SMX and PH) were needed in order to later solve the corresponding mathematical equations. This method was successfully employed for similar purposes in a previous study (Vel Leitner and Roshani, 2010). In the present case, six reactions were considered to simultaneously take place in the described system. They are gathered in Table 1, along with the corresponding kinetic constant values found in literature.

The second-order rate constant for the reaction of MC with hydroxyl radicals was calculated by solving the system formed by Eqs. (2) and (3). Detailed information about the obtaining of these expressions can be found in Text S2 (supplementary information).

$$ln\frac{[MC]}{[MC]_0} = \frac{(k_{MC,O_3} + k_{MC,OH}\cdot Rct)}{(k_{SMX,O_3} + k_{SMX,OH}\cdot Rct)}\,ln\frac{[SMX]}{[SMX]_0} \tag{2}$$

$$ln\frac{[MC]}{[MC]_0} = \frac{(k_{MC,O_3} + k_{MC,OH}\cdot Rct)}{(k_{PH,O_3} + k_{PH,OH}\cdot Rct)}\,ln\frac{[PH]}{[PH]_0} \tag{3}$$

From the above equations, it can be deduced that by plotting the natural logarithm of the relative concentration of MC versus the natural logarithm of the relative concentration of each one of the competitors, per separate, two linear relations are obtained. Together with the experimentally obtained slopes, if all the required kinetic constant values are known the system can be solved in order to determine $k_{MC,OH\cdot}$, as well as *Rct*. The latter corresponds to a time-independent relation which represents the ratio $[OH\cdot]/[O_3]$ in a reaction medium subject to ozonation (Elovitz and Von Gunten, 1999).

A good agreement was observed between the three replicates that were performed: slope values of 0.90 ± 0.02 and 0.98 ± 0.01

Table 1
Reactions considered during competition experiments for $k_{MC,OH\cdot}$ determination.

Reaction	k [$M^{-1}\ s^{-1}$]	Reference
$MC + O_3 \rightarrow k_{MC,O3}$	$1.7\cdot10^6$	This study
$MC + OH\cdot \rightarrow k_{MC,OH\cdot}$	Unknown	–
$SMX + O_3 \rightarrow k_{SMX,O3}$	$2.0\cdot10^6$	(Jin et al., 2012)
$SMX + OH\cdot \rightarrow k_{SMX,OH\cdot}$	$5.5\cdot10^6$	(Huber et al., 2003)
$PH + O_3 \rightarrow k_{PH,O3}$	$1.8\cdot10^6$	(Hoigné and Bader, 1983)
$PH + OH\cdot \rightarrow k_{PH,OH\cdot}$	$6.6\cdot10^9$	(Buxton et al., 1988)

resulted for MC-SMX and MC-PH corresponding relationships, respectively. All the linear coefficients were above 0.99 (see Fig. S3 of the supplementary information). The kinetic constant was determined to be $(8.2 \pm 0.2)\cdot 10^9$ M^{-1} s^{-1}, which indicates the high reactivity of MC with hydroxyl radicals. In that case, the fast kinetics was not attributable to a single specific reaction like the one exhibited between molecular ozone and the thioether group: although this sulfur moiety is also highly reactive to hydroxyl radicals, with reported rate constants in the order of 10^9 to 10^{10} M^{-1} s^{-1} (Rózsa et al., 2017; Szabó et al., 2015), the characteristic non-selectivity of OH· could promote other reaction mechanisms usually exhibited by this transient species (e.g. electron or hydrogen abstraction) (Gligorovski et al., 2015).

3.3. MC degradation by ozone and hydroxyl radicals

During the ozonation process, methiocarb can react with molecular ozone but also with hydroxyl radicals generated by ozone decomposition (Gligorovski et al., 2015). Degradation experiments applying different ozone dosages were performed in order to observe the removal profile by means of the direct route (attack of molecular ozone), as well as to demonstrate the contribution of hydroxyl radicals to the overall depletion of MC at neutral pH. Results are shown in Fig. 1. Transformation by means of O_3/OH· combination was more effective than the removal only due to O_3 attack: the ozone dose required to deplete over a 99% of the initial MC concentration was about 2.5 times lower in the first case than in the second (1.1 mg L^{-1} vs 2.8 mg L^{-1}). At pH 7, therefore, the indirect degradation pathway could play an important role in the global depletion of MC. This means that efficiency of ozonation for MC depletion will strongly depend on water pH, among other characteristics, since decomposition of ozone in hydroxyl radicals is accelerated under alkaline conditions (Gligorovski et al., 2015).

According to bibliography (Gerrity et al., 2012; Lee et al., 2013), doses until 1 mg O_3/mg DOC are considered reasonable for disinfection and trace pollutant oxidation in drinking and wastewater treatment plants. In the case of study, the normalized ozone dose of 0.4 mg O_3/mg DOC was calculated to be enough to completely remove MC by means of the O_3 and OH· joint action. As stated before, besides the chemical reactivity of the pollutant with ozone, the efficiency of the process strongly depends on water characteristics like pH or organic matter content. For instance, and given the high value obtained for the second-order rate constant of MC reaction with O_3 ($1.7\cdot 10^6$ $M^{-1}s^{-1}$), in waters containing natural organic matter (NOM) or soluble microbial compounds (SMP) at concentration levels of mg L^{-1}, MC (from ng L^{-1}-µg L^{-1}) removal is expected to happen mainly via ozone oxidation. It is clear, therefore, that the required ozone doses to deplete MC in real waters are difficult to determine only on the basis of the above results. Carrying out experiments with realistic matrices and MC concentrations could constitute a good idea on that purpose. However, inherent difficulties related to MC hydrophobic properties, which led to the adsorption of this chemical onto many materials, made complicated the performance of this experimental work. A good alternative could be the use of kinetic models, like the ones based on the *Rct* concept (Elovitz and Von Gunten, 1999; Ning et al., 2007): the obtaining of this parameter for particular waters, together with the second-order rate constants provided in this study, should allow the prediction of MC removal and thus the estimation of the ozone dosage required for the complete depletion of this contaminant in real aqueous matrices (Elovitz and Von Gunten, 1999; Lee et al., 2013).

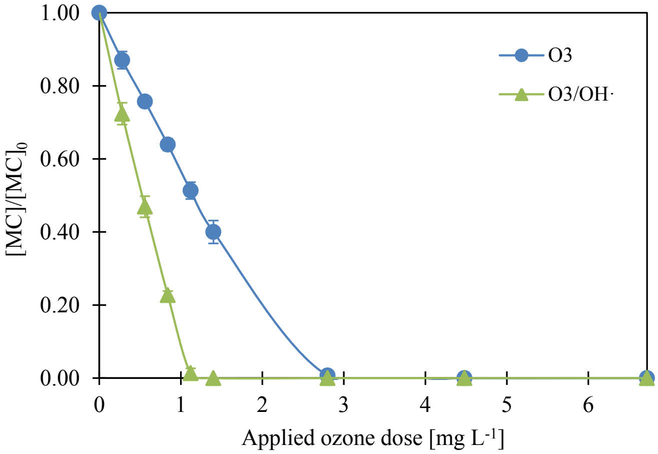


Fig. 1. Profile of MC degradation ($[MC]_0 = 20$ µM) as a function of the applied ozone dose, for experiments with (O_3) and without (O_3/OH·) radical scavenger.

After viewing the results obtained up to this point of the study, and without forgetting their limitations, what is clear is that ozonation could constitute a suitable treatment option regarding MC removal from water. Its high reactivity with O_3 and OH·, together with the significant contribution of hydroxyl radicals to its degradation at neutral pH, allows to suggest that this contaminant could be totally removed during ozonation stages. However, and because of mineralization capability of ozonation is low, it was necessary to explore other basic aspects of the process like the generation of reaction intermediates and the associated toxicity changes.

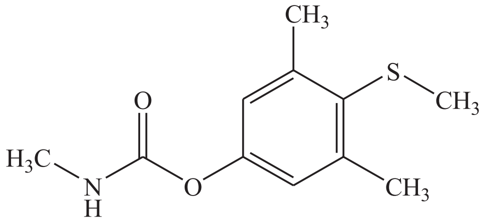
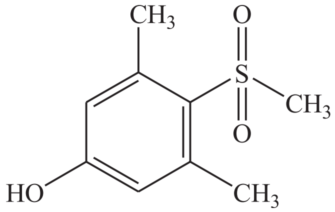
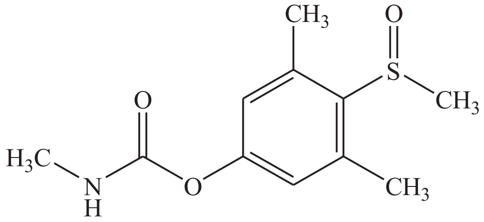
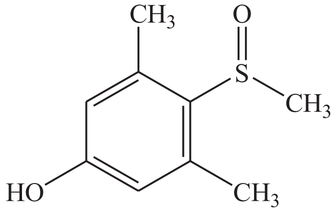
3.4. Reaction intermediates and possible mechanisms

The identification of relevant TPs generated during MC ozonation, with or without the presence of a radical scavenger was performed by means of HPLC-MS. The same signals were observed in both processes, leading this fact to the idea that all the identified TPs could have been formed simultaneously through the two possible ozonation degradative routes. An example of chromatogram illustrating the appearance of TPs signals can be found in Fig. S2 (supplementary information).

The proposed molecular structures of peaks for which the identification procedure was successful are gathered in Table 2. The observed differences between them were two: the relative degree of oxidation presented by the original thioether moiety, on one hand, and the loss of the carbamate group caused by hydrolysis of TP's, on the other. Both reactions are possible, well-known, and indeed have been considered in several papers regarding the environmental fate and degradation of MC by other oxidants (Qiang et al., 2014; Tian et al., 2013, 2010; UNFAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization), 1999). In the case of O_3 and OH· attack to thioether groups, the mechanisms are reported in studies concerning the degradation of organic compounds containing this moiety (Jeon et al., 2016; Jin et al., 2012; Szabó et al., 2015). By this way, methiocarb sulfoxide (MCX), methiocarb sulfoxide phenol (MCXP), and methiocarb sulfone phenol (MCNP) were identified as the major TPs formed during MC ozonation process. The generation of these species, as well as the formation of other byproducts like methiocarb sulfone (MCN) and methiocarb phenol (MCP) (not observed in this work), are reported in previous studies regarding MC oxidation by chlorine dioxide (Tian et al., 2010), free chlorine (Tian et al., 2013) and monochloramine (Qiang et al., 2014).

Fig. 2 shows the semi-quantitative evolution of MC and its major formed TPs during ozonation process, as a function of the applied ozone dose. Since non-reference standards were available for all

Table 2
Detected TPs and corresponding structures.

m/z	Name	Proposed structure
226 (m+1)	Methiocarb (MC)	
201 (m+1)	Methiocarb sulfone phenol (MCNP)	
242 (m+1)	Methiocarb sulfoxide (MCX)	
185 (m+1)	Methiocarb sulfoxide phenol (MCXP)	

the species, the graphs provide the relative variation of the TPs presence in the reaction medium, but not the evolution of their absolute concentrations. As early commented, the major formed byproducts were the same ones in the process only involving the direct attack of ozone (Fig. 2 A) than in the process that involved the attack of both, molecular ozone and hydroxyl radicals (Fig. 2 B). Besides, the evolution profiles as a function of the applied ozone dose presented shape similarities, being the main difference related to the relative efficiency of each degradative process in terms of required oxidant dosage: since the removal of MC for the process only involving the attack of molecular ozone needed larger oxidant doses than for the process in which both ozone and hydroxyl radicals participated, the generation and subsequent destruction of the TPs also required larger ozone doses in the first case than in the second. Another key difference was the relative residual signal of these products at each experimental point, always significantly lower when the radical route played its role. Without the presence of *tert*-butanol, formed hydroxyl radicals were supposed to oxidize part of the remaining MC and TPs, thereby contributing to their global depletion. Since these organic species are generally more reactive to hydroxyl radicals than molecular ozone, that contributed to an enhanced efficiency of the degradative process.

Taking into account the observed TPs and their semi-quantitative evolution with the ozone dosage, the sequential pathway shown in Fig. 3 was proposed for MC ozonation. It has to be cleared that this mechanism attempted to explain what seems to constitute the first steps of the degradation pathway followed by the pesticide during the process, considering that further oxidation products were not possible to be identified. MC oxidation by ozone or hydroxyl radicals firstly occurred at the thioether moiety. Additionally, and due to its demonstrated potential to undergo hydrolysis in water at pH values up to 6.5 (Qiang et al., 2014; Tian et al., 2013), the carbamate group was prone to disintegration generating MCXP as side-product. Then, the concentrations of MCX and MCXP increased by means of these mechanisms until MC was totally depleted. In the view of the profiles presented in Fig. 2, it seems like MCX and MCXP signals decreased at different rates from this moment, being the disappearance of MCXP slightly faster than the one for MCX. It is possible that MCXP was easier to oxidize than MCX, as happened in the study employing monochloramine as oxidant (Qiang et al., 2014). Finally, higher ozone doses allowed further oxidation of MCXP, leading to MCNP generation.

It is known that as a carbamate pesticide, the specific action of MC against pests is based on the inhibition of the vital enzyme cholinesterase by its carbamate group (Padilla et al., 2007). Because of that, MCNX and MCNP probably did not maintain their activity as pesticides after losing their carbamate moiety, which did not mean that these species were non-toxic. Following the same reasoning, MCX probably kept its activity as pesticide, since its carbamate moiety remained unaltered. Because this TP is more toxic than the parent compound (Marss, 1998), the observed increase in toxicity could be attributable to the only difference between both molecular structures: the sulfoxide moiety of MCX, in contrast with the sulfur group presented by MC.

3.5. *Toxicity during MC ozonation process as a function of the applied ozone dose*

The chemical alterations produced during the ozonation-hydrolysis process implied changes in the properties of the resulting species, including toxicity. The variation of *1/EC$_{50}$* versus the applied ozone dose is presented in Fig. 4. This parameter provides a direct idea about the ecotoxicity of the solution, since higher values imply a higher inhibition in bacteria bioluminescence. Initial toxicity for both experiments was relatively high (*EC$_{50}$* about 4.5%), which is not surprising considering that MC had already demonstrated to be highly toxic (Marss, 1998; World Health Organization, 2010). For the untreated solution, the corresponding *EC$_{50}$* value expressed in concentration units could be also calculated, since the composition of this sample was known. With an *EC$_{50}$* of 0.2 mg L^{-1}, and according to the toxicity classification stablished in Directive 93/67/EEC (very toxic to aquatic organisms (0.1–1 mg L^{-1}), toxic (1–10 mg L^{-1}), harmful (10–100 mg L^{-1}), non-toxic (>100 mg L^{-1})) (European Commission Joint Research Centre, 2003), MC would be considered as very toxic to aquatic organisms, which would confirm again the previous knowledge about MC ecotoxicity. For the rest of experimental points, only the *EC$_{50}$* in terms of sample dilution (% v/v) could be provided since the corresponding samples compositions were unknown.

For experiments in the presence of *tert*-butanol, solution toxicity increased to a maximum (*EC$_{50}$* about 1.5%) for applied O$_3$ concentrations about 3.5–4 mg L^{-1}, and decreased for higher dosages. However, this decrement was not significant and for larger ozone doses the acute toxicity was even higher (*EC$_{50}$* about 2%) than that for the untreated solution. For experiments without the presence of radical scavenger, a small increase in toxicity (*EC$_{50}$* about 4%) was observed at O$_3$ doses about 0.5–1 mg L^{-1}, followed by a significant drop of this parameter: for ozone doses about 7 mg L^{-1}, *EC$_{50}$* value was about 95%, which represented a relatively low toxicity.

Changes in toxicity observed in both experiments can be attributed to the generation of TPs more toxic than the parent compound, as concluded in many other related studies (Borowska et al., 2016; Dantas et al., 2008, 2007). In the current case, reaction intermediate MCX is the main suspect of increasing toxicity, since is known to be about 2–3 times more toxic than MC based on oral *LD$_{50}$* values in rats (Marss, 1998). Also, other TPs like MCXP and MCNP, as well as hydrogen peroxide formed through ozone

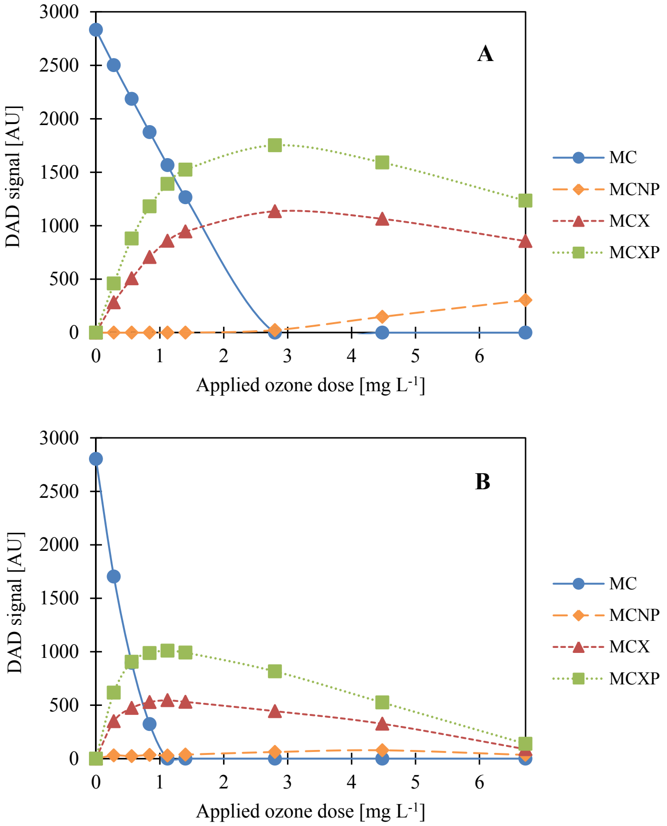


Fig. 2. Semi-quantitative monitoring of MC TPs generated during reaction of the pesticide (C$_0$ = 20 μM) with O$_3$ (A) and O$_3$/OH·(B), as a function of the applied ozone dose.

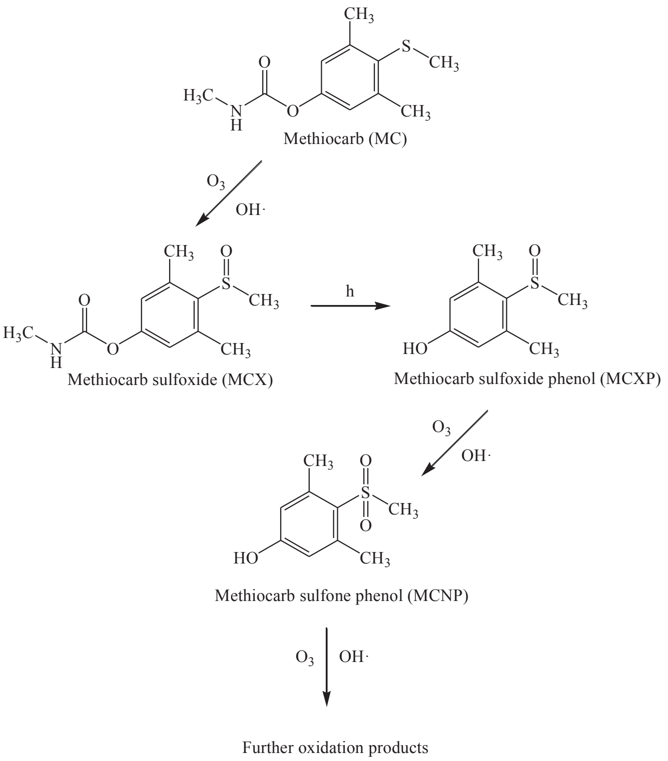


Fig. 3. Proposed reaction mechanism for MC attack by molecular ozone and formed hydroxyl radicals.

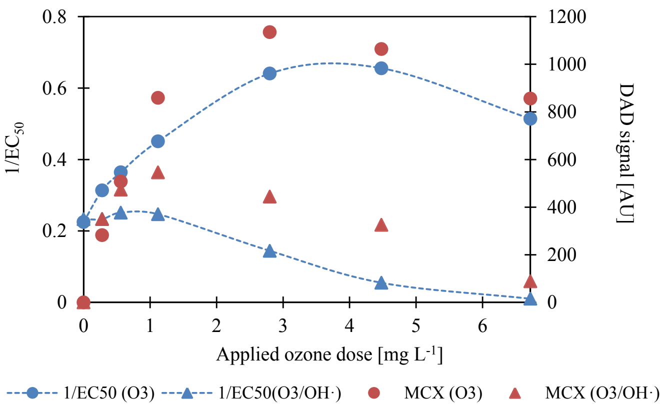


Fig. 4. Acute toxicity and remaining DAD signal of MCX, as a function of the applied ozone dose.

decomposition (Hoigné, 1982) could contribute to this increase in bacteria bioluminescence inhibition. Of course, it was not possible to exactly quantify the contribution of this species to the total toxicity of the solution, but by comparing the MCX and toxicity profiles, a correlation between both parameters appears to be suitable: in all experiments, the maximum $1/EC_{50}$ value is reached at approximately the O_3 dosage in which the maximum relative amount of MCX (DAD signal) is also observed. In addition, when the concentration of this intermediate starts to decrease, the toxicity of the solution also starts to diminish. Since toxicity changes appears to be mainly caused by variations of the MCX concentration, the rest of TPs generated during the process and contained in the analyzed samples should necessarily present similar or lower toxicity levels than MC. This fact would be in total agreement with the previous literature regarding this issue (Marss, 1998; Tian et al., 2013, 2010).

In the view of the last results, ozonation of MC contributed to increase the toxicity of the reaction medium when low oxidant doses were applied. The relative resistance of the formed TPs towards direct ozone attack caused a drop in the overall efficiency of the process, thus enlarging the oxidant dosage required to reach relatively low toxicities. Thus, a normalized ozone dose of approximately 2.5 mg O_3/mg DOC, which probably would be considered as economically non-reasonable (Gerrity et al., 2012; Lee et al., 2013), would be needed under the studied conditions. Since the attack of hydroxyl radicals during MC ozonation revealed to be essential if the removal of its toxic TPs (especially MCX) is wanted to be achieved, an enhancement of the indirect degradation route should be promoted. It is important to mention, however, that in waters with pH values up to 7 the indirect degradative route would be naturally favored, thus enlarging the process efficiency.

4. Conclusions

For the first time, the kinetics, pathways and toxicity changes associated to MC degradation during ozonation process at neutral pH were investigated. The second-order rate constants for reactions of MC with ozone and hydroxyl radicals were determined to be $1.7 \cdot 10^6$ and $8.2 \cdot 10^9$ M^{-1} s^{-1}, respectively. Both ozone and hydroxyl radicals showed to play an important role in the overall depletion of MC at neutral pH, thus indicating the potential of the ozonation process to remove MC from water. Specifically, the $OH\cdot$ attack highly contributed to increase the efficiency of the process by reducing to more than half the oxidant dose necessary to completely degrade MC. MCX, MCXP and MCNP were the major intermediates identified in the MC ozonation process. These byproducts were generated through a sequential combination of both O_3 and $OH\cdot$ oxidation and hydrolysis. The toxicity changes observed in MC ozonation were principally attributed to variations in the MCX concentration. Despite its demonstrated capacity to oxidize MC, direct ozone attack was unable to completely degrade MCX. Although the oxidation by $OH\cdot$ showed its ability to degrade MC and all its TPs, the resistance towards ozone attack exhibited by these compounds increased the oxidant dosage necessary to achieve a relative low toxicity in the medium. In order to overcome these problems and enhance the overall efficiency of the process, the indirect degradation route through hydroxyl radicals should be favored.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.08.040.

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Supplementary information for

Exploring ozonation as treatment alternative for methiocarb and formed transformation products abatement

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List of supplementary data:

Text S1. Preparation of ozone stock solutions

Ozone stock solutions were prepared by continuously bubbling 30 L/h of a gaseous ozone/oxygen mixture with an ozone concentration of 48 mg/L, coming from a 301.19 Sander Labor Ozonator (Germany), into a 1000 mL jacketed reactor containing Milli-Q water, to reach a dissolved ozone concentration of 14 mg L^{-1}. The O_3 concentration in aqueous phase was continuously monitored by means of a Q45H/64 ozone probe (Analytical technology, US) connected to a liquid recirculation stream. To avoid ozone loses, ozone stock solutions were withdrawn from the reactor and immediately kept in an ice bath. Figure S1 shows a scheme of the experimental setup.

Text S2. Determination of second-order rate constants for the reaction between MC and hydroxyl radicals

The removal of each compound (MC, SMX and PH) can be described by second-order kinetic equations involving ozone and hydroxyl radicals:

$$-\frac{d[MC]}{dt} = k_{MC,O3}[MC][O_3] + k_{MC,OH\cdot}[MC][OH\,\cdot] \tag{1}$$

$$-\frac{d[SMX]}{dt} = k_{SMX,O3}[SMX][O_3] + k_{SMX,OH\cdot}[SMX][OH\,\cdot] \tag{3}$$

$$-\frac{d[PH]}{dt} = k_{PH,O3}[PH][O_3] + k_{PH,OH\cdot}[PH][OH\,\cdot] \tag{4}$$

Dividing Eq. (1) by Eq. (2) and Eq. (3), the following two expressions are respectively obtained:

$$\frac{d[MC]}{d[SMX]} = \frac{k_{MC,O_3}[O_3][OH\,\cdot] + k_{MC,OH\cdot}[O_3][OH\,\cdot]}{k_{SMX,O_3}[O_3][OH\,\cdot] + k_{SMX,OH\cdot}[O_3][OH\,\cdot]} \tag{5}$$

$$\frac{d[MC]}{d[SMX]} = \frac{k_{MC,O_3}[O_3][OH\,\cdot] + k_{MC,OH\cdot}[O_3][OH\,\cdot]}{k_{SMX,O_3}[O_3][OH\,\cdot] + k_{SMX,OH\cdot}[O_3][OH\,\cdot]} \tag{6}$$

The *Rct* concept can be introduced into the previous equations. This parameter represents the ratio of OH· exposure over the O_3 exposure in a reaction medium subject to ozonation. Because of this relation is time-independent, it corresponds directly to the ratio *[OH·]/[O₃]*. Substitution of *Rct* into Eq. (5) and Eq. (6) yields:

$$\frac{d[MC]}{d[SMX]} = \frac{[MC](k_{MC,O_3} + k_{MC,OH^{\cdot}}.Rct)}{[SMX](k_{SMX,O_3} + k_{SMX,OH^{\cdot}}.Rct)} \tag{7}$$

$$\frac{d[MC]}{d[PH]} = \frac{[MC](k_{MC,O_3} + k_{MC,OH^{\cdot}}.Rct)}{[PH](k_{PH,O_3} + k_{PH,OH^{\cdot}}.Rct)} \tag{8}$$

Integration of Eq. (7) and Eq. (8) gives the following expressions:

$$ln\frac{[MC]}{[MC]_0} = \frac{(k_{MC,O_3} + k_{MC,OH^{\cdot}}.Rct)}{(k_{SMX,O_3} + k_{SMX,OH^{\cdot}}.Rct)} ln\frac{[SMX]}{[SMX]_0} \tag{9}$$

$$ln\frac{[MC]}{[MC]_0} = \frac{(k_{MC,O_3} + k_{MC,OH^{\cdot}}.Rct)}{(k_{PH,O_3} + k_{PH,OH^{\cdot}}.Rct)} ln\frac{[PH]}{[PH]_0} \tag{10}$$

From Eq. (9) and Eq. (10), it is deduced that plotting the natural logarithm reduction of MC versus the natural logarithm reduction of each one of the references, separately, allows obtaining two linear relations. The corresponding slopes can be expressed as follows:

$$A = \frac{(k_{MC,O_3} + k_{MC,OH^{\cdot}}.Rct)}{(k_{SMX,O_3} + k_{SMX,OH^{\cdot}}.Rct)} \tag{11}$$

$$B = \frac{(k_{MC,O_3} + k_{MC,OH^{\cdot}}.Rct)}{(k_{PH,O_3} + k_{PH,OH^{\cdot}}.Rct)} \tag{12}$$

Experimentally knowing the values of *A* and *B*, as well as the rest of the required second-order kinetic constant values, the system formed by Eq. (11) and Eq. (12) can be solved in order to determine $k_{MCOH^{\cdot}}$ and *Rct*.

Figure S1. Ozonation system

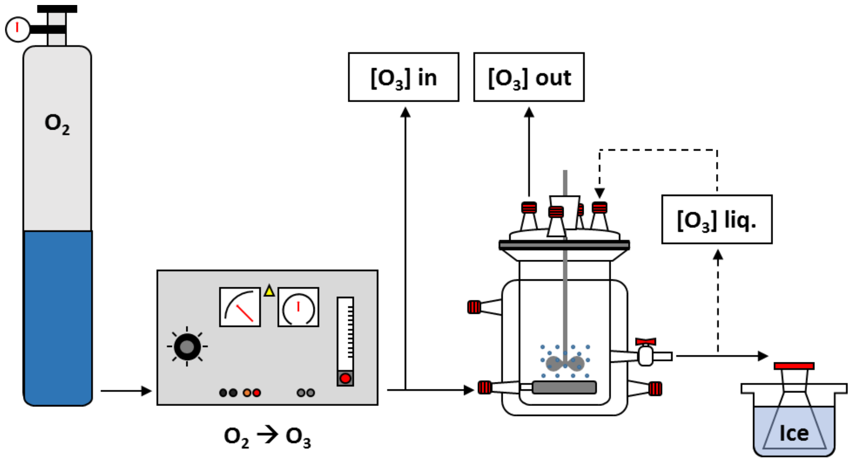
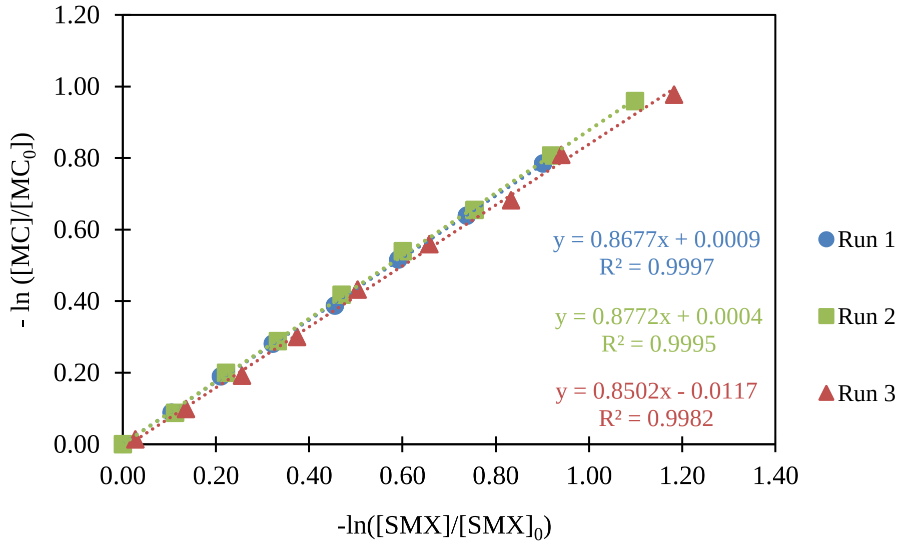
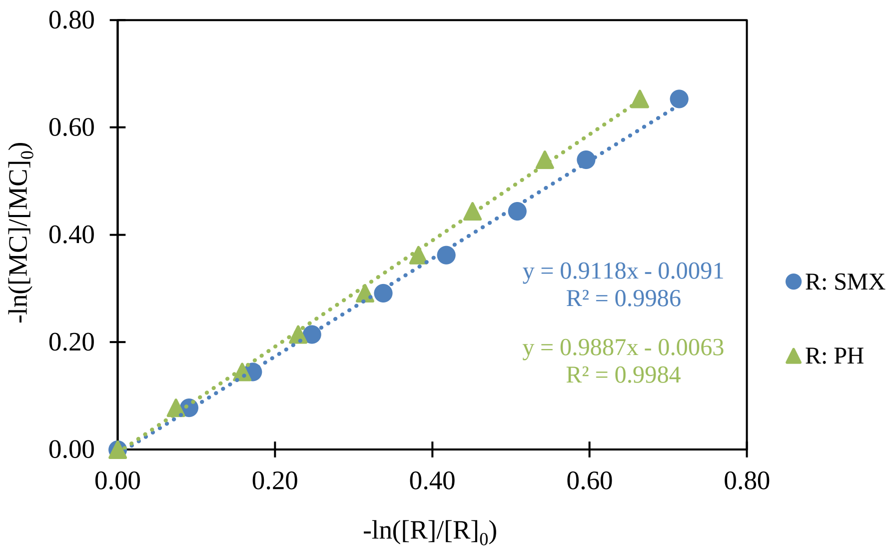


Figure S2. Determination of $k_{MC,O3}$ by competition kinetics



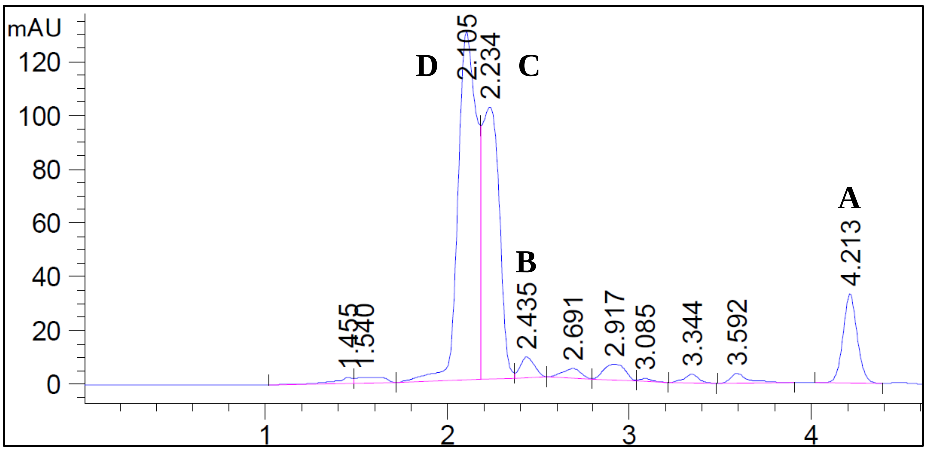
Determination of $k_{MC,O3}$ by competition kinetics: -ln([MC]/[MC]$_0$) versus -ln([SMX]/[SMX]$_0$) for the simultaneous reaction of ozone with MC and SMX ([MC]$_0$=[SMX]$_0$=20 µM), at pH 7.

Figure S3. Determination of $k_{MC,OH}$ by competition kinetics



Determination of $k_{MC,O3}$ by competition kinetics: -ln([MC]/[MC]$_0$) versus -ln([R]/[R]$_0$) for the simultaneous reaction of ozone with MC and the references (R) SMX and PH ([MC]$_0$=[SMX]$_0$=[PH]$_0$=20 µM), at pH 7. The plots correspond to one of the three experimental runs that were performed.

Figure S4. Chromatogram showing the appearance of MC intermediates signals



Initial concentration of MC: 5 mg L^{-1}; pH 7; Applied ozone dose: 2 mg L^{-1}; without radical scavenger addition. The peaks whose identification was possible are named by capital letters. A: MC; B: MCNP, C: MCX and D: MCXP.

Table S1. Chromatographic conditions for MC, SMX and PH separation and quantification.

Compound	Mobile phase	Flow rate [mLmin^{-1}]	Wavelength of detection [nm]
MC	60:40 (ACN:H2O)	1.4	225
SMX	40:60 (ACN:H2O)	1.0	270
PH	50:50 (MeOH: H2O)	0.8	270

Appendix II

Priority pesticides abatement by advanced water technologies: The case of acetamiprid removal by ozonation

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Priority pesticides abatement by advanced water technologies: The case of acetamiprid removal by ozonation

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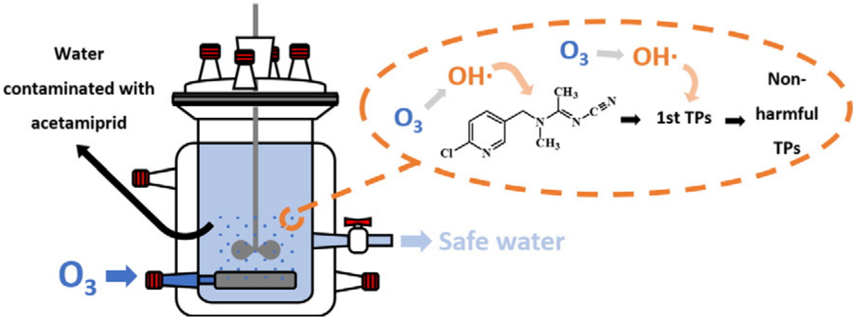
HIGHLIGHTS

- Acetamiprid is highly resistant to direct molecular ozone attack.
- Reaction between acetamiprid and hydroxyl radicals exhibits fast kinetics.
- α-aminoalkyl moieties are the main reaction sites for OH•-mediated oxidation.
- Oxidation through OH• guarantees ACMP, TPs and associated toxicity abatement.

GRAPHICAL ABSTRACT



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ABSTRACT

With the aim of exploring treatment alternatives for priority insecticide acetamiprid (ACMP) abatement, the removal of this compound from water by ozonation was studied for the first time, paying special attention to the kinetic, mechanistic and toxicological aspects of the process. The second order rate constants of reactions between ACMP and both molecular ozone (O_3) and hydroxyl radicals (OH•) were determined to be $0.25\ M^{-1}\ s^{-1}$ and $2.1 \cdot 10^9\ M^{-1}\ s^{-1}$, respectively. On the basis of kinetic results, the degradation of ACMP during ozonation could be well-explained by the reactivity of this pesticide with OH•. HPLC/MS analysis of the ozonated ACMP showed ACMP-*N*-desmethyl, 6-chloronicotinic acid, *N′*cyano-*N*-methyl acetamidine and *N′*-cyano acetamidine as the major transformation products (TPs), all of them formed through amine α carbon oxidation in combination with hydrolysis. Microtox bioassays revealed an increase in the toxicity of the medium during ACMP ozonation process, followed by a decrease to relatively low values. These changes could be attributed to the synergistic effects between TPs as well as to the presence of toxic intermediate aldehydes. Even though adopting strategies to further promote ozone decomposition to hydroxyl radicals appears to be essential, ozonation can be an effective treatment process for ACMP removal and associated toxicity abatement.

1. Introduction

Since 2013 some regulations regarding the identification, monitoring and control of priority substances/groups of substances in aquatic compartments have been published (Barbosa et al., 2016; Ribeiro et al., 2015). For example, the 1st watch list of substances for Union-wide monitoring, Decision 2015/495/EU (The European Commission, Decision 2015/495/EU, 2015), promotes the study of alternative water and wastewater treatment options aimed to remove these substances from aqueous resources. Several pesticides belonging to different families are included as priority pollutants. One of these groups, neonicotinoids, are nowadays one of the most employed class of

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0048-9697/

pesticides (Cimino et al., 2016). They offer insect selectivity, excellent physicochemical properties, wide spectrum of efficacy and a relative safe use in comparison with other pesticide classes like organophosphorus, carbamates or pyrethroids (Simon-Delso et al., 2015a; Jeschke et al., 2011). The widespread use of these chemicals has resulted in their occurrence in all environment compartments, including water (Simon-Delso et al., 2015a). According to previous studies, the presence of neonicotinoids in nature could be harmful to a broad range of invertebrate (Pisa et al., 2015) and also vertebrate (Gibbons et al., 2015) non-target organisms. Regarding the risks for human health, several recent studies have associated the chronic exposure to neonicotinoids with certain types of developmental disorders like congenital heart defects (CHD) (Carmichael et al., 2014), neural tube defects (NTD) (Yang et al., 2014) and autism spectrum disorder (ASD) (Keil et al., 2014).

(*E*)-N-(6-chloro-3-pyridylmethyl)-*N*′-cyano-*N*-methylacetamidine, better known as acetamiprid (ACMP) is a pesticide belonging to neonicotinoid insecticides class. It is one of the most applied insecticides nowadays, being the fourth most employed neonicotinoid in USA (Cimino et al., 2016) and representing more than a 10% of the total sales of this group of insecticides in the last years (Simon-Delso et al., 2015b). China, one of the largest ACMP producers, had in 2013 a production of 8000 tons of this insecticide, 5000 of which were exported (Shao et al., 2013). Because of its extensive usage, this micropollutant has been detected in surface (20–380 ng L^{-1} (Sánchez-Bayo & Hyne, 2014); 2.7–59.3 ng L^{-1} (Struger et al., 2017); 2–410 ng L^{-1} (Kreuger et al., 2010); up to 41 μg L^{-1} (Anderson et al., 2013)) and also wastewater (50 ng L^{-1} (Bernabeu et al., 2011)) samples worldwide. The presence of ACMP in the environment can pose risks to human health. Based on a previous work by Kimura-Kuroda (Kimura-Kuroda et al., 2012), the European Food Safety Authority (EFSA) recently delivered a Scientific Opinion concluding that chronic exposure to ACMP could affect neural development and function in humans (EFSA J., 2013). A more recent study associated the chronic exposure to this insecticide with some adverse effects on human health, including memory loss and finger tremors (Marfo et al., 2015). Moreover, ACMP has been demonstrated to negatively affect other species like aquatic (Li et al., 2010) and soil (Yao et al., 2006) microorganisms, as well as beneficial insects (Iwasa et al., 2004; El Hassani et al., 2008). However, despite its presence in water compartments pose a serious threat to environmental and human safety, scientific literature regarding the removal of ACMP by means of non-conventional treatment technologies is still incomplete (Barbosa et al., 2016). Regarding the use of Advanced Oxidation Processes (AOPs) for this purpose, some studies concerning the application of Fenton-based treatments (Carra et al., 2015; Mitsika et al., 2013), heterogeneous photocatalysis (Fenoll et al., 2015; Guzsvány et al., 2012) and other related technologies like the innovative low temperature plasma (Li et al., 2014) have been published in the last few years, all of them demonstrating their potential for efficiently remove ACMP from different water matrices. However, no reports concerning the employment of ozone for ACMP abatement have been found.

Ozone-based processes have demonstrated to have great potential for micropollutants removal from water (Acero et al., 2000; Borowska et al., 2016; Dantas et al., 2007; Dantas et al., 2008; Huber et al., 2003; Zhao et al., 2017). This technology is based on the strong oxidizing capacity of ozone (O_3), which also yields hydroxyl radicals (OH•) during ozone decay (Gligorovski et al., 2015). Although ozone and hydroxyl radicals can be effective in removing pollutants, transformation products (TPs) which may also be toxic can be formed during ozonation. It is important, therefore, to possess full knowledge of this process by studying reaction kinetics, transformation products, and residual toxicity of the treated water.

The present work aimed, for the first time, to go in-depth with the fundamentals (i.e., reaction kinetics, transformation products and associated toxicity evolution) of ACMP ozonation process. The objective was to determine the reaction kinetics of this pesticide when reacting with both, molecular ozone and formed hydroxyl radicals, as well as to elucidate the possible reaction pathways and potential negative effects of the resulting transformation products from ACMP degradation.

2. Materials and methods

2.1. Chemicals and reagents

Acetamiprid and *p*-chlorobenzoic acid analytical standards, as well as potassium indigotrisulfonate, were acquired from Sigma-Aldrich (Germany). Na_2HPO_4, NaH_2PO_4, H_3PO_4 and acetonitrile were purchased from Panreac (Spain), and were all analytical grade. Milli-Q water was produced by a filtration system (Millipore, USA). Pure oxygen (≥ 99.999%) was supplied by Abelló Linde (Spain).

In order to control the effects of side mechanisms like hydrolysis, adsorption or UV–Vis photolysis on ACMP disappearance during ozonation experiments, several control assays were performed. All runs were carried out in 250 mL closed glass beakers, with initial ACMP concentrations of 1 mg L^{-1}. For hydrolysis and adsorption experiments, the beaker was covered with aluminum foil in order to avoid the possible influence of ambient radiation. The pH in hydrolysis tests was adjusted to a value of 2 or 7 by adding adequate quantities of H_3PO_4 and Na_2HPO_4. For adsorption experiments, several plastic materials (different types of silicones, PVDF and PTFE) usually employed in laboratory were put in contact with the pesticide solution. In all experiments, the medium was under stirring conditions. Samples were withdrawn at 0, 1, 5 and 24 h, and analyzed by HPLC-DAD. Results showed that ACMP remained stable prior to oxidant addition.

2.2. Ozonation experiments

All experiments in this work were performed by mixing aqueous ozone stock solutions with aqueous stock solutions of ACMP. Ozone stock solutions (10–12 mg L^{-1}) were prepared in a 1000 mL jacketed reactor by continuously bubbling a gaseous ozone/oxygen mixture (~ 48 mg L^{-1}) into Milli-Q water at a rate of 40 L/h, using a 301.19 Sander Labor Ozonator (Germany). The medium was maintained at a temperature of 10 ± 1 °C. The O_3 concentration in aqueous phase was continuously monitored by means of a Q45H/64 ozone probe (Analytical technology, US) connected to a liquid recirculation stream. All kinetic and degradation experiments were performed in triplicate, at a controlled temperature of 20 ± 2 °C.

The second-order rate constant for the reaction between ACMP and molecular ozone was directly determined under pseudo-first order conditions (David Yao & Haag, 1991), with a 50-fold molar excess of ozone with respect to the target compound. In order to avoid the presence of hydroxyl radicals in the system, the reaction medium was adjusted to pH 2 by adding adequate quantities of H_3PO_4 and Na_2HPO_4 (Ning et al., 2007a). Experiments were performed in a closed 250 mL bottle, in which the headspace was almost removed in order to avoid aqueous ozone losses. ACMP and ozone stock solutions were mixed to reach initial reactant concentrations of 4 and 200 μM, respectively, and the medium was stirred for 10 s to obtain homogeneous conditions. Aliquots of 0.5 mL were withdrawn at prefixed reaction times, and immediately quenched with 2.5 mL of an indigo solution. These samples were finally employed to determine the dissolved ozone concentration (Bader & Hoigné, 1981), as well as to quantify the remaining concentration of ACMP by HPLC-DAD.

Due to the fast reaction rates expected for the reaction between ACMP and indirectly formed hydroxyl radicals, competition kinetics method (Acero et al., 2000; Huber et al., 2003) must be employed in order to determine the corresponding second-order rate constant. The selected reference was *p*-chlorobenzoic acid (pCBA), since the reactivity of this chemical with molecular ozone is very low (≤0.15 M^{-1} s^{-1}, (David Yao & Haag, 1991)), whereas its reaction with hydroxyl radicals is fast ($5 \cdot 10^9$ M^{-1} s^{-1}, (Neta, 1968)). In order to guarantee the proper generation of OH• while maintaining a relative stability of aqueous ozone, experiments were performed at pH 7 by adding adequate quantities of a $H_2PO_4^-/HPO_4^{2-}$ buffer (1 mM). Reactions were conducted employing a multi-reactor system, successfully used in several previous works (Borowska et al., 2016; Ning et al., 2007b): in a series of 25 mL vials containing 4 μM of ACMP and 4 μM of pCBA, different doses (from 5 to 35 μM) of the ozone stock solution were injected and mixed. Samples were taken when the total consumption of ozone was achieved (all within 2 h). The residual concentrations of ACMP and pCBA were determined by HPLC-DAD.

With the aim of demonstrating the relative contribution of each oxidant involved in ozonation (i.e., molecular ozone and hydroxyl radicals) to ACMP degradation, two additional sets of experiments were performed. Again, the multi-reactor methodology was used. For direct reaction with ozone, each reaction vial (total volume of 25 mL) contained 10 μM of ACMP and 25 mM of *tert*-butanol as radical scavenger. The pH of the solution was adjusted to 7 by adding adequate quantities of a phosphate buffer (1 mM). For reaction involving both, the attack of ozone and hydroxyl radicals, a similar procedure was followed but no scavenger was employed. In all experiments, ozone doses between 5 and 175 μM were injected to each vial. Samples were withdrawn when the total consumption of ozone was achieved (all within 2 h). Once the residual concentration of ACMP was chromatographically determined, the corresponding samples were frozen and later employed for TPs and toxicity determinations.

2.3. Analytical procedures

The concentrations of ACMP and pCBA were quantified by means of a high performance liquid chromatograph (HPLC) equipped with a diode array detector (DAD), all supplied by Agilent (1260 Infinity). The column employed was a Teknokroma Mediterranea Sea18 (250 mm × 4.6 mm and 5 μm size packing). For ACMP analysis, the mobile phase consisted on a 30:70 volumetric mixture of acetonitrile and Milli-Q water acidified at pH 3 by the addition of H_3PO_4. The flow rate was maintained at 1.4 mL min^{-1}, and the detection wavelength was set to 250 nm. For pCBA quantification, the mobile phase consisted on a 50:50 volumetric mixture of acetonitrile and pH 3 Milli-Q water. The flow rate was set to 1 mL min^{-1} and the UV detection was performed at 236 nm. The limits of detection (LODs) for ACMP and pCBA were 0.018 and 0.029 μM, respectively.

With the aim of elucidating the ACMP degradation pathways given in ozonation process, samples in which different ozone doses were applied were analyzed by Liquid Chromatography-Mass Spectrometry (LC-MS). An Agilent 1100 HPLC coupled with a G1969A LC/MSD-TOF mass spectrometer was employed. MS data were collected in full scan mode (25–1100 *m*/*z*), employing positive electrospray ionization. The separation of chemical species was achieved by operating with the following elution program: a 5:95 volumetric mixture of ACN and Milli-Q (pH 3) was maintained as initial mobile phase for 5 min; then, a linear gradient changed the eluent composition from 5:95 to 30:70 in 5 min; the 30:70 mixture was maintained during the next 10 min and, finally, a linear gradient returned back the eluent initial composition (5:95) in 5 min.

In order to assess the toxicity changes along the ACMP ozonation process, Microtox® bioassays were performed. This method measures the inhibition of light emission of bioluminescent bacteria *Vibrio fischeri* caused by the presence, in aqueous media, of toxic compounds. The results of this assay are usually expressed as $EC_{50,15min}$, which represents the percentage of sample dilution (% v/v) that causes a 50% reduction in bacteria luminescence after 15 min of exposure. All the tests were carried out in duplicate in a Microtox® M500 (Modern Water, UK) toxicity analyzer.

3. Results and discussion

3.1. Kinetics of ACMP reactions with ozone and hydroxyl radicals

Under the experimental conditions employed in these assays (i.e. pH 2), the half-life of molecular ozone in pure aqueous solutions was observed to be >6 h, thus evidencing that no radical chain reaction occurred. It was assumed, therefore, that molecular ozone was the only oxidant in the reaction medium. Thus, the second-order rate constant for the reaction between ACMP and O_3 could be calculated from Eq. 1, being obtained by integrating the corresponding kinetic equation.

$$-\ln\left(\frac{[ACMP]}{[ACMP]_0}\right) = k_{MC,O_3}\int_0^t [O_3]dt \qquad (1)$$

By plotting the natural logarithm of the relative residual concentration of ACMP against the ozone exposure, $\int[O_3]dt$, a linear relation was obtained. The slope of the function corresponds to the second-order kinetic constant for the reaction between ACMP and molecular ozone. Fig. 1 shows the relative concentration of ACMP and ozone during the experiment (A), as well as the logarithmic relative concentration of ACMP as a function of $\int[O_3]dt$ (B). The ozone exposure was determined by calculating the area under the ozone decay curve, employing the trapezoidal method of numerical integration. $k_{ACMP\text{-}O3}$ was determined to be 0.25 ± 0.02 M^{-1} s^{-1}.

In the view of the above results it is clear that reactivity of ACMP towards direct ozone attack is very low, as expected from preliminary experiments. It is important to note that the determined value corresponds to ACMP deprotonated form, since the pKa value of this pesticide is 0.7 (EPA, 2002). Therefore, the rate constant value should remain unaltered for higher pH values, including the ones exhibited by most water and wastewater real matrices.

Since the reactivity of ACMP and pCBA with molecular ozone is very low, and reactions between these chemicals and OH• were expected to be fast, it was assumed that depletion of both compounds under the employed experimental conditions (pH = 7) was only due to OH• attack. Therefore, the second-order rate constant for the reaction between

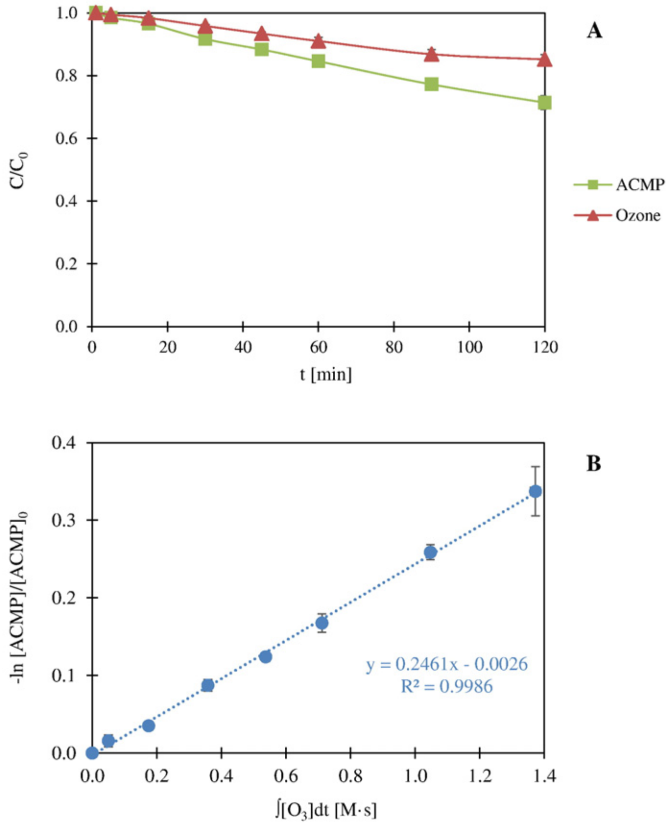


Fig. 1. Determination of second-order rate constant ($k_{ACMP\text{-}O3}$) for the reaction of ACMP and ozone. A) Relative concentration of ACMP and ozone vs reaction time. B) Natural logarithm of the relative concentration of ACMP vs ozone exposure. Conditions: $[ACMP]_0 = 4$ μM, $[O_3]_0 = 200$ μM, pH 2, temperature = 20 ± 2 °C.

ACMP and OH• could be calculated from Eq. 2, being obtained by dividing the kinetic equations corresponding to reactions between OH• and both ACMP and pCBA.

$$-\ln\left(\frac{[ACMP]}{[ACMP]_0}\right)=\frac{k_{ACMP,OH\cdot}}{k_{pCBA,OH\cdot}}\left(-\ln\left(\frac{[pCBA]}{[pCBA]_0}\right)\right) \qquad (2)$$

According to the above expression, a linear dependence between the natural logarithm of the relative ACMP concentration and the natural logarithm of the relative pCBA concentration was expected. The slope of this relationship represents the ratio between the second-order rate constants of OH• with target (ACMP) and reference (pCBA) compound, respectively. Fig. 2 shows the relative concentration of both ACMP and pCBA as a function of the ozone dose (A), as well as the natural logarithm of ACMP relative concentration as a function of the natural logarithm of the relative pCBA concentration (B). A value of $(2.1 \pm 0.1)\cdot 10^9\ M^{-1}\ s^{-1}$ was finally determined for $k_{ACMP,\ OH\cdot}$. The high reactivity of ACMP with hydroxyl radicals is explained by the non-selective character of the oxidant (Gligorovski et al., 2015) which readily undergo reactions with different points of organic molecules.

3.2. ACMP degradation by ozone and hydroxyl radicals

It is well known that during ozonation, a compound can directly react with molecular ozone but also with hydroxyl radicals formed through O_3 decomposition (Gligorovski et al., 2015). With the aim of observing and comparing the removal of ACMP by both possible transformation routes, degradation experiments were conducted at pH 7 with and without the presence of a radical scavenger. Results are shown in Fig. 3. Degradation by means of the direct reaction barely occurred, which was not surprising considering the extremely low rates exhibited by the reaction between ACMP and O_3 during the preceding kinetic runs. Besides, under the employed neutral pH conditions, ozone self-decomposition becomes relevant and therefore the stability of this oxidant in the medium is reduced with respect to more acidic conditions. For its part, indirect transformation trough hydroxyl radicals demonstrated the effectiveness usually exhibited by this transient species in organics oxidation, and showed to be in total agreement with the findings of the previously mentioned studies dealing with the removal of ACMP by means of other AOPs (Carra et al., 2015; Fenoll et al., 2015). With an ozone dosage of approximately 5.50 mg L^{-1}, the complete removal of ACMP was achieved.

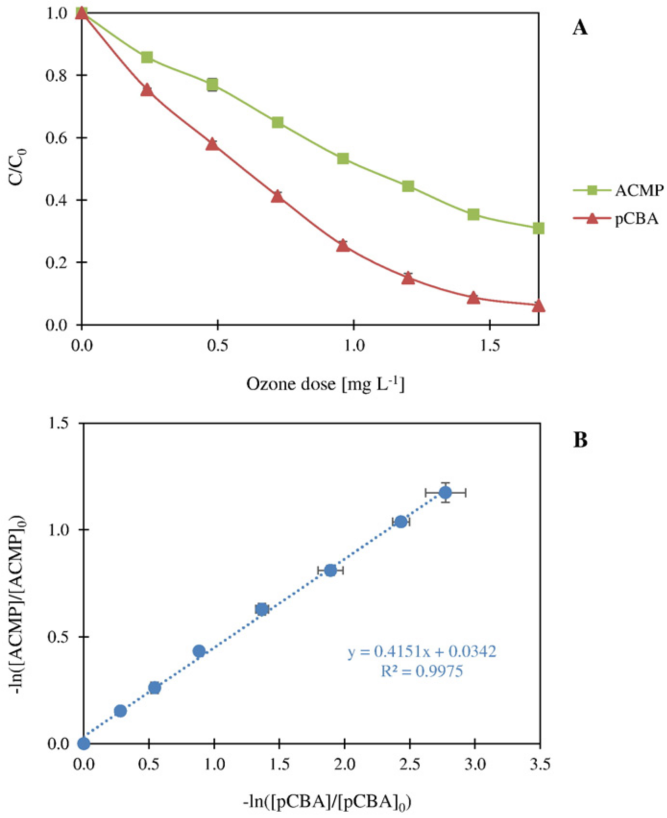


Fig. 2. Determination of second-order rate constant ($k_{ACMP,OH\cdot}$) for the reaction of ACMP and OH• by competition kinetics. A) Relative concentrations of ACMP and pCBA as a function of the ozone dose. B) Natural logarithm of ACMP relative concentration vs natural logarithm of pCBA relative concentration. Conditions: $[ACMP]_0 = [pCBA]_0 = 4\ \mu M$, pH 7, temperature = 20 ± 2 °C.

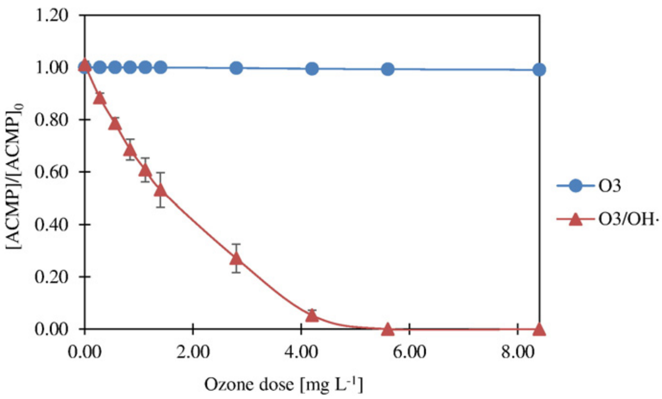


Fig. 3. Profile of ACMP degradation as a function of the ozone dose, for experiments with (O_3) and without (O_3/OH•) the presence of *tert*-butanol (25 mM). Conditions: $[ACMP]_0 = 10\ \mu M$, pH 7, temperature = 20 ± 2 °C.

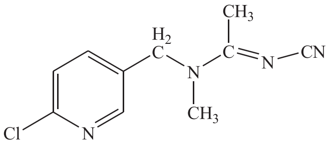
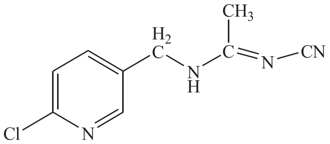
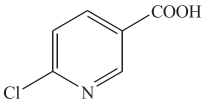
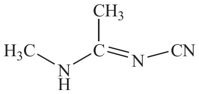
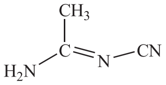
Considering the initial concentration of ACMP in degradation experiments, a normalized ozone dose of approximately 2.50 mg O_3/mg DOC (Dissolved Organic Carbon) was required to 100% eliminate ACMP under the studied conditions. This oxidant dosage, according to literature (Gerrity et al., 2012; Lee et al., 2013), would probably be considered expensive since doses up to 1 mg O_3/mg DOC are usually enough for disinfection and trace pollutant removal in drinking and wastewater treatment plants (Gerrity et al., 2012; Lee et al., 2013). Because of that reason, and considering that ozone decomposition to hydroxyl radicals is the key of ACMP removal by ozonation, strategies aimed to further promote this indirect route should be pursued to make the process a competitive treatment option for waters contaminated by this compound. It is important to note, however, that since the process performance would always depend on water characteristics, like pH or inorganic and organic matter type and concentrations, the application in real matrices should be properly evaluated in future studies. With that purpose, experiments with real water matrices and pesticide concentrations should be performed. Another good option would be the employment of kinetic models based on the use of water specific information and the rate constants determined in this study (Gerrity et al., 2012; Lee et al., 2013).

3.3. Reaction intermediates and possible mechanisms

The identification of major TPs generated during ACMP ozonation was performed by means of LC-MS, being the corresponding chemical structures proposed on the basis of the detected masses. Since ozone was shown to be ineffective degrading ACMP molecules, it could be stated that all the detected species were reaction intermediates corresponding to products of OH• reactions, that is, the indirect reaction pathway. The molecular structures of the TPs that were identified are shown in Table 1.

According to the detected structures and the experimental conditions employed in the study, the first stages of ACMP degradation during ozonation process could consist on a combination of OH• oxidation and fast hydrolysis of the metabolites generated during the first step, as

Table 1
ACMP, detected TPs and corresponding molecular structures.

m/z	Name	Proposed structure
223 (m + 1)	Acetamiprid (ACMP)	
209 (m + 1)	ACMP-209 Acetamiprid-*N*-desmethyl	
158 (m + 1)	ACMP-158 6-Chloronicotinic acid	
98 (m + 1)	ACMP-98 *N*′-cyano-*N*-methyl acetamidine	
84 (m + 1)	ACMP-84 *N*′-cyano acetamidine	

shown in Fig. 4. The brackets in some of the proposed intermediates indicate that these species could not be detected during the analysis, probably due to their low concentration or fast tendency to undergo hydrolysis or become oxidized.

The identification of ACMP-158, ACMP-98 and ACMP-84 suggests that the initial attack by hydroxyl radicals takes place at the methylene group (C α) of the ACMP amine. After the fast H-abstraction carried out by OH•, further oxidation of the α-aminoalkyl radical by molecular oxygen in the presence of OH^- yields the corresponding α-hydroxymethylamine (reaction **1**). This mechanism is similar to the one reported by Das et al. for trimethylamine OH•-induced oxidation (Das et al., 1987). The hydrolysis of the hydroxymethylamine (reaction **2**) would lead to the generation of *N*′-cyano-*N*-methyl acetamidine (ACMP-98) and 6-chloronicotinoid acid (ACMP-158). The latter, however, would require a previous step which should involve the generation of the corresponding aldehyde hydrate and its subsequent transformation to a carboxylic acid (reaction **3**), being the latter step caused by the oxidizing conditions of the medium (Dell'Arciprete et al., 2009). For its part, further attack to ACMP-98 by hydroxyl radicals in the presence of O_2 (reaction **4**) would result on the generation of its demethylated form, or *N*′-cyano acetamidine (ACMP-84), after the hydrolysis of the corresponding, previously formed hydroxymethylamine (reaction **5**). Instead of at the methylene group, the initial H-abstraction from ACMP structure can also take place at the methyl group of its amine moiety (also an alpha C) (reaction **7**). Hydrolysis of the resulting hydroxymethylamine (reaction **8**) would finally give ACMP-*N*-desmethyl (ACMP-209). It is interesting to mention that the hydrated form of formaldehyde would be yielded as a side product of ACMP-97 and ACMP-208 hydrolysis. Under the oxidizing conditions of the medium, this compound could eventually be transformed and yield carbonic acid as final product (reactions **6** and **9**).

The pesticide properties of ACMP are based on its nicotinoid structure, which mimics the vital neurotransmitter acetylcholine (ACh) by binding to the corresponding nicotinic acetylcholine receptor (*n*AChR) (Jeschke et al., 2011). Due to the fact that this specific neural pathway is more abundant in insects than in warm-blooded animals, ACMP and those of its family (i.e. neonicotinoids) are more toxic to insects than to mammals (Tomizawa & Casida, 2005). Since the presence of the nicotinoid structure appears to be fundamental to maintain this selectivity against pests, TPs ACMP-98 and ACMP-84 could have lost its ability to bind the insect *n*AChRs and thus their insecticide features, which did not necessarily mean that these side products were non-toxic. By the same argument, the intermediates ACMP-209 and ACMP-158 (i.e. acetamiprid-*N*-desmethyl and 6-chloronicotinic acid) could still maintain certain specificity in their pesticide action. However, in order to ensure a proper interaction with the *n*AChRs and therefore a high selective action against insects, it is also important for neonicotinoid species to possess an electronegative moiety on their molecule to bind to the unique, positive charged amino acid residue present in the nicotinic cholinergic receptor (Tomizawa & Casida, 2005; Shao et al., 2011). In relation with that, it has been found that nitro or cyano substituents could be the most adequate electron-withdrawing moieties to enhance the affinity between the pesticide and the receptor subsite (Tomizawa & Casida, 2005; Shao et al., 2011). Therefore, in the present case it is expected for 6-chloronicotinic acid to present less affinity with *n*AChRs and thus, an also less selective pesticide action than the exhibited by acetamiprid-*N*-desmethyl, which would still keep the original cyano group of ACMP.

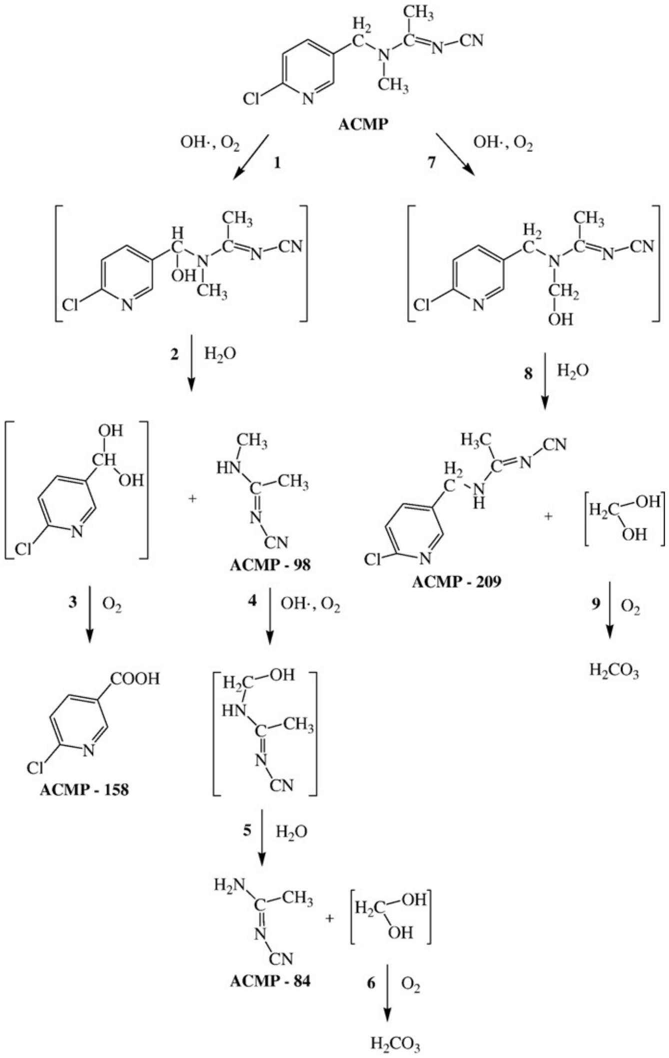


Fig. 4. Proposed reaction pathways for ACMP degradation by OH• during ozonation process.

3.4. Toxicity evolution during ACMP ozonation process

Due to the changes on the reaction medium composition, caused by the generation of new products and the degradation of parent compound, ACMP ozonation process also involved changes in the solution

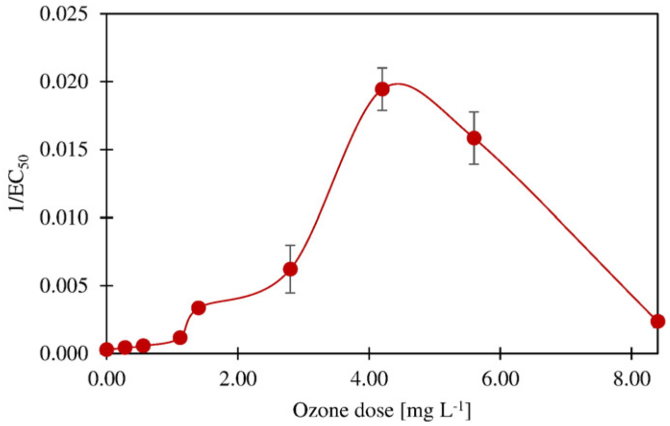


Fig. 5. Acute toxicity of the reaction medium during ACMP ozonation, as a function of the ozone dose.

toxicity. The evolution of this property is represented in Fig. 5 by the $1/EC_{50}$ value for *Vibrio fischeri* assays, as a function of the ozone dosage. It is important to remember that higher $1/EC_{50}$ values mean higher toxicities, and vice versa. Initial EC_{50} value, that is, the effective concentration that inhibits a 50% of the bacteria light emission, was determined to be 86 mg L^{-1} (about 40 times the initial concentration, in terms of sample dilution), which clearly represents a low toxicity to non-target species. This value is lower than the one reported by Dell'Arciprete et al. (129 mg L^{-1}), which was obtained by exposing bioluminescent bacteria to solutions with different concentrations of ACMP. For the rest of samples, only EC_{50} in terms of percentage of dilution (% v/v) could be determined since their compositions were unknown. The toxicity of the medium notably increased for ozone doses above 3 mg L^{-1}, reaching a maximum (EC_{50} 51.6%) for an O_3 dosage of approximately 4.50 mg L^{-1}. The application of larger ozone doses resulted on significant toxicity abatement, as observed in the $1/EC_{50}$ profile. A similar value than the starting one was practically achieved for an ozone dose about 8.5 mg L^{-1}.

In previous works regarding ACMP degradation by oxidation processes in which hydroxyl radicals and other ROS (Reactive Oxygen Species) were involved, an increase in the medium toxicity was observed after the treatment with respect to the untreated solution (Dell'Arciprete et al., 2009; Dell'Arciprete et al., 2010). The same happened in a previous research regarding the photocatalytic degradation of 6-chloronicotinic acid, one of the ACMP TPs detected in this work (ACMP-158) (Žabar et al., 2011). Although the results in this study agree with the previous related literature, a larger extent of the oxidation reaction in the present case with respect to the preceding researches also led to the degradation of the intermediate species that caused the observed increase in the medium toxicity.

The changes in toxicity observed during ACMP ozonation can be attributed, as in many other works (Dantas et al., 2007; Dantas et al., 2008; Žabar et al., 2011) to the generation of TPs more toxic than the parent compound, as well as to the possible synergistic effects between initial and newly formed species present in the reaction medium. Because of the relative loss in their pesticide selectivity, it would be reasonable to consider ACMP-158, ACMP-98 or ACMP-84 as the most suitable candidates leading to the bacteria bioluminescence inhibition, as *Vibrio fischeri* could be considered as a non-target species. ACMP-209, for its part, should still maintain a similar activity than the parent compound, and therefore a relative high specificity against insects. However, ACMP-158 (6-chloronicotinic acid) has been reported to be less toxic to *Vibrio fischeri* than ACMP itself (Dell'Arciprete et al., 2009), and no information regarding the response of this bioluminescent bacteria under ACMP-98 and ACMP-84 exposure has been found. Given the scarcity of data on that topic, it was not possible to attribute the increase in toxicity to the single presence of one of the detected TPs. In addition to the possible synergistic effects between all the present species, as earlier mentioned, it is possible that the observed changes were related to the presence of other toxic intermediates that could not be identified during the LC-MS analyses. In the preceding section it has been stated that aldehyde hydrate compounds (formaldehyde and 6-chloronicotinaldehyde hydrates) could be involved in the ACMP degradation pathway. Since these compounds are typically in equilibrium with their parent aldehydes, and the latter have already proven to be highly toxic to Microtox® bacteria (EC_{50} of 1.35 mg L^{-1} for formaldehyde versus 89 mg L^{-1} for ACMP determined in this study) (Zhao et al., 2017; Blum & Speece, 1991), that could constitute an alternative good explanation to the observed increase in toxicity.

Considering the Microtox results, it is clear that ozonation applied to waters contaminated by ACMP could cause an increase in the toxicity of the medium, at least within a certain range of ozone doses. Since the employment of this treatment will always pursue the complete depletion of the pesticide while ensuring the lowest possible toxicity in the treated water matrix, this could enlarge the necessary ozone dosage to prohibitive values, economically speaking. Moreover, because of ACMP is resistant to molecular ozone oxidation, the degradation through hydroxyl radicals will be the main removal mechanism of this priority pesticide during ozonation. Therefore, the water matrix characteristics will play a decisive role in the ACMP degradation efficiency. In addition to the conditions that naturally favor the ozone decomposition process to hydroxyl radicals, like neutral and alkaline pH conditions, strategies aimed to further promote the indirect pathway should be equally investigated and employed. This, of course, would be essential in order to enhance the degradation efficiency and consequently reducing the oxidant dose to be applied.

4. Conclusions

The kinetics, reaction pathways and toxicity evolution during ACMP ozonation process were explored for the first time. The second-order kinetic constant for the reactions of ACMP with molecular ozone and hydroxyl radicals were determined to be 0.25 M^{-1} s^{-1} and $2.1 \cdot 10^9$ M^{-1} s^{-1}, thus clearly indicating the resistance of the pesticide structure towards O_3 attack. This ozone-recalcitrance was confirmed through degradation experiments at neutral pH, in which the direct reaction was barely observed. Formed hydroxyl radicals showed to completely remove ACMP (initial concentration 10 μM) with an ozone dosage of 5.5 mg L^{-1}, while their major intermediate products needed higher doses. The proposed ACMP degradation pathways consisted of combinations of oxidation and hydrolysis steps, which would yield different TPs depending on the initial site in which the hydrogen abstraction by hydroxyl radicals took place. Toxicity of the reaction medium increased to reach a maximum, and then decreased to relatively low values. Since these changes could not be related to the single presence of some of the detected TPs, they were attributed to synergistic effects among different species as well as to the presence, although not identified, of intermediate aldehydes which even at very low concentrations, exhibited acute toxicity to bacteria. In the view of the obtained results, further promoting ozone decomposition to hydroxyl radicals appears to be necessary to achieve a complete ACMP and associated toxicity abatement while maintaining a reasonable efficiency.

Acknowledgements

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Appendix III

Priority pesticides dichlorvos removal from water by ozonation process: Reactivity, transformation products and associated toxicity

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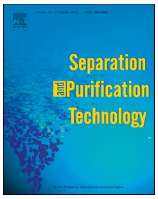

Priority pesticide dichlorvos removal from water by ozonation process: Reactivity, transformation products and associated toxicity

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ABSTRACT

The treatability of waters contaminated with priority pesticide dichlorvos (DDVP) by means of ozonation has been assessed for the first time. In order to do so, reaction kinetics, transformation mechanisms and associated toxicity have been inspected in detail. Second-order rate constants of DDVP reactions with O_3 and $OH^{\cdot}$ were determined to be 590 and $2.2{\cdot}10^9\ M^{-1}s^{-1}$, respectively. These values partly explained the degradation profiles obtained during experiments with and without the presence of an $OH^{\cdot}$ scavenger, in which the significant contribution of the indirect degradative route in the removal of DDVP was revealed. LC-MS analyses for ozonated samples allowed the elucidation of desmethyl dichlorvos (d-DDVP), dichloroacetic acid (DCA) and dimethyl phosphate (DMP) as main transformation products (TPs). DMP was found to be present in both O_3 and $OH^{\cdot}$-mediated oxidation pathways. Three possible degradation routes were proposed for $OH^{\cdot}$ degradation, whereas the direct oxidation by O_3 was only well-explained by the addition of this oxidant to the double bond of DDVP dichlorovinyl moiety. Microtox® bioassays revealed the inability of molecular ozone to reduce the toxicity of the medium and pointed out the importance of $OH^{\cdot}$ contribution in the degradation process. In general, ozonation could be a suitable treatment alternative for DDVP, formed TPs and associated toxicity abatement.

1. Introduction

Although discharge limits for micropollutants have not been legally stablished yet, some regulations regarding the identification, monitoring and control of some of these substances in the aquatic environment have been released over the last few years [1]. Directive 2013/39/EU, for instance, recommended attention to the monitoring of 45 compounds/groups of compounds considered as priority substances, giving special importance to the development and implementation of innovative remediation technologies aimed to remove these chemicals from water and wastewater [2].

About half (22/45) of the priority substances considered in the list are pesticides [2], fact that points out the special concern regarding the presence of this kind of pollutants in water compartments. Increases in cancer incidence, endocrine disruption, birth defects and genetic mutations are some of the chronic consequences to human health that have been directly linked to pesticide exposure [3]. Also, it is well-known that pesticides can pose a risk to other living species [4]. However, since the agricultural use of these chemicals is still necessary to ensure harvest quality and food protection, pesticides continuously enter aquatic resources mainly via runoff, soil leaching or spray drifting [5]. Moreover, and far of contributing to improve this problematic situation, most of these compounds are resistant to conventional water and wastewater treatments [6] thus increasing their environmental persistence and associated potential risks.

Dichlorvos (2,2-Dihclorovinyl dimethyl phosphate, DDVP) is a chlorinated organophosphorus pesticide. It has been traditionally employed as insecticide in agriculture, food storage areas, workplaces and homes [7], as well as to treat parasite infections in livestock and domestic animals [8]. As most organophosphorus insecticides, DDVP is highly toxic to humans: the acute exposure to this chemical can cause breathing problems, coma or even death [9]. Chronic exposure to DDVP has been related to increased risk of diabetes [10], whereas some studies suggest this pesticide could negatively affect liver [11] and renal [12] function. Moreover, and according to the International Agency for Research on Cancer (IARC), DDVP probably presents carcinogenic activity in humans [13]. DDVP can also affect other living species. For instance, it has been found that the chronic exposure to this chemical induces oxidative damage, developmental changes, mutagenesis and carcinogenicity in fish [14]. Because of all these reasons, DDVP has been classified by the World Health Organization (WHO) as a highly hazardous pesticide [15] and has been excluded from the list of insecticides approved for use in some world regions like the European Union [16]. In other countries like USA [17] or Australia [18], the use

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of DDVP has been restricted but still continues. Moreover, DDVP is still largely used in many developing countries where poor environmental controls are applied [19,20]. The widespread employment of this insecticide has therefore caused its detection in surface waters worldwide, in concentrations ranging from 1.4 to 5630 ng L^{-1} [21–25].

Despite the serious risks to human and environmental health posed by the presence of DDVP in water resources, the knowledge regarding the removal of this compound by means of unconventional water treatments is still incomplete. Concerning the use of Advanced Oxidation Processes (AOPs) on that purpose, some works in which heterogeneous photocatalysis [8,26–28], Fenton [29] and different combinations of oxidative processes [7] were applied can be found in literature. Even so, the use of other advanced treatments like ozonation has been barely explored.

Ozonation process has extensively demonstrated to have a great potential for micropollutant abatement [30–33]. Ozone (O_3) is a strong oxidizing agent that also decomposes in water to yield hydroxyl radicals ($OH^{\cdot}$), a transient species with extraordinary oxidation capacity [34]. However, although ozonation can be a suitable alternative to remove these contaminants from water it is important, prior to its full-scale application, to deeply investigate the fundamentals of the degradative process by studying the kinetics and mechanisms of the principal reactions involved. This information is crucial to proper assess the process efficiency since harmful transformation products (TPs) can be formed during the treatment, even though the parent compound becomes completely removed [34].

To the best of our knowledge this is the first time in which the degradation of priority pesticide DDVP by means of ozonation process is explored. The study aimed to determine the reaction kinetics of this compound with both, molecular ozone and hydroxyl radicals, as well as to elucidate the possible reaction mechanisms involved in the process. In order to evaluate the potential risks that formed TPs could pose, the residual toxicity of the treated water was also determined.

2. Materials and methods

2.1. Chemicals and reagents

Dichlorvos, metoprolol, and *p*-benzoquinone analytical standards were acquired from Sigma-Aldrich (Germany). NaH_2PO_4, Na_2HPO_4, H_3PO_4, *tert*-butanol and acetonitrile were purchased from Panreac (Spain), and were all analytical grade. Milli-Q water was produced by a filtration system (Millipore, USA). Pure oxygen (> 99.999%) was supplied by Abelló Linde (Spain). Finally, all the reagents employed during toxicity bioassays were purchased from Modern Water (UK).

2.2. Ozonation experiments

Several control experiments were performed in order to determine the possible effects of hydrolysis, adsorption or UV–Vis photolysis on DDVP disappearance during ozonation experiments. All the assays were carried out in 250 mL closed glass beakers, with initial DDVP concentrations of 1 mg L^{-1}. For hydrolysis and adsorption experiments, the beakers were covered with aluminum foil in order to prevent the possible influence of radiation. The pH in hydrolysis tests was adjusted to a value of 7 by adding adequate quantities of a H_3PO_4/Na_2HPO_4 buffer solution. For adsorption experiments, different types of silicones, PVDF and PTFE were put in contact with the pesticide solutions. Samples were taken at 0, 1, 5 and 24 h, and analyzed by HPLC-DAD. Results showed that DDVP remained stable for hydrolysis, photolysis and most of the adsorption experiments. Only in the case of silicones a significant disappearance of DDVP (5–10%) was observed, after 24 h. The use of this kind of materials was therefore discarded during experimentation.

All ozonation experiments were carried out in triplicate, at a controlled temperature of 20 ± 2 °C and neutral pH conditions, in Milli-Q water. A multi-reactor methodology, successfully employed in several previous works [30,35,36], was employed for kinetic and degradation experiments. Detailed information regarding ozone stock solutions preparation can be found elsewhere [35].

For $k_{DDVP,O3}$ measurement, competition kinetics method [30,37] was employed. Experiments were carried out in a series of 25 mL vials containing 20 μM of DDVP and 20 μM of metoprolol (MPL), the reference compound. This competitor was selected considering the moderate reactivity of DDVP with molecular ozone, revealed during preliminary experiments. To avoid the presence of hydroxyl radicals ($OH^{\cdot}$), *tert*-butanol (100 mM) was employed as scavenger. Adequate quantities of the phosphate buffer were also added in order to maintain the medium pH at a constant value of 7. Different doses (from 5 to 40 μM) of the ozone stock solution ($[O_3] = 14$ mg L^{-1}) were injected to each vial to initiate the reaction. The mixtures were shaken for a few seconds to obtain homogeneous conditions. Samples were withdrawn when the total consumption of ozone was achieved (all within 2 h). The residual concentrations of DDVP and MPL were determined by HPLC-DAD. For $k_{MC,OH^{\cdot}}$ determination, a similar procedure was followed. This time, however, two references were employed instead of one since reactions of DDVP with O_3 and $OH^{\cdot}$ took place at the same time and needed to be considered due to their significant contribution to DDVP degradation. MPL and *p*-benzoquinone (pBZQ) were selected as competitors since both were expected to present similar overall reactivity than DDVP. pBZQ residual concentration was also determined by HPLC-DAD.

In order to demonstrate the relative contribution of each oxidant (i.e., O_3 and $OH^{\cdot}$) to DDVP degradation, two extra sets of experiments were carried out. For direct degradation by molecular ozone, each reaction vial contained 20 μM of DDVP, 25 mM of *tert*-butanol and adequate quantities of the pH 7 phosphate buffer. Different doses (from 5 to 175 μM) of the ozone stock solution were applied. Samples were withdrawn when the total consumption of ozone was achieved (all within 2 h). Once the DDVP concentrations were analyzed by HPLC-DAD, samples were frozen and lately employed for TPs and toxicity determinations.

2.3. Analytical procedures

The concentrations of DDVP, MPL and pBZQ were quantified by means of a high performance liquid chromatograph (HPLC) equipped with a diode array detector (DAD), all supplied by Agilent (1260 Infinity). The column employed was a Teknokroma Mediterranea Sea18 (250 mm × 4.6 mm and 5 μm size packing). The mobile phase consisted on a 35:65 volumetric mixture of acetonitrile and Milli-Q water acidified at pH 3 by the addition of H_3PO_4. The flow rate was set to 1 mL min^{-1} and the UV detection was performed at 205, 220 and 254 nm for DDVP, MPL and pBZQ, respectively.

In order to elucidate the possible reaction pathways during DDVP ozonation, samples in which different ozone doses were applied were analyzed by LC-MS. An Agilent 1100 HPLC coupled with a G1969A LC/MSD-TOF mass spectrometer was employed. MS data were collected in full scan mode (25–1100 *m/z*), employing negative electrospray ionization.

With the aim of assessing the toxicity changes during DDVP ozonation process, Microtox® assays were performed for samples withdrawn from degradation experiments. This method measures the inhibition of light emission of bioluminescent bacteria *Vibrio fischeri* caused by the presence of toxic compounds in the aqueous media. The results of this assay are usually expressed as $EC_{50,15min}$, which represents the percentage of sample dilution (v/v) that causes a 50% reduction in bacteria luminescence after a contact time of 15 min. All the tests were carried out in duplicate in a Microtox® M500 (Modern Water, UK) toxicity analyzer.

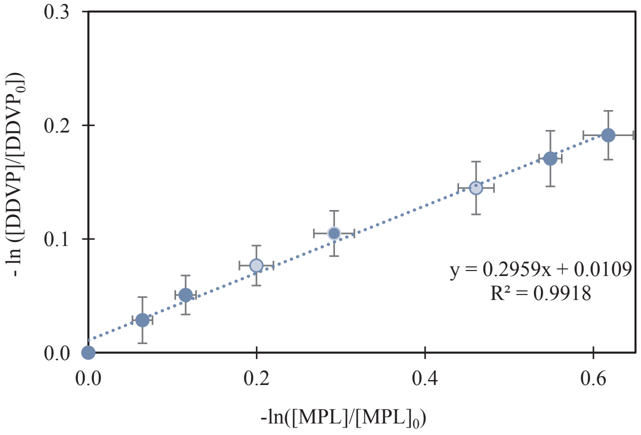


Fig. 1. Determination of second-order rate constant ($k_{DDVP\text{-}O3}$) for the reaction of DDVP and ozone by competition kinetics. Conditions: $[DDVP]_0 = [MPL]_0 = 20\,\mu M$, pH 7, temperature = 20 ± 2 °C.

3. Results and discussion

3.1. Kinetics of DDVP reactions with ozone and hydroxyl radicals

The second-order rate constant of DDVP reaction with molecular ozone was calculated from Eq. (1), obtained by dividing the kinetic equations corresponding to reactions between O_3 and both DDVP and MPL.

$$-ln\left(\frac{[DDVP]}{[DDVP]_0}\right) = \frac{k_{DDVP,O_3}}{k_{MPL,O_3}}\left(-ln\left(\frac{[MPL]}{[MPL]_0}\right)\right) \tag{1}$$

According to this expression, a linear dependence between the natural logarithm of the relative DDVP concentration and the natural logarithm of the relative MPL concentration was expected. The ratio between the second-order rate constants of O_3 with target (DDVP) and reference (MPL) compound would represent the slope of this line.

Fig. 1 shows the experimental results, in which a good linear adjustment was obtained ($R^2 > 0.99$). By knowing the second-order rate constant value for the reaction between ozone and the reference compound, the second-order rate constant for the reaction between DDVP and molecular ozone could be easily calculated. Under pH 7 conditions, and according to the results obtained in previous works [38], MPL reaction with ozone presented a second-order rate constant of $2.0 \cdot 10^3\ M^{-1}s^{-1}$. A value of $590 \pm 20\ M^{-1}s^{-1}$ was finally determined for $k_{DDVP\text{-}O3}$ at pH 7 and 20 °C, which indicates a moderate reaction rate of DDVP with molecular ozone, according to the classifications stablished by Von Gunten and coworkers regarding the reactivity of micropollutants with this oxidant [39,40]. Since DDVP does not show basic or acidic properties in water, the reactivity of this compound with O_3 was not expected to change with the medium pH, as happens with many other chemicals [37].

The second-order rate constant of DDVP reaction with hydroxyl radicals was calculated by solving the system formed by Eqs. (2) and (3). Detailed information about the obtaining of these expressions can be found in previous works, in which this methodology was successfully employed [35,41].

$$ln\frac{[DDVP]}{[DDVP]_0} = \frac{(k_{DDVP,O_3} + k_{DDVP,OH^{\cdot}} Rct)}{(k_{MPL,O_3} + k_{MPL,OH^{\cdot}} Rct)} ln\frac{[MPL]}{[MPL]_0} \tag{2}$$

$$ln\frac{[DDVP]}{[DDVP]_0} = \frac{(k_{DDVP,O_3} + k_{DDVP,OH^{\cdot}} Rct)}{(k_{pBZQ,O_3} + k_{pBZQ,OH^{\cdot}} Rct)} ln\frac{[pBZQ]}{[pBZQ]_0} \tag{3}$$

It is important to note that since this protocol employed two reference compounds (MPL and pBZQ) and each one of them could react with both ozone and hydroxyl radicals, six reactions needed to be considered to simultaneously take place in the studied system. These are gathered in Table 1 along with their corresponding second-order rate constant values.

Table 1
Reactions considered during competition experiments for $k_{DDVP,OH^{\cdot}}$ determination.

Reaction	2nd-order k value $[M^{-1}s^{-1}]$	Reference
$DDVP + O_3 \rightarrow k_{DDVP,O3}$	590	This study
$DDVP + OH^{\cdot} \rightarrow k_{DDVP,OH^{\cdot}}$	Unknown	–
$MPL + O_3 \rightarrow k_{MPL,O3}$	$2.0 \cdot 10^3$	[38]
$MPL + OH^{\cdot} \rightarrow k_{MPL,OH^{\cdot}}$	$7.3 \cdot 10^9$	[38]
$pBZQ + O_3 \rightarrow k_{pBZQ,O3}$	$2.5 \cdot 10^3$	[42]
$pBZQ + OH^{\cdot} \rightarrow k_{pBZQ,OH^{\cdot}}$	$1.2 \cdot 10^9$	[43]

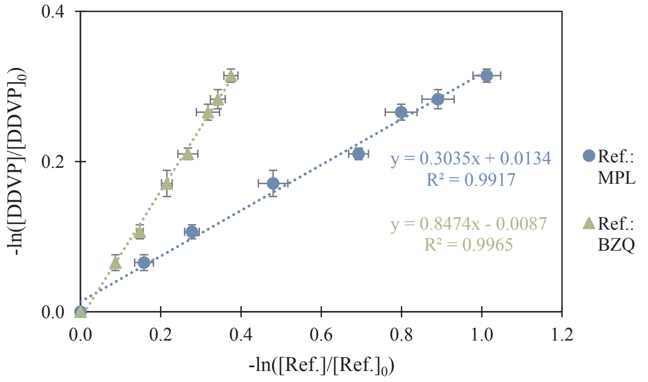


Fig. 2. Determination of $k_{DDVP,OH^{\cdot}}$ by competition kinetics: $-\ln([DDVP]/[DDVP]_0)$ versus $-\ln([Ref.]/[Ref.]_0)$ for the simultaneous reaction of ozone and hydroxyl radicals with DDVP and the references (Ref.) MPL and pBZQ. Conditions: $[DDVP]_0 = [MPL]_0 = [pBZQ]_0 = 20\,\mu M$, pH 7, temperature = 20 ± 2 °C.

From Eqs. (2) and (3) it was deduced that by plotting the natural logarithm of DDVP relative concentration versus the natural logarithm of both MPL and pBZQ relative concentrations, two linear relationships could be obtained. The slope values of these lines, together with the second-order rate constant values shown in Table 1 were required to solve the equation system.

Fig. 2 shows the experimental results, in which good linear adjustments ($R^2 > 0.99$) were obtained for both plots. The second-order rate constant of DDVP reaction with hydroxyl radicals was determined to be $(2.2 \pm 0.1) \cdot 10^9\ M^{-1}s^{-1}$, thus pointing out the high reactivity of DDVP with $OH^{\cdot}$. This was explained by the non-selective character of the oxidant, which can readily undergo reactions with different points of organic molecules [37].

3.2. DDVP degradation by ozone and hydroxyl radicals

During ozonation, DDVP could react with molecular ozone and also with hydroxyl radicals formed as a consequence of ozone decay. In order to determine the relative contribution of $OH^{\cdot}$ to overall DDVP removal, degradation experiments were conducted at pH 7 with and without the presence of *tert*-butanol. Results are presented in Fig. 3.

Degradation through the combination of ozone and hydroxyl radicals was more effective than the lonely attack by O_3: an ozone dose of approximately $2.8\ mg\ L^{-1}$ was required for the complete removal of DDVP, while the double of this dose ($5.5\ mg\ L^{-1}$) was necessary in the presence of *tert*-butanol. Therefore, the contribution of hydroxyl radicals to the pesticide removal was significant at neutral pH. Higher pH values, of course, would probably enhance this contribution since ozone decomposition is accelerated under basic conditions [37]. Besides the pH, other water characteristics like the organic and inorganic matter content can also affect the process efficiency. Thus, performing experiments with real water matrices and more realistic pesticide

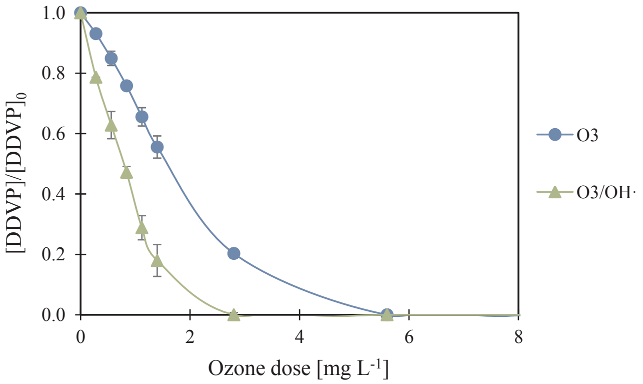


Fig. 3. DDVP degradation as a function of the ozone dose, for experiments with (O_3) and without ($O_3/OH^{\cdot}$) the presence of *tert*-butanol (25 mM). Conditions: $[DDVP]_0$ = 20 μM, pH 7, temperature = 20 ± 2 °C.

concentrations would be convenient in order to properly determine the ozone dose necessary to remove DDVP. Also, models based on the kinetic data here determined and water specific information [40,45] could be useful on that purpose.

Besides the degradation of DDVP, the study of the formed TPs was thought to be essential in order to assess the process efficiency: intermediates presenting higher toxicity than the parent compound could be formed, thus enlarging the oxidant dosage necessary to obtain a water relatively free of harmful substances.

3.3. Reaction intermediates and possible mechanisms

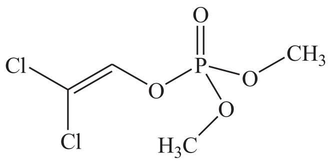
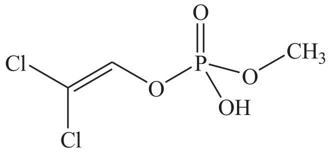
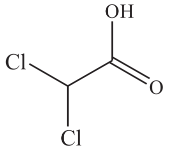
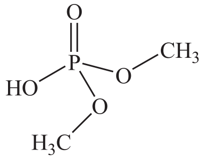
Relevant TPs generated during DDVP ozonation with and without radical scavenger addition were identified by means of LC-MS, on the basis of the detected masses. The proposed molecular structures are shown in Table 2.

Only one of the observed intermediates, DDVP-125 or dimethyl phosphate (DMP), was detected in both experiments (i.e., experiments with and without the presence of hydroxyl radicals). For their part, DDVP-207 and DDVP-128 (desmethyl dichlorvos (d-DDVP) and dichloroacetic acid (DCA), respectively) were only detected in experiments in which $OH^{\cdot}$ were present in the reaction medium. These findings appeared to indicate that DMP could be generated through both molecular ozone and hydroxyl radicals mediated oxidation, whereas d-DDVP and DCA were only formed via $OH^{\cdot}$. The first degradation steps during DDVP ozonation process, therefore, could be explained by the reaction pathways illustrated in Fig. 4.

The identification of d-DDVP suggests an initial H-abstraction, carried out by $OH^{\cdot}$, at one of the methyl groups of DDVP's phosphate moiety (pathway 1). A subsequent $OH^{\cdot}$ addition after this first step, followed by the yielding of a formaldehyde molecule from the resulting structure would finally end in the d-DDVP (DDVP-207) formation. Alternatively, this TP could be formed through $OH^{\cdot}$ addition to the phosphate moiety of DDVP, followed by the elimination of a methanolate (CH_3O-) group from the resulting structure (pathway 2). The attack by hydroxyl radicals to DDVP molecule could also take place at its dichlorovinyl moiety. This pathway would consist on the addition of $OH^{\cdot}$ to the corresponding double bound, followed by the hydrolysis of the resulting radical to yield DMP (DDVP-125) and dichloroacetaldehyde (pathway 3). Under the oxidizing conditions of the reaction medium, the latter would easily undergo oxidation to yield DCA, the last detected TP (DDVP-128). As before commented, in addition to the $OH^{\cdot}$-mediated oxidation and according to the LC-MS results obtained for samples in which *tert*-butanol was added as $OH^{\cdot}$ scavenger, the intermediate DDVP-125 (DMP) could be formed via double bond cleavage by O_3 (pathway 4). The primary ozonide would be rapidly decomposed into a phosgene molecule and a zwitterion, being the latter subsequently transformed into DMP through CO_2 release.

As an organophosphate, the insecticide properties of DDVP are based on the irreversible inhibition of the vital enzyme acetyl cholinesterase. This inhibition is called cholinergic effect and is caused by the phosphorylation of the active site of the enzyme, which is no longer able to hydrolyze the acetylcholine neurotransmitter. This causes the overstimulation of the insect nervous system [9]. Since the presence of the phosphate structure is necessary to maintain the cholinergic effect, the intermediate DDVP-128 was not expected to present that pesticide mode of action. In addition, DDVP dichlorovinyl moiety enhances the

Table 2
DDVP, detected TPs and their corresponding molecular structures.

m/z	Name	Proposed structure	Observations
220 (m-1)	Dichlorvos (DDVP)		Parent compound in both experiments
207 (m-1)	DDVP-207 Desmethyl Dichlorvos (d-DDVP)		Only detected in the presence of $OH^{\cdot}$
128 (m-1)	DDVP-128 Dichloroacetic Acid (DCA)		Only detected in the presence of $OH^{\cdot}$
125 (m-1)	DDVP-125 Dimethyl phosphate (DMP)		Detected in both experiments

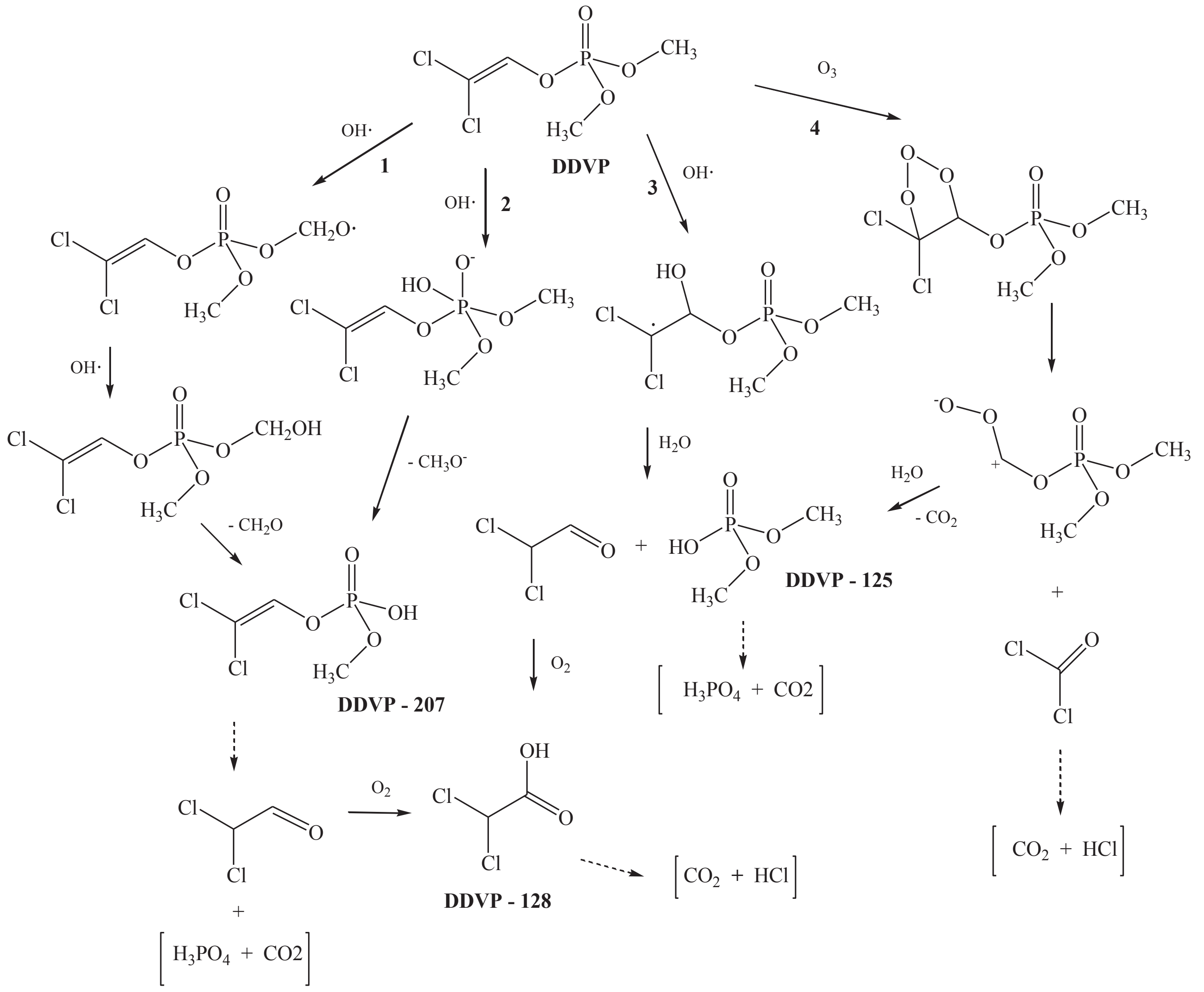


Fig. 4. Proposed reaction pathways for DDVP oxidation by molecular ozone and hydroxyl radicals during ozonation process.

binding between the enzyme's active site and the pesticide due to the electronegativity of its terminal chlorine. Because of that, it is probable that DDVP-127 had lost its cholinergic properties. It is important to note, however, that losing the cholinergic capacity does not mean to be non-toxic since other toxicity mechanisms affecting the life of target and non-target organisms could be manifested. For its part, intermediate DDVP-207 still maintains the DDVP dichlorovinyl phosphate structure and, as a consequence, this compound was expected to present similar insecticide activity than the parent compound.

3.4. Toxicity evolution during DDVP ozonation

Changes in the chemical species involved in DDVP ozonation process could imply alterations in the properties of the reaction medium. Among these properties, toxicity is of special interest since DDVP and formed TPs could affect target (insects) but also non-target organisms. The evolution of $1/EC_{50}$ as a function of the ozone dose is presented in Fig. 5, for samples corresponding to degradation experiments with and without the presence of a radical scavenger. It has to be remembered that higher $1/EC_{50}$ values mean higher inhibition of bacteria luminescence (i.e., higher toxicity), and vice versa. Initial EC_{50} value, that is, the sample concentration that causes mortality in the 50% of the bacteria population after 15 min contact was determined to be 3.8 mg L^{-1} (EC_{50} about 80% in terms of sample dilution). For the rest of samples, only EC_{50} expressed as sample dilution could be obtained since the medium compositions were unknown.

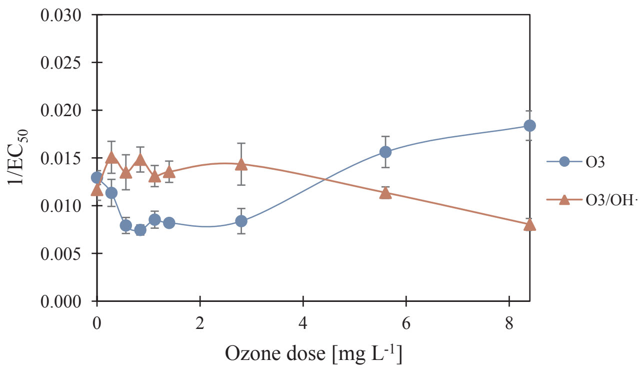


Fig. 5. Acute toxicity of the reaction medium during DDVP ozonation, in experiments with (O_3) and without ($O_3/OH^{\cdot}$) the presence of *tert*-butanol. Conditions: $[DDVP]_0 = 20$ μM, pH 7, temperature = 20 ± 2 °C.

The toxicity during experiments with the addition of *tert*-butanol initially decreased to a minimum, being this caused by the reduction of DDVP concentration in the reaction solution. For low ozone doses, the amount of formed TPs is low and thus the contribution of these intermediates and the synergies between them to the medium toxicity are not expected to be significant. After this first drop, toxicity started to increase for oxidant doses above 3 mg L^{-1}. The final *EC$_{50}$* value (51.3%), higher than the initial one (86.2%) indicates a global growth in the toxicity of the medium that could be caused by synergistic effects between residual DDVP and newly formed species like DDVP-125 (DMP) or phosgene, a well-known toxic agent. The latter, although not detected during LC-MS analyses, was expected to be generated according to the proposed degradation pathways (see Fig. 4). However, this compound rapidly hydrolyzes [46]. Perhaps other toxic, non-detected species formed during DDVP ozonation process (i.e. aldehydes or H_2O_2 formed through ozone decomposition [34,47] could be present and contribute to enhance the medium toxicity. Also, dimethyl phosphate, the TP generated through direct molecular ozone attack, presents a saturated, aliphatic molecular structure. Therefore, the reactivity of this byproduct with molecular ozone is expected to be low [48,49], and this would cause its accumulation in the system thus increasing the residual toxicity of the medium. In the case of experiments without the presence of *tert*-butanol, toxicity slightly increased for low oxidant dosages (0–0.3 mg L^{-1}), remained without major variations for doses up to 3 mg L^{-1} and then started to decrease, reaching 1/*EC$_{50}$* values below the initial one. The initial rise of this parameter, although not very significant, was probably due to synergistic effects between remaining DDVP and early-formed TPs like DDVP-207, which as before commented, could maintain a similar toxicity than the parent compound. For doses above 3 mg L^{-1}, DDVP was no longer present in the reaction medium (see Fig. 3) and synergistic effects apparently disappeared. From this point, therefore, further $OH^{\cdot}$-mediated oxidation of the TPs that were present in the reaction system allowed the final toxicity abatement of the solution.

In the view of the Microtox® results, it can be stated that O_3 oxidation alone contributed to increase the toxicity of the medium. The low reactivity of formed TP (i.e., DMP) with this oxidant probably caused the accumulation of this chemical species in the reaction medium, thus inducing the observed increase in toxicity. However, hydroxyl radicals formed through ozone decomposition allowed to solve this problem since this transient species were able to remove both DDVP and TPs. Therefore, it is concluded that ozonation process could be a suitable treatment alternative for DDVP removal and associated toxicity abatement, provided that the indirect degradative route (i.e., $OH^{\cdot}$-mediated oxidation) is properly promoted.

4. Conclusions

The obtained results allow drawing some conclusions regarding the degradation of dichlorvos by means of ozonation. The moderate and high values for second-order rate constants of DDVP reactions with O_3 and $OH^{\cdot}$, respectively, point out the treatability by ozone-based processes of water matrices containing traces of this priority pesticide. Both ozone and hydroxyl radicals can play an important role in DDVP abatement, although studies dealing with real waters and lower concentrations of the contaminant are required in order to properly assess the process performance. Proposed reaction mechanisms indicate the formation of dimethyl phosphate as a common TP for both O_3 and $OH^{\cdot}$ degradation routes. This intermediate is expected to present low reactivity towards ozone, even though can be degraded by hydroxyl radical-mediated oxidation. The acute toxicity analyses in experiments with $OH^{\cdot}$ scavenger demonstrates that a rise in the bacteria luminescence inhibition occur for increasing oxidant dosages. However, results of experiments without *tert*-butanol show that formed hydroxyl radicals are able to abate the toxicity of the reaction medium. It is clear, therefore, that the contribution of the $OH^{\cdot}$ degradation route during ozonation process is required in order to remove DDVP, formed TPs and reduce the associated toxicity. Strategies aimed to enhance this indirect via need to be assessed to improve the process efficiency.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.09.069.

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4.2 Ozonation for enhanced treatment of wastewater effluents

Ozonation was applied to biotreated municipal wastewater effluents with the aim of get novel insights into the effective abatement and fate control of ozone-recalcitrant micropollutants during this treatment. Six different effluents were employed: three collected from MBR treatments (M-VAC, M-VAL and M-GAV), and three others from CAS systems (C-PRA, C-GAV and C-LLA). The process was first explored in terms of the abatement of a model micropollutant (ACMP) spiked at low concentrations, developing this way novel tools for performance characterization and kinetic modelling based on the use of this class of compound as probe for hydroxyl radicals. Then, by combining these tools with the measurement of water quality parameters, a potential online control strategy was developed. Results obtained in that work led to the publication presented in Appendix IV. Through additional ozonation experiments employing the same effluents, a comprehensive assessment on the fate of EfOM during the process was performed. Potential scenarios in which higher ozone doses are applied for a more effective abatement of ozone-refractory MPs were considered in this part of the work. Obtained results led to the publication presented in Appendix V.

4.2.1 Abatement of ozone-recalcitrant species, kinetic modelling and potential control strategies (Appendix IV)

The oxidation of ACMP during semi-batch ozonation experiments of different wastewater effluents was assessed and compared, with especial focus on employed ozone doses, to literature works including data on ozone-resistant MPs abatement. In general, specific (*i.e.*, DOC-normalized) ozone doses employed in lab-, pilot- and full-scale investigations ranged up to 2 mg O_3 mg C^{-1}, which as claimed in many scientific reports are often enough to effectively abate most compounds with high to moderate reactivity to ozone [136,138,188,189]. However, and because of its low reactivity with that oxidant (see Table 14 in section 4.1.1), ACMP abatement ranged from 30 to 80% depending on the effluent (see Figure 2 in Appendix IV). It is clear, therefore, that an increase of the applied ozone doses in wastewater ozonation with respect to the currently employed ones would be required to also remove refractory compounds during ozone application. However, if absolute ozone doses (i.e., mg O_3 L^{-1}) are considered, it is possible that this strategy would be considered economically feasible for only those effluents with a lower pollution load and alkalinity, such as MBR effluents and C-PRA (see Table 11 in section 3.2 or Table 1 in Appendix IV). On the contrary, for more polluted effluents such as C-GAV and C-LLA, this option would be probably dismissed due to very high operational expenses.

ACMP abatement data obtained in batch ozonation experiments was employed to determine hydroxyl radical exposures ($\int[\bullet OH]dt$) for all effluents throughout the entire ozonation time. This could be done by assuming that observed removals were entirely due to hydroxyl radical oxidation, which is valid given the extremely low reactivity of this chemical with ozone. Eq. (23) (section 1.4.1) and the rate constant value of reaction between ACMP and •OH ($2.1 \cdot 10^9$ $M^{-1}s^{-1}$) previously determined in batch ozonation experiments (see section 4.1.1 and Appendix II) were applied, according to a previously, well established methodology [150]. As explained in section 1.4.1, •OH exposure is key to assess the abatement of MPs, particularly ozone-recalcitrant species. Due to significant differences in water quality between effluents (see Table 11 in section 3.2), which were well reflected by the estimated ozone demands (IOD values of 14, 9, 11, 16, 28 and 19 mg O_3 L^{-1} for effluents M-VAC, M-VAL, M-GAV, C-PRA, C-GAV and C-LLA, respectively), •OH exposures were normalized to TOD in order to compare oxidation efficiencies in terms of radical availability per consumed ozone. Thus, the recently defined $R_{OH,O3}$ concept (section 1.4.1 and ref. [159]) was tested as a potential tool for performance characterization of wastewater ozonation. Linear correlations between •OH exposure and TOD data were observed in all cases ($R^2 > 0.98$), and since two regimes of ozone consumption –as usual in wastewater ozonation [142,143]– were observed, two linear plots were obtained for each one of the tested effluents (see Figure 3 of Appendix IV). IOD values, also represented in Figure 3 of Appendix IV, indicated the limit between both of them. $R_{OH,O3}$ values corresponded to the slope values of these lines. For initial or IOD stage, obtained R_{OHO3} values ranged from $1.53 \cdot 10^7$ to $7.60 \cdot 10^7$ s, whereas values between $0.61 \cdot 10^6$ and $2.95 \cdot 10^6$ s were obtained after IOD completion (secondary ozonation stage). Values found for $R_{OH,O3}$ and other parameters later on discussed can be consulted in Table 3 of Appendix IV. R_{OHO3} values, and particularly those corresponding to the initial or IOD stage, were closely related to effluent characteristics, mainly organic matter concentration/properties and alkalinity. Being so, MBR effluents displayed in general a higher oxidation efficiency in terms of hydroxyl radical availability per consumed ozone. On the contrary, •OH exposure per consumed ozone was markedly lower in effluent samples with significantly higher content of dissolved or even suspended organics (*e.g.*, GAV-V).

The ultraviolet absorbance at 254 nm (UVA_{254}), a typical and easily measurable parameter employed in wastewater characterization was monitored during ozonation experiments, and a good correlation ($R^2 > 0.98$) was observed with TOD, according to Eq. (33). A two-stage behavior, similar to that for $R_{OH,O3}$ plots, was also observed in this relationship. The corresponding plots are found in Figure 4 of Appendix IV. The parameter $k_{UVA,O3}$ was defined as the coefficient of proportionality between the negative, natural logarithm of the relative UVA_{254} and TOD. Values estimated for this parameter can be consulted in Table 3 of Appendix IV.

$$-\ln\left(\frac{\mathrm{UVA}_{254}}{\mathrm{UVA}_{254,0}}\right) = k_{\mathrm{UVA,O3}} \cdot \mathrm{TOD} \qquad (33)$$

Considering the existing correlations between •OH exposure and TOD [Eq. (24)], on one hand, and between UVA_{254} and TOD [Eq. (33)], on the other, an additional correlation between •OH exposure and UVA_{254} could be deducted and experimentally verified (see Figure 5 and Table 3 in Appendix IV). Similarly to the above mentioned correlations, $k_{UVA,OH}$ was defined as the slope of the linear relationship between $\int[\bullet\mathrm{OH}]\mathrm{d}t$ and the negative, natural logarithm of the relative absorbance, according to Eq. (34). R^2 coefficients above 0.98 were again obtained in all cases.

$$-\ln\left(\frac{\mathrm{UVA}_{254}}{\mathrm{UVA}_{254,0}}\right) = k_{\mathrm{UVA,OH}} \cdot \int [\bullet\ \mathrm{OH}]\mathrm{d}t \qquad (33)$$

The relationship between UVA_{254} decrease and hydroxyl radical exposure suggested that absorbance monitoring throughout ozonation of wastewater effluents could be used for online prediction of •OH exposure. Combining this relationship with Eq. (23), a new relationship (Eq. 34) might be employed to predict the abatement of ozone-recalcitrant species. In addition to continuous UVA_{254} measurement, both the rate constant of reactions between •OH and the target compound and the value of $k_{UVA,OH}$ –empirically known for a given effluent– would be required.

$$\frac{[\mathrm{MP}]}{[\mathrm{MP}]_0} = \left(\frac{\mathrm{UVA}_{254}}{\mathrm{UVA}_{254,0}}\right)^{\frac{k_{\bullet\mathrm{OH}}}{k_{\mathrm{UVA,OH}}}} \tag{34}$$

In order to validate this approach, additional ozonation experiments were performed in effluents spiked with low concentrations of two known ozone-recalcitrant micropollutants: the drug ibuprofen (IBU) [176] and the pesticide atrazine (ATZ) [190]. Predictions were performed according to the described methodology. In addition, predictions based on the use of the R_{OHO3} concept were employed with the aim of demonstrate its usefulness as tool for controlling the fate of ozone-recalcitrant species during ozone application. Eq. (35) was employed to that purpose, which was the result of combining Eqs. (23) and (24).

$$-\ln\left(\frac{[\mathrm{MP}]}{[\mathrm{MP}]_0}\right) = k_{\bullet\mathrm{OH}} \cdot R_{\mathrm{OH,O3}} \cdot TOD \tag{35}$$

Good agreements ($R^2 > 0.98$) between measured and predicted abatements were observed for different compounds (IBU and ATZ), tested effluents (six, three from MBR systems and three other from CAS bioreactor) and prediction models (based on $R_{\mathrm{OH,O3}}$ and TOD monitoring, on one hand, and on $k_{\mathrm{UVA,OH}}$ and UVA_{254} monitoring, on the other). Plots of predicted and measured degradation data can be found in Figures 6 and 7 of Appendix IV, respectively, and also in the corresponding Supplementary Information (Figures 8 and 9).

4.2.2 Assessment of EfOM changes taking place through ozone application for micropollutants abatement, including ozone-refractory compounds (Appendix V)

EfOM transformation during ozonation of M1-M3 and C1-C3 wastewater effluents was assessed. The effective degradation of the ozone-refractory compound ACMP was selected as reference to establish a range of potentially practical ozone dosages (up to 1 mM, see Figure 1 in Appendix V)). Under those treatment conditions, typical wastewater parameters related to the organic matter content were measured, and changes taking place in the dissolved EfOM fractions were also evaluated through SEC-OCD determinations.

General quality parameters such as UVA_{254}, COD and DOC revealed changes in aromaticity, oxidation state and variations in the concentration of dissolved organic carbon in all effluents. Corresponding data is presented in Figures 2, 3 and 4 of Appendix V. Aromaticity reduction was substantial in all effluents even at low or moderate ozone doses, which was normal as ozone readily reacts during its initial stage with electron-rich moieties of EfOM [107]. COD reduction were in comparison lower (up to 45% reduction versus up to 80% observed for UVA_{254}), indicating that even though aromaticity is reduced after some changes in the moieties responsible for this property, structural changes required for significant oxidation of organic matter are only achieved if stronger oxidation conditions are applied. Reduction in both UVA_{254} and COD strongly depended on the effluent properties, being these more effective in those samples with a lower content in organic and inorganic carbon (*i.e.*, MBR effluents). DOC analyses, on its part, revealed that relatively low mineralization was achieved in MBR effluents (up to about 20-25% for the highest ozone doses, that is, 0.6 mM). CAS effluents, on their part, increased organic carbon content (about 5, 35 and 20% in effluents C1, C2 and C3, respectively, for O_3 doses between 0.7 and 1 mM) during the process. This was most noticeable for those samples with a higher content in suspended EfOM (*i.e.*, C2 and C3), and it was attributed to solubilization of this matter upon oxidation.

A closer look at the evolution of specific fractions of dissolved EfOM through the SEC-OCD technique revealed in CAS effluents an increase in the concentration of humic substances with increasing TOD values, especially in samples C2 and C3 (see Figure 5 in Appendix V). As this was the only fraction for which a rise was observed, the increase in DOC content previously described was attributed to the solubilization of this class of matter. This behavior was not so clearly observed in effluent C1, for which it a slight increase in the humic fraction content was observed at low ozone dosages, followed by an also slight decrease for higher TOD values. Similarly, the DOC gain observed in the other CAS samples was not so clear in the case of C1. The lower content in particulate EfOM of this wastewater was probably the reason why this occurred. Concerning the other investigated fractions of EfOM in CAS effluents, accumulation of lower molecular weight compounds such as the so-called building blocks, organic acids and neutrals was in general observed along the process.

In MBR samples, which were free of suspended EfOM because of their previous treatment through ultrafiltration membranes, the humic fraction experimented a sustained decrease in all samples, which in general led to the generation of smaller components such as building blocks or low molecular weight organic acids. This data is represented in Figure 6 of Appendix V. The latter fraction was also presumably enriched through oxidation of low molecular weight neutrals. The concentration in biopolymers, on its part, slightly decreased during the process, although the initial content in this fraction in the untreated effluent was not very significant compared to other EfOM fractions.

Changes in humic contents for MBR samples were related to some effluent quality and ozonation parameters, in an attempt of stablishing useful relationships potentially allowing a first assessment and estimation of EfOM evolution during ozonation. It was observed that humics content significantly decreased only after an also significant abatement of UVA_{254} was observed (see Figure 7A in Appendix V). Thus, although humic substances have always been related to EfOM aromaticity [191–193], a lag between both (*i.e.*, the content in humic substances and UVA_{254}) during ozonation was revealed in this study. Interestingly, this lag (*i.e.*, the observed % in UVA_{254} reduction from which a significant abatement of humic substances was observed) and the rate through which humics were removed from MBR samples correlated well with IOD (0.29, 0.19 and 0.23 mmol O_3 L^{-1} for M1, M2 and M3, respectively) and the IOD-normalized •OH exposure ($\int$[•OH]dt/IOD) values ($3.1 \cdot 10^{-7}$, $7.3 \cdot 10^{-7}$ and $4.9 \cdot 10^{-7}$ s for M1, M2 and M3, respectively) determined for each effluent (Appendix V, Table 3). In general, lower oxidant (both O_3 and •OH) demands at the beginning of the process resulted in a more immediate (*i.e.*, lower observed lag) and faster abatement of humic moieties.

Appendix IV

Abatement of ozone-recalcitrant micropollutants during municipal wastewater ozonation: Kinetic modelling and surrogate-based control strategies

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Abatement of ozone-recalcitrant micropollutants during municipal wastewater ozonation: Kinetic modelling and surrogate-based control strategies

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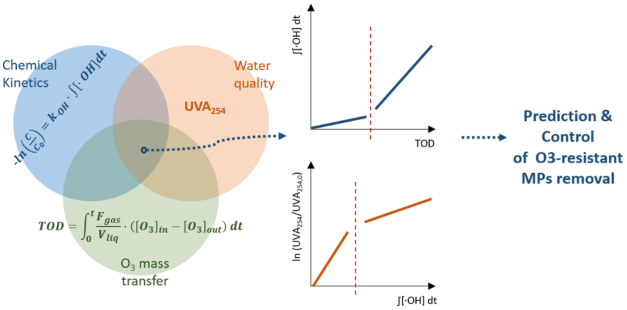
HIGHLIGHTS

- O_3:DOC ratios up to 2 are not effective for significant removal of O_3-resistant MPs.
- Two-stage models based on R_{OHO3} allow complete performance description of ozonation.
- R_{OHO3} concept can be useful for prediction of O_3-recalcitrant species removal.
- A novel method based on UVA_{254} monitoring is proposed for removal prediction.

GRAPHICAL ABSTRACT



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ABSTRACT

Although ozonation is nowadays recognized as one of the most efficient technologies for micropollutants abatement in municipal wastewater effluents, several of the compounds potentially present in those waters exhibit a strong resistance to direct ozone oxidation. In addition, the real-time control of the removal process is still challenging. In this work, the abatement of ozone-recalcitrant micropollutants during wastewater ozonation of six different wastewater effluents was explored using the pesticide acetamiprid as hydroxyl radical (·OH) probe. By means of this data, the oxidation efficiency (*i.e.*, hydroxyl radical exposure per consumed ozone) could be described by means of a two-stage model based on the R_{OHO3} concept. This was possible using a semi-continuous bubbling ozone contactor in all experiments, which permitted the inclusion of the ozone mass balance in the model. R_{OHO3} values of $(1.53–7.60)\cdot 10^{-7}$ s for initial ozonation stage and $(0.61–2.95)\cdot 10^{-6}$ s for the secondary stage were obtained allowing the characterization and comparison of the process performance in a wide range of effluent qualities, including water matrices with a high content of dissolved and particulate organic matter (total organic carbon (TOC), dissolved organic carbon (DOC) and turbidity tested ranges: 6.7–50 mg C L^{-1}, 6.6–27.6 mg C L^{-1} and 0.3–28.6 NTU, respectively). Finally, a surrogate strategy involving ·OH exposure estimation by means of ultraviolet absorbance at 254 nm (UVA_{254}) measurements was proposed based on the R_{OHO3} concept, and by means of its application the removal of atrazine and ibuprofen in six different wastewaters could be rightly predicted ($R^2 > 0.98$).

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1. Introduction

Ozonation has largely demonstrated to be one of the most effective and easily implementable advanced treatment technologies for micropollutants (MPs) abatement in municipal wastewater effluents. From laboratory to full-scale studies, a considerable number of works have reported the benefits, in terms of water quality, derived from ozone (O_3) application after the secondary stage of a wastewater treatment train [2,11,20,24,28]. However, and although this technology is nowadays increasingly implemented in wastewater treatment plants (WWTPs) around the world [5], the control of MPs removal during the process – necessary to optimize the required oxidant doses – is still challenging. Despite the vast advances in chromatographic techniques, which currently allow the simultaneous determination of a few hundred compounds from μg L^{-1} to ng L^{-1} levels [2], the huge number of chemicals [9,22] potentially present in wastewater effluents makes the measurement of their individual oxidation efficiencies a completely prohibitive option from a practical and economical perspective. A helpful alternative could be the employment of chemical kinetics, which establishes that the removal of any MP during ozonation can be predicted if the second-order rate constants of reactions between this compound and both ozone (k_{O3}) and hydroxyl radicals ($k_{\cdot OH}$), as well as the ozone and hydroxyl radical exposures ($\int [O_3]dt$ and $\int [\cdot OH]dt$) are known, according to Eq. (1).

$$-\ln\left(\frac{[MP]}{[MP]_0}\right) = k_{O_3}\int [O_3]\mathrm{d}t + k_{\bullet OH}\int [\bullet OH]\mathrm{d}t \qquad (1)$$

Despite the great potential of ozonation process, some of the organic compounds typically present in secondary effluents present a strong recalcitrance towards direct ozone oxidation. They are known as ozone-resistant micropollutants, and they are characterized by second-order rate constants with molecular ozone generally below 10 M^{-1} s^{-1} [16]. As most of these chemicals are only effectively eliminated by hydroxyl radical ($\cdot OH$) oxidation, they are considered to be one of the main limiting factors for ozone applications [25]. In some parts of the world, obtaining a high quality water from wastewater may be required in a near future for applications involving further human exposure. In these situations, the monitoring and control of the fate of ozone-recalcitrant MPs during ozonation might be essential, especially considering that some of these compounds can pose risks to human and environmental health. In such cases, and according to chemical kinetics (see Eq. (1)), if these species (ozone-resistant compounds) are effectively removed from the effluent, it can be fairly hypothesized that those other compounds presenting a certain degree of reactivity with O_3 (*i.e.*, in general, k_{O3} values larger than 10 $M^{-1}s^{-1}$) would be faster oxidized. It is clear, therefore, that a potential approach to ensure the removal of MPs during the ozonation step in a WWTP could be the control of those MPs whose abatement is more difficult to achieve, that is, O_3-resistant compounds. In accordance with this hypothesis of work, Eq. (1) could be simplified to Eq. (2).

$$-\ln\left(\frac{[MP]}{[MP]_0}\right) = k_{\bullet OH}\int [\bullet OH]\ \mathrm{d}t \qquad (2)$$

Regarding $k_{\cdot OH}$ values, there is a large kinetic database in literature for reactions between organic compounds and hydroxyl radicals [4,27]. With respect to $\cdot OH$ exposure, this term can be experimentally determined through the monitoring of a $\cdot OH$ probe compound [10]. This method, although useful for prediction of contaminants removal in lab-scale studies or during the planning stage of wastewater ozonation units [17,16,25], is time consuming and hardly has an application in real-time control systems. A possible solution to this limitation could be the use of a water quality parameter as surrogate for online estimation of $\cdot OH$ exposure. A recent work by Chys and coworkers shows the potential of this approach employing the ultraviolet absorbance at 254 nm (UVA_{254}) and total fluorescence (TF) as surrogates [5]. In a parallel – but related – line of work, some studies have also shown that decreases in UVA_{254} and total fluorescence (TF) could be correlated to the abatement of micropollutants [12,23,26].

In general, lab-scale studies dealing with micropollutants oxidative abatement from wastewater by means of ozonation – and especially those working on the kinetic modelling of the process – ignore the ozone mass transfer and the relationship between this factor and the process performance. The performance of batch ozonation experiments with addition of O_3 from aqueous stock solutions, although practical for absolute kinetics determinations, prevents the accurate characterization of the initial, fast O_3-consuming, ozonation stage. Furthermore, in most ozonation studies the oxidation performance is usually described by means of parameters that are strongly dependent from the applied dose of oxidant, such as the R_{ct} concept [10]. Regarding this, Kwon and coworkers [15] have recently proposed the R_{OHO3} concept, a kinetic parameter defined as the $\cdot OH$ exposure (*i.e.*, the time-integrated $\cdot OH$ concentration) per consumed O_3 (*i.e.*, the transferred ozone dose (TOD)) (see Eq. (3)). The R_{OHO3} concept is independent from the O_3 dose and appears to be useful for both, performance characterization and kinetic modelling of ozonation process. However, a single R_{OHO3} value is not enough to characterize the whole ozonation process, as deducted by the work performed by Kwon et al. [15].

$$R_{OHO_3} = \frac{\int [\bullet OH]\mathrm{d}t}{TOD} \qquad (3)$$

The main goal of this study was, on one hand, to assess the oxidation performance of semi-continuous ozonation for enhanced wastewater treatment, particularly focusing on the monitoring and control of ozone-resistant micropollutants removal from effluents. On the other, and by means of kinetic parameters like R_{OHO3} and the monitoring of UVA_{254} as surrogate quality parameter, to establish the fundamentals of potential strategies for the real-time prediction and control of the abatement of these recalcitrant species during the whole process. The proposed models were validated by predicting the abatement of ozone-recalcitrant micropollutants atrazine and ibuprofen in all the employed effluents. The removal of moderate and highly ozone-sensitive micropollutants during the process was also verified.

2. Materials and methods

2.1. Chemicals and reagents

Acetamiprid (ACMP), atrazine (ATZ), ibuprofen (IBU), methiocarb (MC) and dichlorvos (DDVP) analytical standards were acquired from Sigma-Aldrich (Germany). Ultrapure water was produced by a filtration system (Millipore, USA). Pure oxygen (≥99.999%) was supplied by Abelló Linde (Spain).

2.2. Wastewater effluents

Six wastewater effluents from five WWTPs in the province of Barcelona (Spain) were employed in this work. Three of them (M-VAC, M-VAL and M-GAV) came from membrane biological reactor (MBR) systems, whereas the rest (C-PRA, C-GAV and C-C-LLA) were collected from conventional activated sludge (CAS) treatments. All samples were directly collected from the outlet stream of the corresponding biological treatments. Their main quality parameters are gathered in Table 1. The raw CAS effluents were filtered with conventional filter paper to remove the largest particles. For each sample, total organic carbon (TOC) and dissolved organic carbon (DOC) (after being filtered through 0.45 μm PTFE syringe filters) were measured by means of a Shimadzu TOC-VCSN analyzer. The ultraviolet (UV) absorbance was determined with a DR6000 UV VIS spectrophotometer (Hach, USA). Turbidity was measured with a 2100Q portable turbidimeter, also by Hach. Alkalinity was determined by means of an automatic titration device coupled with a pH meter (Crison, Spain). Nitrite (NO_{22}^{-}) concentration was

Table 1
Main effluent water quality parameters (M-: membrane biological systems; C-: conventional activated sludge treatments). All measurements were performed per triplicate. Discrepancies between values were in all cases lower than 5%.

WWTP ID	Location	pH	TOC [mg C L^{-1}]	DOC [mg C L^{-1}]	UV_{254} [cm^{-1}]	Turbidity [NTU]	Alkalinity [mg $CaCO_3$ L^{-1}]	NO_2^- [mg N L^{-1}]
M-VAC	Vacarisses	7.9	6.7	6.6	0.179	0.6	330	0.85
M-VAL	Vallvidrera	7.4	10.5	10.3	0.163	0.9	178	0.03
M-GAV	Gavà-Viladecans	7.7	12.4	12.1	0.149	0.3	200	0.12
C-PRA	El Prat de Llobregat	7.5	14.0	13.6	0.229	1.1	264	0.09
C-GAV	Gavà-Viladecans	7.8	42.1	27.6	0.672	28.6	517	0.09
C-LLA	La Llagosta	7.7	25.6	21.3	0.664	20.1	419	0.03

determined through ion-exchange chromatograph with UV detection. All the effluent samples were stored at 4 °C prior to be used.

The employed wastewater effluents showed broad variations in their main quality parameters. These marked differences were considered highly valuable since allowed the performance of a study whose results could cover a wide range of water qualities.

2.3. Ozonation of wastewater effluents

Wastewater ozonation experiments were performed in a 750 mL jacketed reactor, operated in semi-continuous mode. Ozone was produced by a 301.19 lab ozonizer (Sander, Germany) and injected at the bottom of the reactor by means of a porous diffuser made of sintered glass (pore size: 150–250 µm). A mechanical mixing system ensured the good contact between liquid and gas phases. Experiments were performed at 20 ± 1 °C, without pH adjustment. The gas flow rate and the inlet ozone concentration were maintained at 0.1 NL min^{-1} and 30 mg NL^{-1}, respectively. Inlet and outlet gas-phase ozone concentrations were continuously monitored by two BMT 964 ozone analyzers (BMT Messtechnik, Germany) placed up and downstream the reactor, respectively. The ozone concentration in the aqueous phase was measured by means of a Q45H/64 dissolved O_3 probe (Analytical Technology, USA), which was connected to a liquid recirculation stream (flow rate: 200 mL min^{-1}). A detailed scheme of the ozonation setup is shown in Fig. 1.

The ozone consumption was determined as the transferred ozone dose (TOD), which is defined by Eq. (4) and represents the accumulated amount of ozone that is transferred to the water sample per unit of volume and time.

$$TOD = \int_0^t \frac{F_{gas}}{V_{liq}} \cdot ([O_3]_{gas,\ in} - [O_3]_{gas,\ out}) \cdot dt \tag{4}$$

F_{gas}, V_{liq} are the gas flow rate and the liquid volume, respectively; t stands for the ozonation time; $[O_3]_{gas,in}$ and $[O_3]_{gas,out}$ represent the ozone concentrations measured at the inlet and outlet gas streams, respectively. The trapezoidal method of numerical integration (integration step: 10 s) was employed in these calculations. The existent dead volume between the reactor liquid-gas interface and the outlet ozone gas analyzer was considered for TOD calculations. The reactor headspace was modelled as a continuous stirred-tank reactor (CSTR) to account for ozone dilution in the gas phase, whereas gas streams circulating through standard polytetrafluoroethylene (PTFE) tubing have been considered to follow plug-flow behavior (estimated delay: 2.0 min).

Each wastewater effluent was spiked with 100 µg L^{-1} of ACMP as $\cdot OH$ probe compound ($k_{ACMP,O3} = 0.25\ M^{-1}\ s^{-1}$ and $k_{ACMP,\cdot OH} = 2.1 \cdot 10^9\ M^{-1}\ s^{-1}$ [7], then ozonized for 60 min under the mentioned operational conditions. Samples were withdrawn at known time intervals and kept at room conditions until complete consumption of dissolved ozone was achieved. The residual concentration of ACMP was then measured by high performance liquid chromatography with UV detection (HPLC-UV). The UV absorbance data was determined with a DR6000 UV–Visible spectrophotometer (Hach, USA). Additional ozonation experiments were performed in order to test the proposed strategy for the control of micropollutants abatement. In this case, each wastewater effluent was spiked with low concentrations (25–50 µg L^{-1}) of the pesticides atrazine (ATZ), methiocarb (MC) and dichlorvos (DDVP), as well as the anti-inflammatory drug ibuprofen (IBU). The residual concentrations of these micropollutants in samples taken at various reaction times were also determined by HPLC-UV. All experiments were performed in duplicate.

The concentrations of ACMP, ATZ, MC, DDVP and IBU were quantified by means of a HPLC equipped with a diode array detector (DAD), all supplied by Agilent (1260 Infinity). The column employed

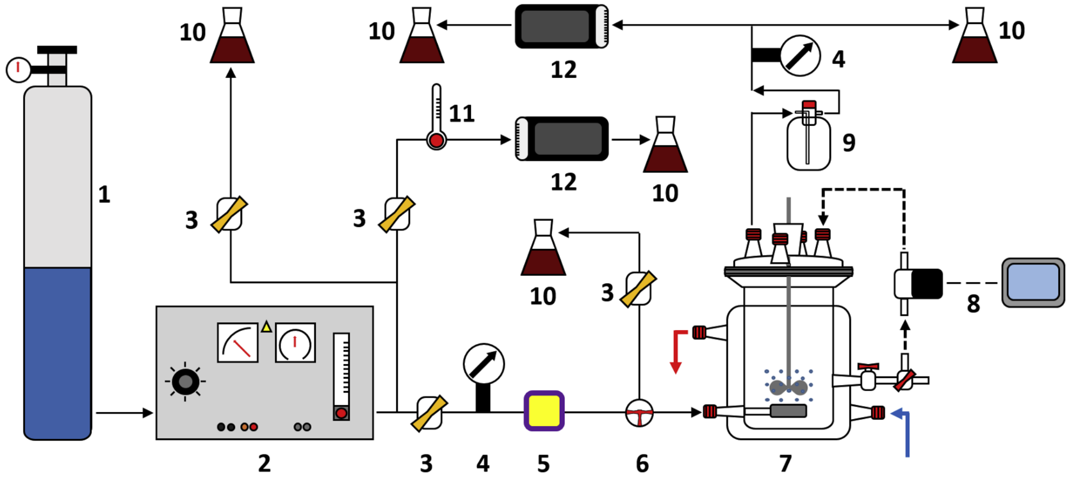

Fig. 1. Ozonation setup. 1. Oxygen bottle; 2. Ozonizer; 3. Regulating valve; 4. Manometer; 5. Gas flow-meter; 6. Three-way valve; 7. Reactor; 8. Dissolved ozone measuring system; 9. Foam trap; 10. KI solution for O_3 quenching; 11. Thermometer; 12. Ozone analyzer (gas-phase).

was a Teknokroma Mediterranea Sea18 (250 mm × 4.6 mm and 5 µm size packing). The flow rate and injection volume were set, respectively, at 1.0 mL min^{-1} and 100 µL in all determinations. For ACMP and DDVP analyses, the mobile phase consisted of 30:70 volumetric mixtures of acetonitrile and Milli-Q water acidified at pH 3 by the addition of H_3PO_4. The detection wavelength was set to 250 nm (ACMP) and 225 (DDVP) nm, respectively. For ATZ, MC and IBU quantification, the mobile phase consisted of 70:30 volumetric mixtures of acetonitrile and pH 3 Milli-Q water, and the UV detection was performed at 225 nm. The limits of quantitation were: 3.3 µg/L (ACMP), 9.2 µg/L (DDVP), 0.9 µg/L (ATZ), 8.3 µg/L (MC) and 2.1 µg/L (IBU).

3. Results and discussion

3.1. *Ozone mass transfer and demand*

During wastewater ozonation experiments, inlet and outlet (gas phase), as well as dissolved (liquid phase) ozone concentrations were continuously measured and registered (see Fig. S1 of the Supplementary Information (SI)). The monitoring of these data allowed a complete assessment of the ozone mass balance and the estimation of some parameters describing key aspects of the process, such as the ozone transfer efficiency (η_{tr}), the volumetric mass transfer coefficient (K_La), the rate of ozone decay (k_d) and the immediate ozone demand (IOD). The corresponding values for each effluent are gathered in Table 2. Further information regarding these parameters and their estimation procedures can be found in the SI (Texts S1-S3 and Figs. S2–S5).

Differences observed between effluents in ozone transfer behavior could be explained by the properties of each sample, especially – but not exclusively – the initial concentrations of dissolved and particulate organic matter (OM) (see TOC and DOC data in Table 1). This is clearly illustrated by results obtained for IOD. This parameter describes the ozone demand at the initial stage of ozonation, where this oxidant is instantaneously consumed by the reactive components of the water matrix. Thus, this parameter represents the dose of ozone for which the transition between primary (fast) and secondary (slow) ozonation stages takes place. In general, increasing contents in organic matter leads to larger ozone demands. DOC-normalized IODs (*i.e.*, IOD/DOC) were in general in the range between 0.9 and 1.2 mg O_3 mg C^{-1}, being this a proof of the similar effluent organic matter (EfOM) character and ozone needs for different effluent sources. The only exception was found to be the M-VAC sample, which presented an IOD/TOC of 1.7 (ozone demand exerted by nitrite [21] already deducted). This particular result could be probably attributed to the also individual properties of that effluent – besides nitrite content: highest pH, high alkalinity, and one of the highest UVA_{254}/DOC ratios. For the rest of parameters gathered in Table 2, in general, the relationship between ozone transfer and effluent quality observed in the present study was in agreement with previous findings and fundamental concepts [14,18,19].

Table 2
IOD, k_d and η_{tr} values determined for wastewater effluent samples.

Sample ID	IOD [mg O_3 L^{-1}]	k_d [min^{-1}]	K_La [min^{-1}]	η_{tr}, 1st-phase [tr. O_3/app. O_3]	η_{tr}, 2nd-phase [tr. O_3/app. O_3]
M-VAC	14	0.170	0.451	0.705	0.115
M-VAL	9	0.175	0.389	0.771	0.121
M-GAV	11	0.181	0.396	0.742	0.141
C-PRA	16	0.221	0.397	0.725	0.154
C-GAV	28	0.621	0.210	0.853	0.247
C-LLA	19	0.582	0.228	0.840	0.233

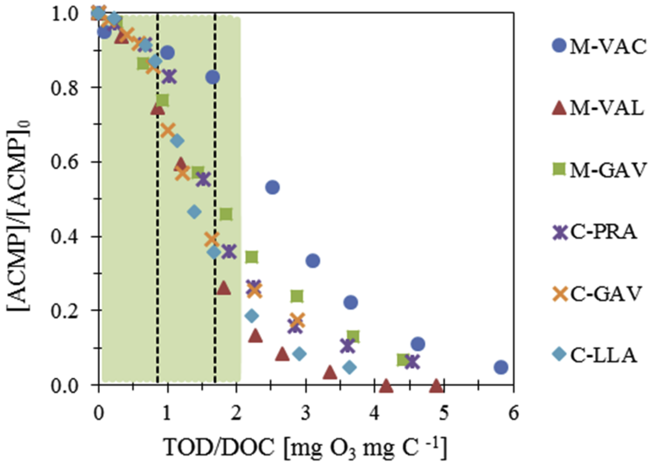

Fig. 2. Abatement of acetamiprid from different wastewater effluents during ozonation, as a function of the TOD/DOC ratio. The shaded area represents the typical range of O_3:DOC ratios applied in ozonation studies (up to 2 mg O_3 mg C^{-1}). Maximum and minimum DOC-normalized IOD values are also represented by dashed vertical lines.

3.2. *Removal of a model ozone-resistant micropollutant and determination of R_{OHO3} values*

Fig. 2 shows ACMP degradation evolution during ozonation experiments as a function of the employed O_3:DOC ratios (determined as TOD/initial DOC). Ozonation was extended to applied ozone doses significantly higher than that reported in related lab-, pilot- and full-scale ozonation works, where O_3:DOC ratios mainly between 0.5 and 1.5 mg O_3 mg C^{-1} but up to 2 mg O_3 mg C^{-1} [2,5,11,15,16] have been employed. Typical conditions applied in actual ozonation units are characterized by none or limited ozone residual in the aqueous phase during the process, that is, working within the initial ozonation stage in which all the applied ozone is instantaneously consumed, before IOD completion. In Fig. 2, the maximum and minimum DOC-normalized IOD values (IOD/DOC) determined during experimentation are represented by dashed lines.

It is clear, in the view of recent research, that currently employed ozone doses are not able to completely remove ozone-recalcitrant chemicals [2,16]. That is also obvious in the view of the findings of the present work, where ACMP removals for a maximum O_3:DOC ratio of 2 mg O_3 mg C^{-1} ranged between 30 and 80%, depending on the water source. If ozone was dosed up to IOD completion, the following ACMP degradation levels would be approximately obtained: 17% for M-VAC, 25% for M-VAL, 22% for M-GAV; 20% for C-PRAT; 31% for C-GAV and 25% for C-LLA. Definitely, if a significant abatement of ozone-recalcitrant micropollutants is wanted to be reached, ozonation should be extended beyond IOD. However, and due to the high pollution loads (*i.e.*, high DOC) of samples from conventional activated sludge effluents, the absolute doses of oxidant to apply for the abatement of O_3-resistant compounds would be considered uneconomical. Thus, for these effluents other alternatives should be explored for the removal of these chemical species from wastewaters. On the contrary, extended ozonation could be considered for clearer effluents, such as the MBR systems employed in this study.

Because of the different O_3 demands and consumptions according to the individual water qualities (see Table 2 and SI, texts S1–S3 and Figs. S1–S5), the use of $\int[\cdot OH]dt$ alone as an absolute indicator of the oxidation performance during ozonation process is not recommended. The R_{OHO3} concept can be used instead. Fig. 3 shows the $\int[\cdot OH]dt$ versus TOD (consumed ozone, according to the employed experimental methodology) plot for all the tested effluents. Linear relationships were obtained in all cases ($R^2 > 0.98$) and, according to Eq. (3), the corresponding R_{OHO3} values could be determined from their slope values

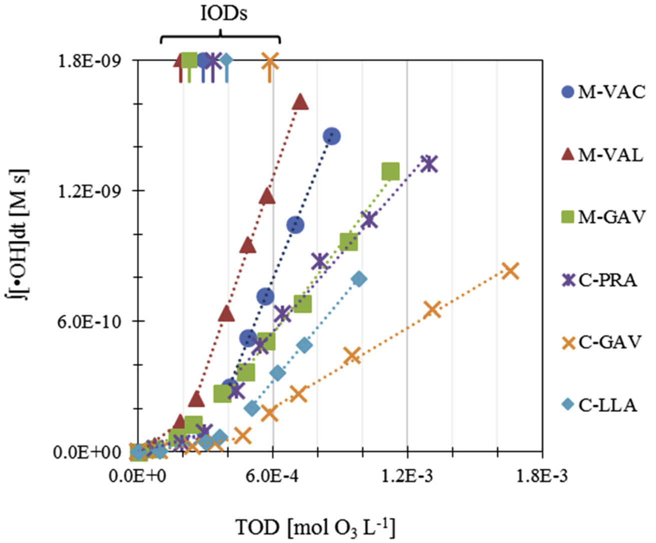

Fig. 3. $\int[\cdot OH]dt$ versus TOD plot obtained during ozonation of wastewater effluent samples spiked with acetamiprid as $\cdot$OH probe compound. The slopes of each linear regression represent the R_{OHO3} values of primary and secondary ozonation stages, which are gathered in Table 2. $[ACMP]_0 = 100\,\mu g\,L^{-1}$; Gas flow rate = 0.100 ± 0.005 NL min^{-1}; Inlet (gas) ozone concentration = 30 ± 1 mg O_3 NL^{-1}; $T_{reaction} = 20 \pm 1\,°C$, T_{in} (gas) = 22 ± 2 °C; P_{in} (gas) = 25 ± 2 mbar. Values of the immediate ozone demand (IOD) for each effluent are marked at the top of the graph and should be read by projecting the symbols on the x-axis.

(Table 3). IOD values representing the transition between both stages are also indicated in Fig. 3.

Two different R_{OHO3} were obtained for each water sample, one per each of the two ozone consumption regimes that were observed during ozonation experiments. According to the typically applied conditions in actual ozonation units, first stage R_{OHO3} value would be enough to estimate the hydroxyl radical exposure during the treatment. If ozonation is extended beyond IOD with the aim of further removing ozone-recalcitrant species, the secondary R_{OHO3} value should be also taken into account. For all effluents, the initial R_{OHO3} value was lower than the secondary one. This means that at the beginning of the reaction there were less radicals available per consumed ozone, when there is a strong mass transfer and an instantaneous ozone consumption exerted by O_3-reacting matter. After IOD completion, the amount of consumed ozone gradually decreased until stationary conditions were reached. In addition, during the early stage of ozonation the water matrix presents larger amounts of $\cdot$OH-scavenging matter. This situation changes when the regime switches to the slow phase, as a fraction of these components have already been consumed. From this point, therefore, both the O_3 consumption and $\cdot$OH scavenging rates diminish.

Changes in ozone transfer regimes turned into ca. 3 to 9-fold R_{OHO3} increases between primary and secondary ozonation stages, depending on the water source. The observed trend in initial R_{OHO3} values were M-VAL > M-GAV > M-VAC ≈ C-PRA > C-LLA > C-GAV. Although M-GAV and C-PRA exhibited similar values for $\cdot$OH exposure, the C-PRA effluent had larger ozone needs caused by a higher content in organic matter and EfOM aromaticity. Therefore, for equal $\int[\cdot OH]dt$ values the M-GAV sample presented a better oxidation efficiency. Similarly, the obtained R_{OHO3} values for M-VAC and C-PRA effluents were very close. The M-VAC effluent presents a NO_2^- content and alkalinity of 0.85 mg N L^{-1} and 329.5 mg $CaCO_3$ L^{-1}, respectively, versus the 0.09 mg N L^{-1} and 263.5 mg $CaCO_3$ L^{-1} exhibited by the C-PRA sample. Thus, differences in OM content between these two waters [M-VAC (TOC: 6.7 mg L^{-1}), C-PRA (TOC: 14.0 mg L^{-1})], were compensated by a larger O_3 consumption without $\cdot$OH generation (nitrite) and also a higher $\cdot$OH scavenging rate (carbonates) in the case of the M-VAC effluent. M-VAL, C-GAV and C-LLA effluents presented the highest and the two lowest oxidation efficiencies, respectively, which could be also explained by their relative water qualities: the M-VAL sample had relatively low values TOC and alkalinity, whereas the opposite situation was observed for C-GAV and C-LLA effluents.

3.3. Effluent organic matter transformation during wastewater ozonation: Evolution of UV_{254} absorbance

The absorbance spectra as a function of the transferred ozone dose (TOD) revealed a proportional decay in the UV absorption of the water throughout the entire ozonation time, at practically any of the studied wavelengths and for all the ozonized effluents (Fig. S6 of the SI). As known, the electron-rich moieties present in wastewater effluents (EfOM), with typically strong UV absorptions [27], are certainly reactive to ozone: a sustained decrease in the UV absorption was therefore expected during the ozonation process. Fig. 4 shows, for all the tested effluents, the plot of the relative decrease in UV absorbance with time (A), as well as negative, natural logarithm of the relative UV absorbance versus the consumed ozone (B), represented in this case by the TOD. A wavelength of 254 nm was chosen for absorbance monitoring since UVA_{254} is one of the parameters typically monitored in practice.

$$-\ln\left(\frac{UVA_{254}}{UVA_{254,0}}\right) = k_{UVA,O3}\cdot TOD \tag{5}$$

The relationship between the absorbance decrease and the TOD is expressed by Eq. (5). This is reasonable here since the decay of UVA_{254} has been demonstrated to follow a first-order kinetic relationship with respect to ozone, and the ozone exposure (*i.e.*, the time-integrated O_3 concentration) is directly proportional to the consumed dose of this oxidant [3]. In the view of the obtained results (Fig. 4B), in which linear relationships with regression coefficients greater than 0.98 were generally obtained, these assumptions were confirmed.

Again, two different regimes were observed regarding the rate of UVA_{254} reduction ($k_{UVA,O3}$, Table 3) in accordance with the relative amount of aromatic and unsaturated moieties contained in the EfOM along ozonation, for each one. M-VAL wastewater effluent exhibited the highest rate constant for UVA_{254} depletion ($2.59{\cdot}10^3$ M^{-1}), whereas for the C-GAV effluent ($0.77{\cdot}10^3$ M^{-1}) resulted to be the lowest one. This

Table 3
Summary of R_{OHO3}, $k_{UVA,O3}$ and $k_{UVA,OH}$ (experimental and determined as $k_{UVA,O3}/R_{OHO3}$) values obtained for ozonized wastewater effluents. Correlation coefficients (R^2) > 0.98 were obtained in all cases. Discrepancies between coefficients values obtained in duplicate experiments were in all cases lower than 5%.

WW ID	R_{OHO3} [s]		$k_{UVA,O3}$ [M^{-1}]		$k_{UVA,OH}$ (experimental) [$M^{-1}s^{-1}$]		$k_{UVA,OH}$ ($k_{UVA,O3}/R_{OHO3}$) [$M^{-1}s^{-1}$]	
	1st (×10^7)	2nd (×10^6)	1st (×10^{-3})	2nd (×10^{-3})	1st (×10^{-9})	2nd (×10^{-8})	1st (×10^{-9})	2nd (×10^{-8})
M-VAC	2.95	2.53	1.64	1.50	5.73	5.90	5.56	5.92
M-VAL	7.60	2.95	2.59	1.79	3.37	6.06	3.41	6.05
M-GAV	5.29	1.35	1.88	0.82	3.49	5.98	3.55	6.08
C-PRA	2.94	1.18	1.48	0.76	4.94	6.46	5.03	6.43
C-GAV	1.53	0.61	0.77	0.25	5.00	4.20	5.05	4.09
C-LLA	1.79	1.23	0.93	0.59	5.13	4.80	5.20	4.80

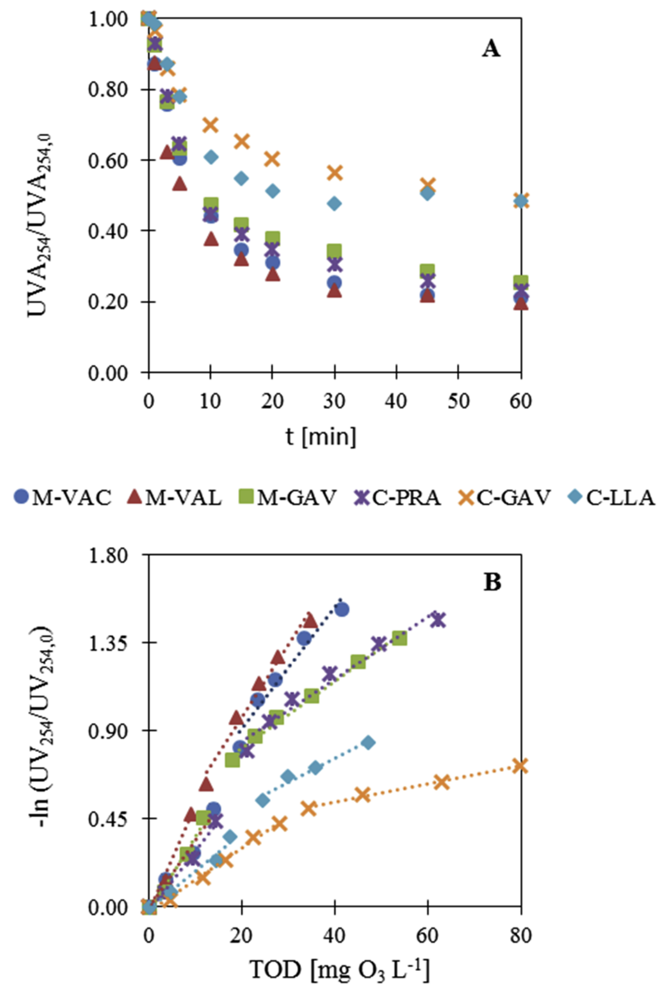

Fig. 4. Changes in UV absorbance during ozonation of wastewater effluents. UVA_{254} evolution with time (A) and logarithmic relative decrease in UVA_{254} (B) as a function of the transferred ozone dose (TOD).

approximately 4-fold factor is partly explained by the huge differences found in particulate/colloidal organic matter content of the CAS effluent with respect to the MBR effluent, (see turbidity, TOC and DOC values in Table 1) [19]. If the focus is put in waters in which less or no solids were present (M-VAL, M-VAC, M-GAV and C-PRA), other water quality parameters with high influence on the ozonation process, such as the carbonate presence (alkalinity) or the EfOM aromaticity can play an important role. So, the MBR effluent with the fastest kinetics (M-VAL) is also the one with a lower carbonate alkalinity content (178 mg $CaCO_3\,L^{-1}$). ·OH oxidation appears to play a significant role in the UVA_{254} reduction process during ozonation, and a significant increase in the carbonate content reduces this important contribution by means of the scavenging effect.

3.4. Kinetic modelling using the R_{OHO3} concept and UVA_{254} monitoring

If the relationship between ·OH exposure and transferred ozone (*i.e.*, R_{OHO3} definition, Eq. (3)) and the relationship between UVA_{254} decay and TOD (Eq. (5)) are both combined, a new expression relating the absorbance decrease and the ·OH exposure can be obtained (Eq. (6)).

$$-\ln\left(\frac{UVA_{254}}{UVA_{254,0}}\right) = k_{UVA,OH}\cdot \int [\bullet OH]\ \mathrm{d}t \tag{6}$$

Therefore, if the logarithm of the relative measured UVA_{254} is graphically represented against the time-integrated hydroxyl radical concentration, a linear correlation is expected. Fig. 5 shows the logarithm of relative UVA_{254} as a function of the hydroxyl radical exposure, determined for all the tested effluents. Experimental data were fitted by straight lines ($R^2 > 0.98$), thus confirming the linear behavior for this data set previously deduced by means of theoretical analysis. Obtained $k_{UVA,OH}$ values, that is, the slope of the obtained linear relationship described by Eq. (6), are gathered in Table 3. To further validate the relationship obtained by the combination of Eqs. (2) and (4), $k_{UVA,OH}$ calculated as $k_{UVA,O3}/R_{OHO3}$ was also included in this table and compared with the experimentally determined values, obtaining differences ranging from 0.1 to 3.0%.

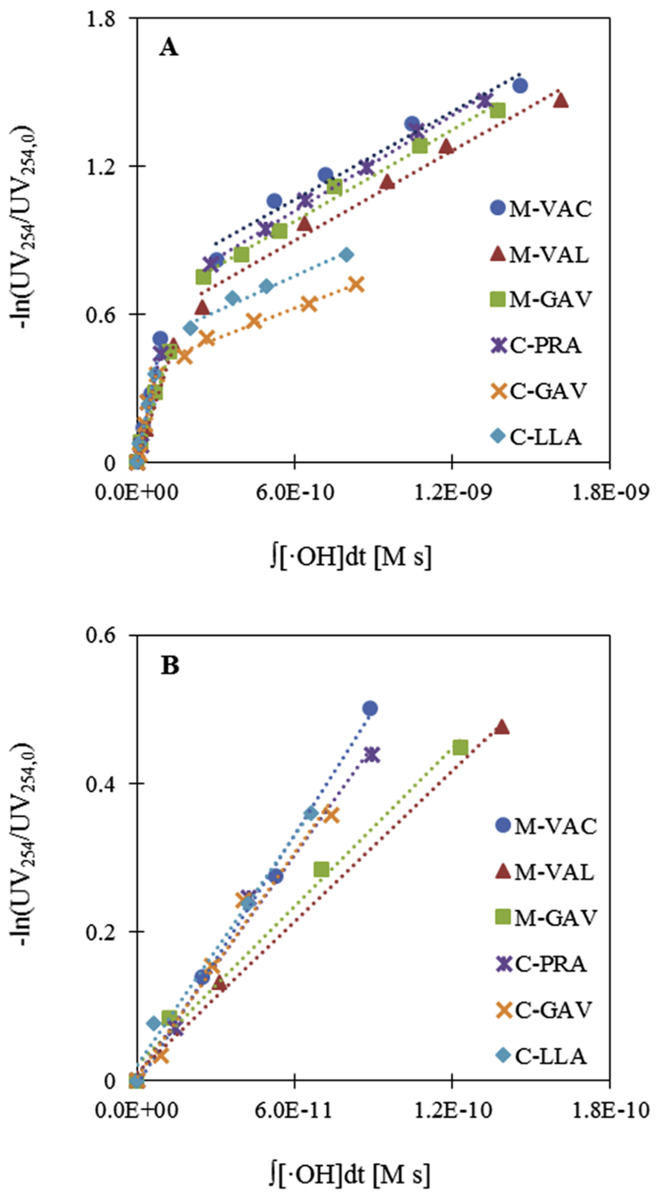

Fig. 5. Natural logarithm of relative UVA_{254} as a function of ·OH exposure, determined during ozonation experiments of different wastewater effluent samples: A, entire ozonation time; B, zoom of data corresponding to initial ozonation stage.

According to the obtained results, good correlations could be established between ·OH-exposure and UVA_{254} attenuation, which opens the door to potential real-time estimations of the $\int [\cdot OH]dt$ term by means of online UVA_{254} measurements. The use of a similar approach has been recently reported by Chys et al., who obtained good correlations between ·OH-exposure and both UVA_{254} and TF attenuation (R^2 in the range of 0.82–0.90) in lab-scale wastewater ozonation

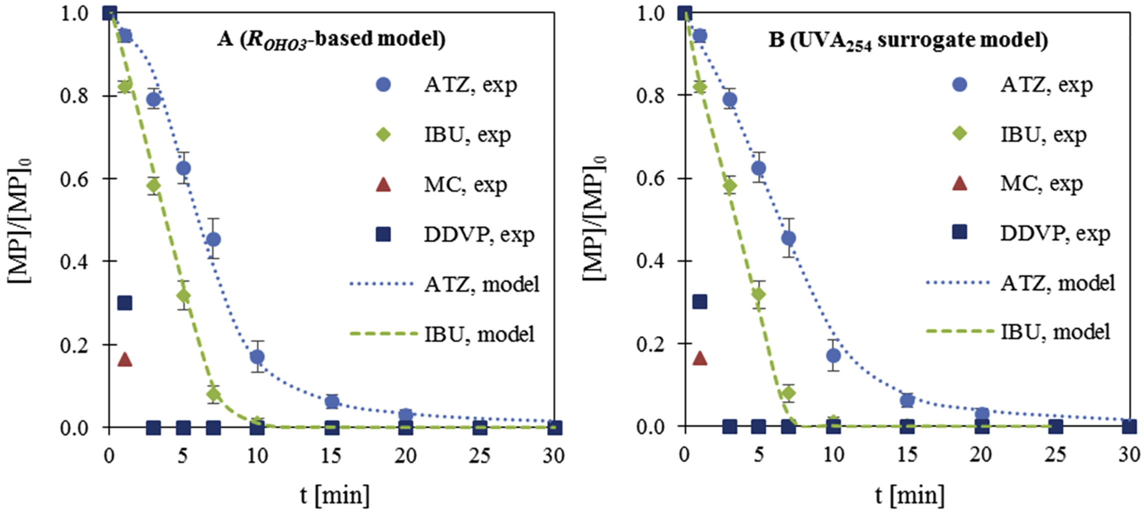

Fig. 6. Prediction of ATZ and IBU removals during ozonation of M-VAC (representative example) effluent, employing both the R_{OHO3} concept (A) and the UVA$_{254}$-based strategy for ·OH exposure prediction (B). $[ATZ]_0 = [IBU]_0 = 25\ \mu g\ L^{-1}$, $[MC]_0 = [DDVP]_0 = 50\ \mu g\ L^{-1}$; Gas flow rate = 0.100 ± 0.005 NL min^{-1}; Inlet (gas) ozone concentration = 30 ± 1 mg O_3 NL^{-1}; $T_{reaction}$ = 20 ± 1 °C, T_{in} (gas) = 22 ± 2 °C; P_{in} (gas) = 25 ± 2 mbar.

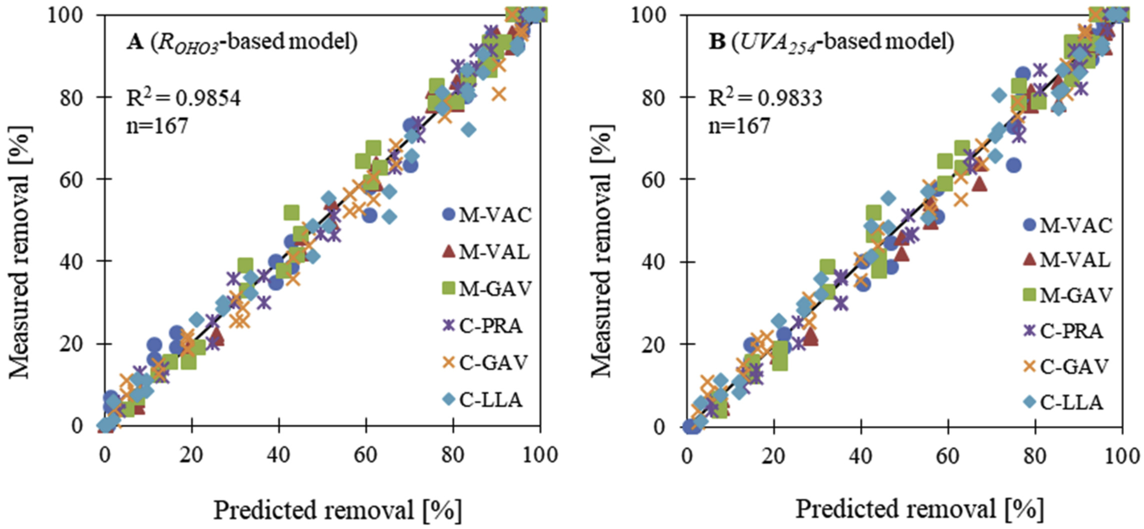

Fig. 7. Measured versus predicted removals for atrazine and ibuprofen in six different wastewater effluents, employing both R_{OHO3} (A) and UVA_{254}-based (B) models.

experiments. Similarly to R_{OHO3} concept, initial $k_{UVA,OH}$ values obtained in the present study would be useful to perform ·OH-exposure estimations during the primary ozonation stage, that is, if working ozone doses are within IOD completion. That situation, as mentioned, would represent typical operational conditions of actual ozone applications for enhanced water and wastewater treatment. However, if ozonation is wanted to be extended up to the application of O_3 doses beyond IOD, the second-stage $k_{UVA,OH}$ value should be used for ·OH-exposure predictions in the secondary ozonation stage. By means of these two values, therefore, a complete characterization of the radical availability during the whole ozonation process is certainly possible.

It seems to be that even a general model for ·OH-exposure prediction by UVA$_{254}$ measurements could be proposed for clearer effluents such as membrane bioreactor effluents and C-PRA (R^2 = 0.94 and 0.92 for initial and secondary ozonation stages, respectively, see SI-Fig. S7). Significant deviations from these predictions, however, would be observed for CAS effluents with relatively high content in OM and inorganic salts (*i.e.*, C-GAV and C-LLA samples). Further investigations, therefore, would be required in these cases to accurately quantify the individual and synergistic effects exerted by main matrix components, so proper corrections according to the water quality could be applied to the model.

3.5. Prediction of ozone-resistant micropollutants removal by means of models based on R_{OHO3} and UVA_{254} measurements

In order to evaluate the usefulness of both the R_{OHO3} concept and the newly developed method for ·OH exposure monitoring by means of UVA$_{254}$ measurements, removal prediction assays were conducted for each wastewater effluent and two typical target compounds: ibuprofen (IBU) and atrazine (ATZ). The deprotonated form of both chemicals, predominant at neutral pH, present low reactivity towards ozone, with second-order rate constants of 9.6 and 6 $M^{-1}s^{-1}$, respectively, and moderate/high reactivity with hydroxyl radicals ($k_{\bullet OH}$ of $7.4 \cdot 10^9$ and $3.0 \cdot 10^9\ M^{-1}s^{-1}$ for IBU and ATZ, respectively) [1,13]. According to Eq. (2) and both the R_{OHO3} and $k_{UVA,O3}$ definitions (Eqs. (3) and (5)), the removal of these two O_3-resistant micropollutants (MPs) can be predicted by Eqs. (7) and (8), respectively.

$$-\ln\left(\frac{[MP]}{[MP]_0}\right) = k_{\bullet OH}\cdot R_{OHO3}\cdot TOD \tag{7}$$

$$-\ln\left(\frac{[MP]}{[MP]_0}\right) = k_{\bullet OH}\cdot\frac{-\ln\left(\frac{UVA_{254}}{UVA_{254,0}}\right)}{k_{UVA,OH}} \tag{8}$$

Consistently with the work developed in this study, and according to the fact that we extended ozonation experiments in order to achieve the complete abatement of ozone-recalcitrant micropollutants, two-phase models were employed for these calculations using the R_{OHO3} and $k_{UVA,O3}$ values determined in primary and secondary ozonation stages, for each tested water source.

Fig. 6 shows the removal profiles of ATZ and IBU predicted for the M-VAC effluent, as representative example, together with the relative residual concentrations experimentally determined during the tests. The concentrations of two additional micropollutants, the pesticides methiocarb (MC) and dichlorvos (DDVP), were also followed during removal prediction tests. MC presents high reactivity towards both O_3 and $\cdot OH$ ($k_{MC,O3} = 1.7{\cdot}10^6\,M^{-1}\,s^{-1}$ and $k_{MC,{\cdot}OH} = 8.2{\cdot}10^9\,M^{-1}\,s^{-1}$, [8], whereas the insecticide DDVP rapidly reacts with hydroxyl radical but has a moderate reaction rate with ozone ($k_{DDVP,O3} = 590\,M^{-1}\,s^{-1}$ and $k_{DDVP,{\cdot}OH} = 2.2{\cdot}10^9\,M^{-1}\,s^{-1}$, [6]. Similar plots were obtained for the rest of tested effluent samples (see SI, Figs. S8 and S9). In all cases, a good agreement between model predictions and experimental measurements was observed. An initial, rapid removal rate followed by a slower degradation period was observed for ATZ and IBU, being the depletion of ATZ always less efficient than that for IBU. This was kinetically consistent, as IBU presents lower rate constant with $\cdot OH$ than ATZ. On the other hand, MC and DDVP pesticides were degraded below their respective detection limits at a contact time less than 5 min. These results highlight again the strong dependence between the removal of micropollutants with low ozone reactivity and $\cdot OH$ exposure, which in turn can represent a limiting factor when implementing ozonation treatments in secondary effluents. Chemicals with significant ozone reactivity here illustrated by the MC and DDVP examples in this work are always faster eliminated by the contribution of direct ozonation. Finally, Fig. 7 shows how the removal of IBU and ATZ could be accurately predicted by employing both R_{OHO3} and $k_{UVA,OH}$ concepts along with chemical kinetics, in a wide range of wastewater effluent qualities ($R^2 > 0.98$ for both models), down to complete recalcitrant micropollutants abatement.

4. Conclusions

The production of a high quality reclaimed wastewater, especially if the final application of this water involves potential human exposure, may require the monitoring and control of ozone-resistant micropollutants from wastewater effluents. In this work, the oxidation performance of the whole semi-continuous ozonation process could be well described by means of a two-stage model based on R_{OHO3} concept. Determining the R_{OHO3} values necessary to describe both initial and secondary ozonation stages was achieved by coupling chemical kinetics with a proper assessment of the ozone mass transfer. This tool was demonstrated to be useful to describe and compare the process in different effluents showing a broad range of water properties. By means of this approach, hydroxyl radical exposures during ozonation could be accurately determined during the whole treatment, provided that the consumed ozone dose was always known. Also derived from a strategy based on the R_{OHO3} concept, a new model involving UVA_{254} monitoring was proposed for the online estimation of hydroxyl radical exposure along the entire process. The fundamentals of a potential strategy for the monitoring and control of ozone-recalcitrant micropollutants abatement during ozonation have been developed and presented in this paper. Further research in this direction is from now on required, including exhaustive studies concerning the influence of water quality and seasonal variations on the kinetic parameters of the model (*i.e.*, R_{OHO3} and $k_{UVA,OH}$).

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2018.10.206.

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Supplementary Information for

Abatement of ozone-recalcitrant micropollutants during municipal wastewater ozonation: kinetic modelling and surrogate-based control strategies

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The SI includes the following 9 figures and 3 additional texts:

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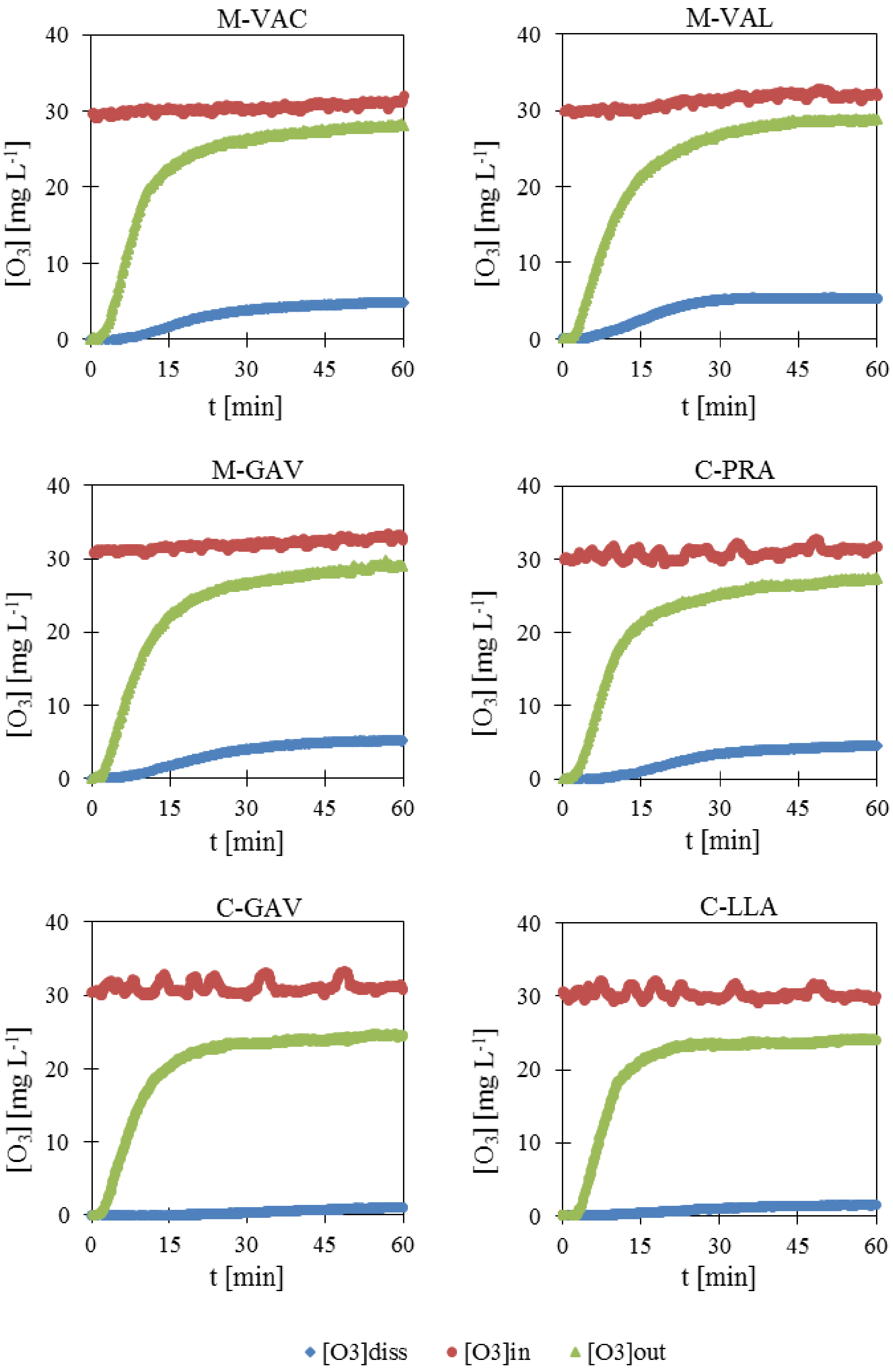

Figure S1. Measured inlet (g), outlet (g) and dissolved (liq.) ozone concentrations during secondary effluent ozonation experiments. Gas flow rate = 0.1 ± 0.005 NL min^{-1}; Inlet (g) ozone concentration = 30 ± 1 mg O_3 NL^{-1}; $T_{reaction}$ = 20 ± 1 °C; T_{in} (gas) = 22 ± 2 °C; P_{in} (gas) = 25 ± 2 mbar.

Text S1 Determination of ozone transfer yields and volumetric mass transfer coefficients (K_La).

The monitoring of inlet and outlet (gas) ozone concentrations during effluents ozonation allowed the assessment of the ozone mass balance. Fig. S2 shows the transferred ozone dose (TOD) and transfer yield evolution as a function of the applied ozone dose, for all the tested effluents. The slope values of the TOD profiles (η_{tr}, see Fig. S2) were employed to estimate the ozone transfer efficiency during primary and secondary ozonation stages and can be found in the main text (Table 2). The volumetric mass transfer coefficient, K_La, was one of the parameters describing ozone mass transfer that could be estimated during wastewater ozonation experiments. A detailed explanation of the employed calculation procedure can be found elsewhere (Marce et al., 2016).

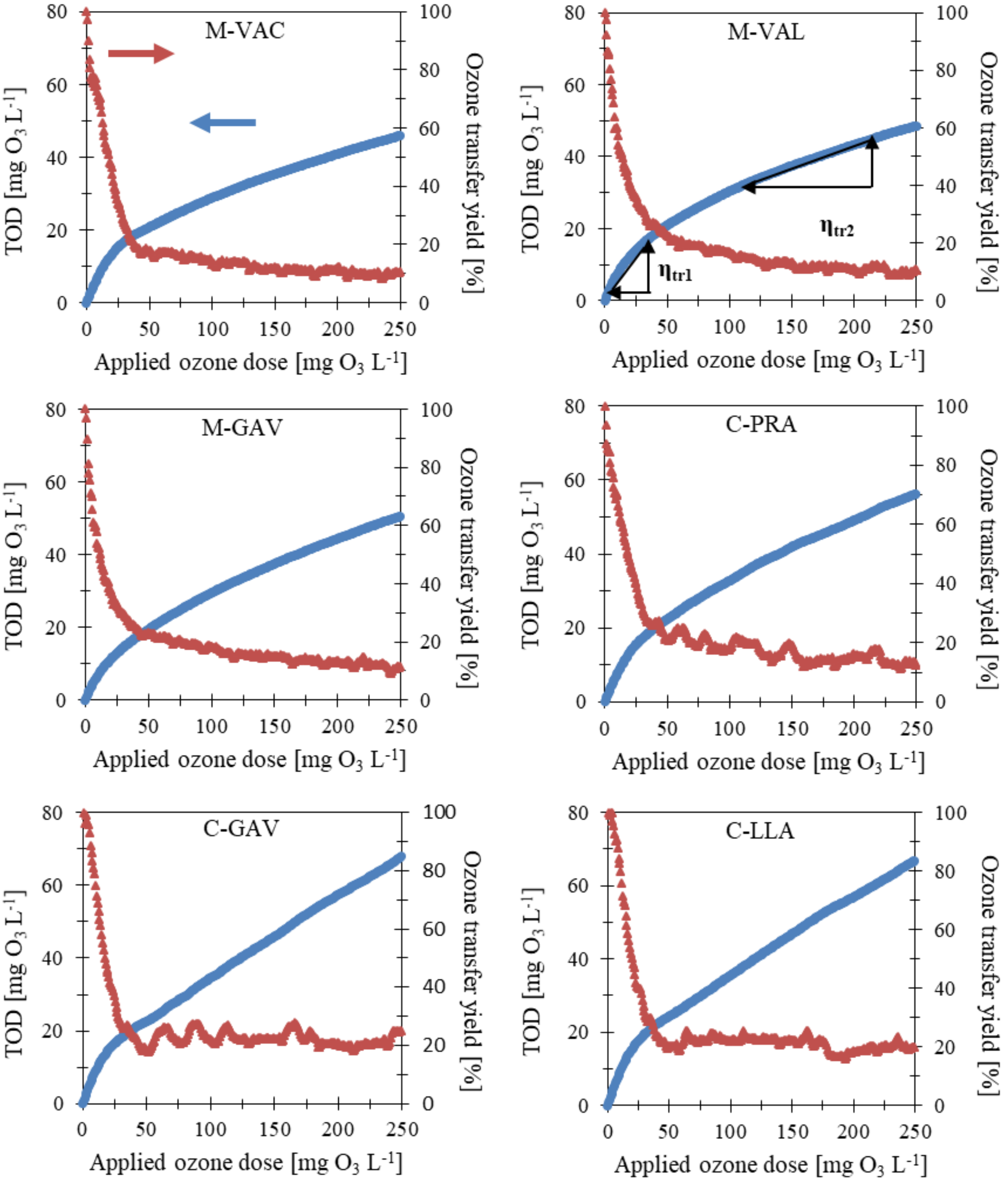

Figure S2. TOD (primary y-axis) and ozone transfer yield (secondary y-axis) evolution for tested wastewater effluents during ozonation experiments.

Text S2 Determination of immediate ozone demand (IOD)

Ozone concentration measurements in the liquid phase allowed the estimation of the immediate ozone demand (IOD). The IOD represents the amount of ozone that is consumed during the initial ozonation stage, in which a fraction of fast, O_3-reacting matter present in the reaction medium is instantaneously transformed by the oxidant. During this period, ozone cannot be detected in the liquid phase. Fig. S3 shows the evolution of dissolved ozone concentration as a function of the transferred ozone dose (TOD) for the six tested effluents. The TOD value from which this oxidant started to be detected in the reaction medium is a good estimate for IOD (Roustan et al., 1998).

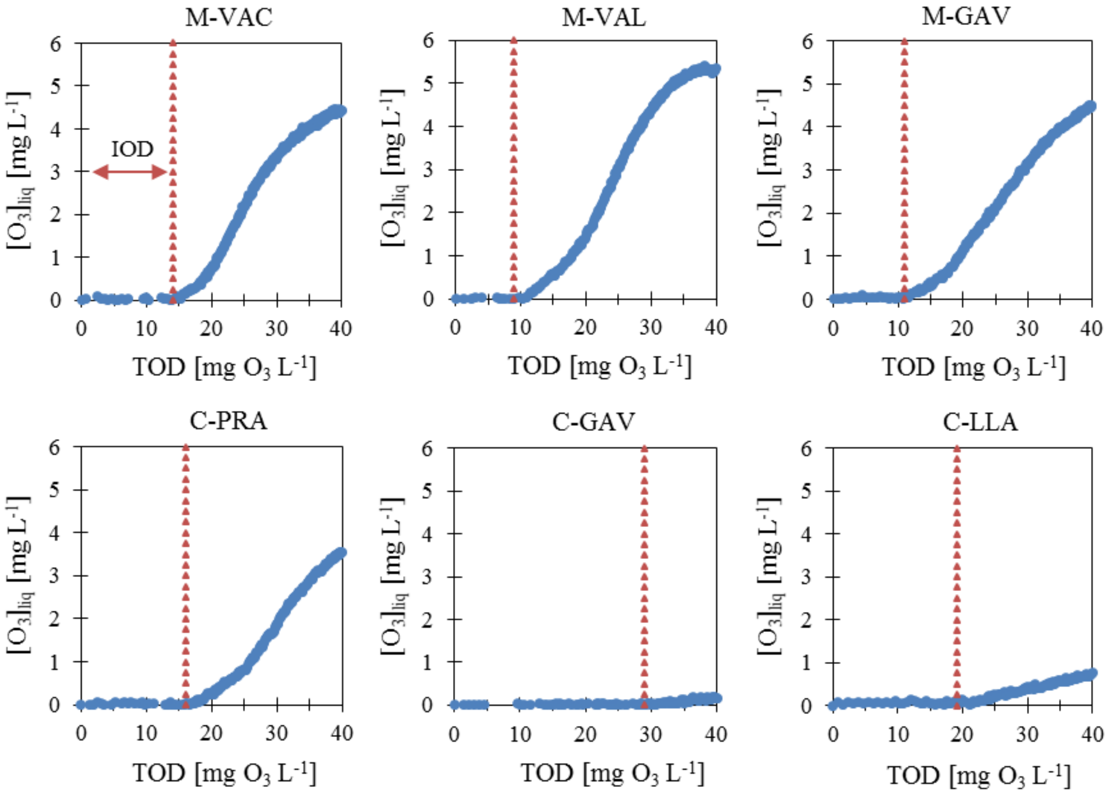

Figure S3. Dissolved ozone concentration as a function of the transferred ozone dose (TOD). These plots were employed to determine the immediate ozone demand (IOD, indicated in the first subplot) of each wastewater effluent.

Text S3 Determination of first-order ozone decay constant (k_d).

The constant k_d represents the overall rate of ozone decay due to moderate and slow reactions in the secondary ozonation stage, and generally follows first-order kinetics (Buffle et al., 2006). This parameter is largely dependent on the water matrix properties, especially the pH, the concentration and nature of OM and the alkalinity (Von Gunten, 2003). The obtained values are shown in Table 2 of the main text. Ozone decay curves and first-order plots employed in k_d determinations can be found in Figs. S4 and S5.

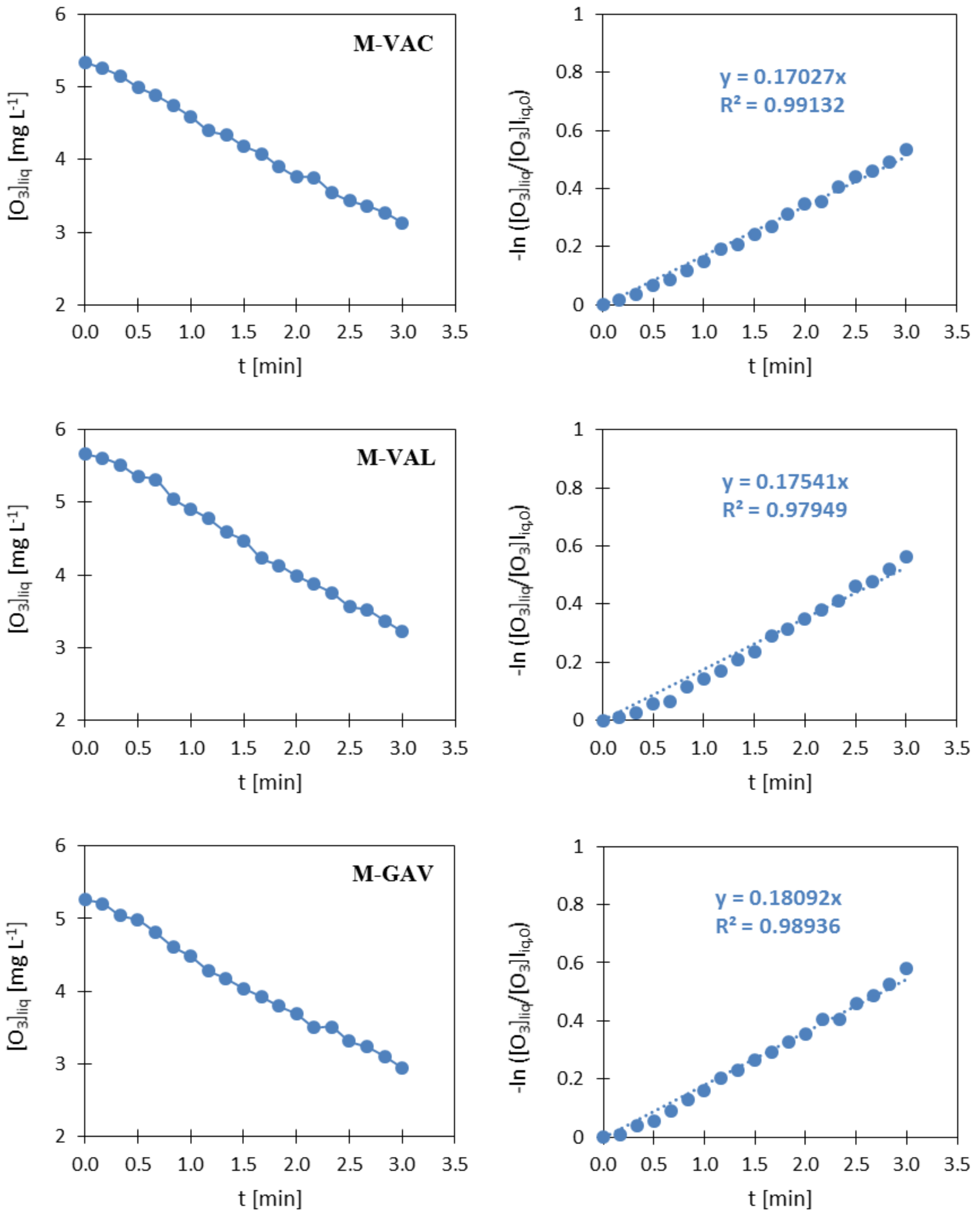

Figure S4. Determination of first-order ozone decay constant k_d (secondary ozonation stage) for MBR effluents, after 60 min of ozonation (stationary conditions were already achieved).

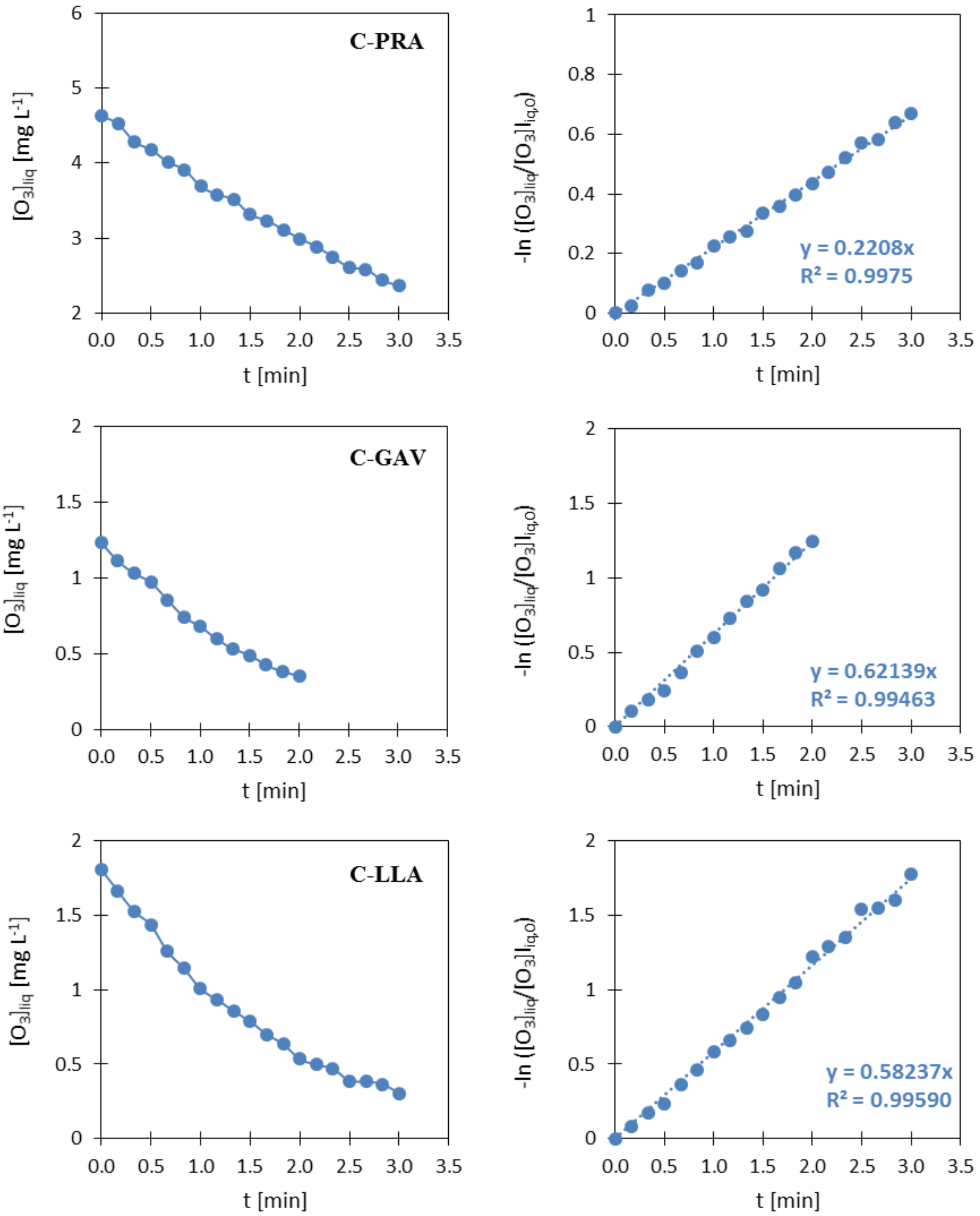

Figure S5. Determination of first-order ozone decay constant k_d (secondary ozonation stage) for CAS effluents, after 60 min of ozonation (stationary conditions were already achieved).

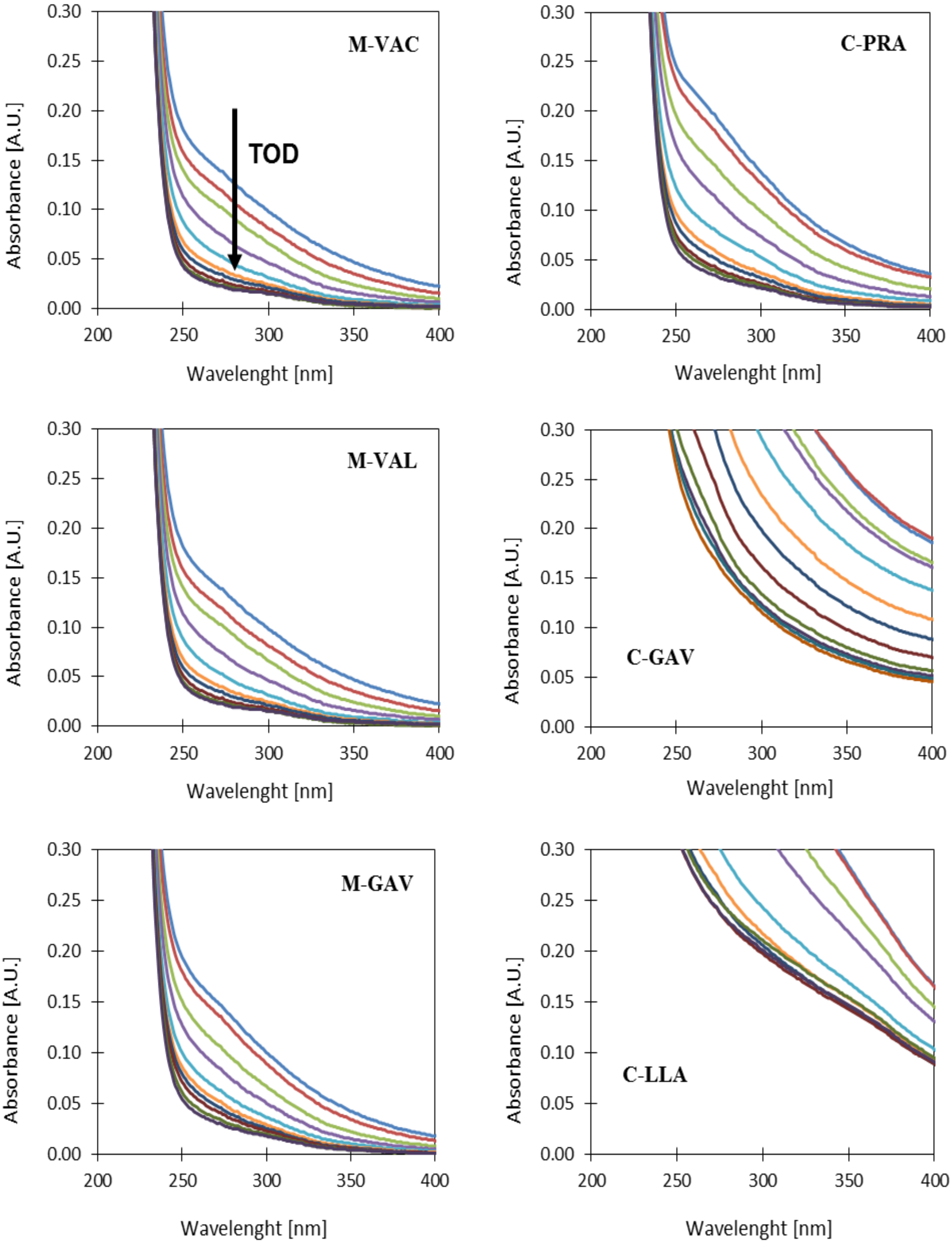

Figure S6. Changes in UV absorbance spectra with increasing ozone consumption (TOD), for all the tested wastewater effluents.

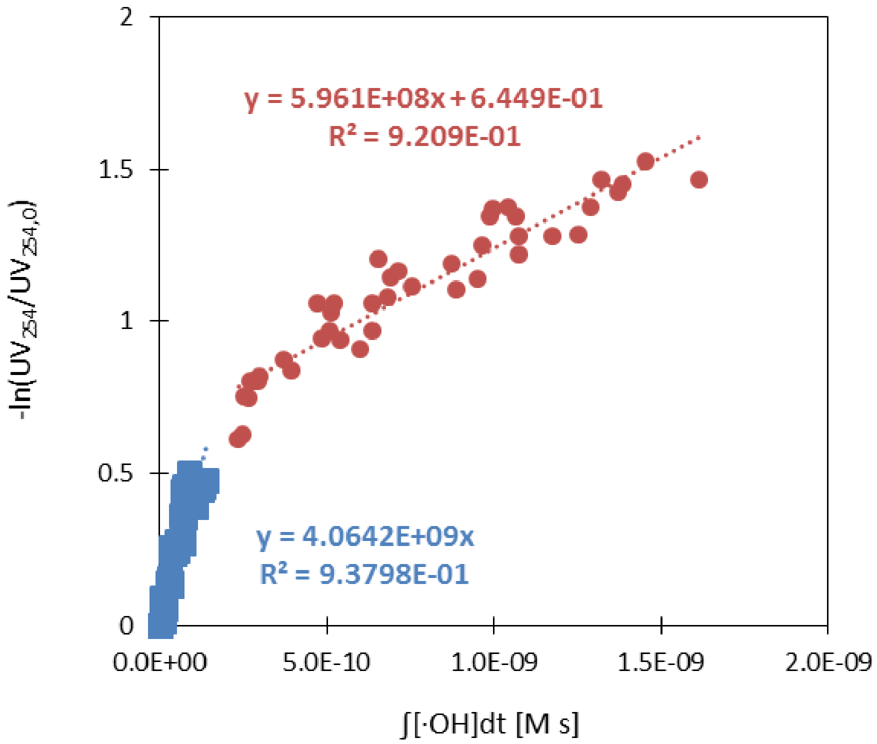

Figure S7. Hypothetic, general model for •OH-exposure prediction by means of UVA254 monitoring for clearer (*i.e.*, those coming from MBR systems and C-PRA) effluents.

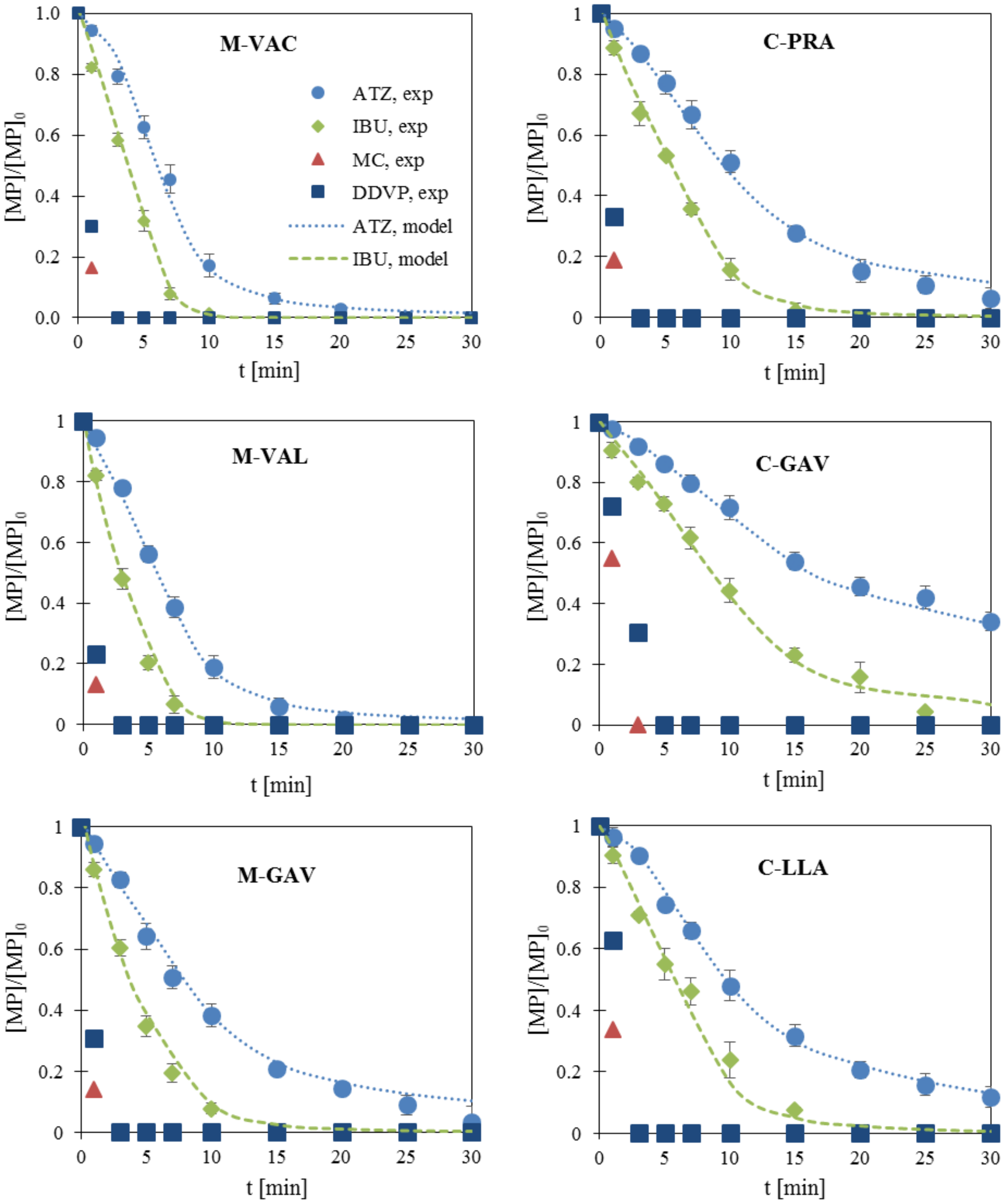

Figure S8. Prediction of ATZ and IBU removals during ozonation of wastewater effluents, employing the model based on R_{OHO_3} experimentally determined values. Results corresponding to the M-VAC effluent are shown in the main text, as representative example. Experimental conditions: $[ATZ]_0 = [IBU]_0 = 25$ µg L^{-1}, $[MC]_0 = [DDVP]_0 = 50$ µg L^{-1}; Gas flow rate = 0.1 ± 0.005 NL min^{-1}; Inlet (gas) ozone concentration = 30 ± 1 mg O_3 NL^{-1}; $T_{reaction} = 20 \pm 1$ °C, T_{in} (gas) = 22 ± 2 °C; P_{in} (gas) = 25 ± 2 mbar.

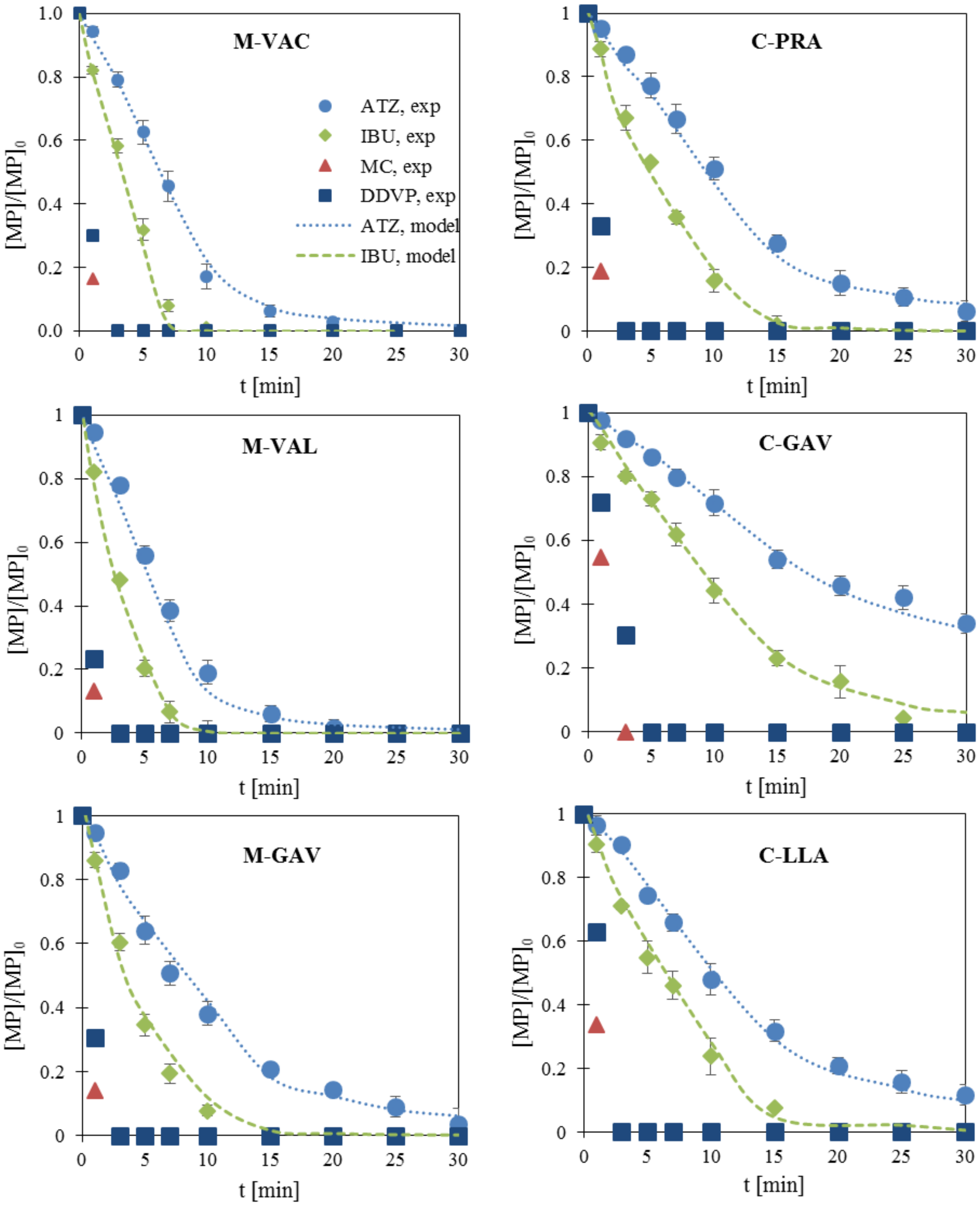

Figure S9. Prediction of ATZ and IBU removals during ozonation of wastewater effluents, employing the model based on the UVA$_{254}$ monitoring for •OH-exposure prediction strategy. Results corresponding to the M-VAC effluent are shown in the main text, as representative example. Experimental conditions: [ATZ]$_0$ = [IBU]$_0$ = 25 μg L^{-1}, [MC]$_0$ = [DDVP]$_0$ = 50 μg L^{-1}; Gas flow rate = 0.1 ± 0.005 NL min^{-1}; Inlet (gas) ozone concentration = 30 ± 1 mg O$_3$ NL^{-1}; T$_{reaction}$ = 20 ± 1 ºC, T$_{in}$ (gas) = 22 ± 2 ºC; P$_{in}$ (gas) = 25 ± 2 mbar.

Appendix V

New insights on the fate of EfOM during ozone application for effective abatement of micropollutants in wastewater effluents

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New insights on the fate of EfOM during ozone application for effective abatement of micropollutants in wastewater effluents

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ABSTRACT

Alterations occurring in the effluent organic matter (EfOM) during ozonation could be detrimental depending on the final application of the treated effluent. In this work, the fate of EfOM in different ozonized wastewaters was assessed through the monitoring of general water quality parameters and organic fractions determined through size-exclusion chromatography combined with organic carbon detection (SEC-OCD) analysis. The abatement of an ozone-refractory micropollutant was employed as reference. UVA_{254} and COD reductions ranged from 40 to 80% and from 10 to 45%, respectively, for ozone doses between 0.6 and 1.0 mM, depending on the organic matter content (both dissolved and suspended) and alkalinity of the effluents. DOC analysis showed 21-27% reductions in MBR effluents, whereas for CAS samples this value increased (6-35%) during the oxidative treatment. This was attributed to the continuous solubilization of humic substances, according to SEC-OCD results. Moreover, accumulation of lower molecular weight fractions such as building blocks or acids was observed in all the tested effluents, attributed to the breakdown of largest EfOM fractions, mainly humic substances. Relationships proposed in this work between humic substances evolution, water quality (UVA_{254}) and process parameters (IOD, $\int[\bullet OH]\,dt$/IOD, TOD) might be useful for EfOM variations estimations along ozonation.

KEYWORDS

Wastewater ozonation, micropollutants oxidation, EfOM fractions, SEC-OCD, humic substances

1. Introduction

In a time in which water scarcity increasingly constitutes one of the most serious threats for human and environmental safety, enhanced wastewater treatment and reclamation consolidates as the strategy to follow if sustainability regarding this vital resource is wanted to be preserved [1–3]. Advanced treatment of effluents released into freshwater bodies minimizes the negative impacts (*i.e.*, pollution of the receiving aqueous compartments) derived from this practice. Reclaimed wastewater can be employed for a variety of non-potable uses, including agricultural and municipal irrigation, environmental applications, recreational activities or industrial processes [3,4]. By means of these practices, significant volumes of freshwater –otherwise wasted– are saved. However, the use of this alternative water source in applications implying further human or animal exposure is limited by the presence of organic micropollutants which, although in general not regulated, pose potential risks for living species [1]. Considering this particular issue, ozonation is nowadays one of the most recognized advanced treatment technologies for enhanced wastewater treatment and reclamation purposes [5–11].

So far, most studies dealing with ozonation of wastewater effluents mainly focus on the fate of micropollutants and harmful oxidation byproducts, such as bromates [12–14]. Changes in effluent organic matter (EfOM) are traditionally set aside or studied, at most, through the variation of general related parameters such as total and dissolved organic carbon (TOC and DOC, respectively), chemical oxygen demand (COD) or ultraviolet absorbance (UVA) [15–20]. There is still, however, a lack of knowledge regarding the fate of the different organic fractions during municipal wastewater ozonation. Deeper information can be obtained by means of size-exclusion chromatography in combination with organic carbon detection, SEC-OCD [21], which is able to separate and quantify biopolymers (BP), humic substances (HS), building blocks (BB), low molecular weight neutrals (LMWN) and low molecular weight acids (LMWA). The sizes and a brief description of these five groups are gathered in Table 1.

Table 1. Properties of dissolved EfOM fractions.

Dissolved EfOM fraction	**Molecular weight**	**Description**
Biopolymers (BP)	50000-2000000	Associated to amino acids and proteins. Do not absorb UV radiation.
Humic substances (HS)	100-100000	Mix of hydrophobic humics and humic/fulvic acids, in varying concentrations
Building blocks (BB)	350 - 500	Degradation intermediates of humic substances
Low molecular weight neutrals (LMWN)	< 350	Short chain, non-acidic degradation products: alcohols, aldehydes, ketones…
Low molecular weight acids (LMWA)	< 350	Final degradation products of organics

Although only few of them use the above classification, there are several publications in literature describing the impact of wastewater effluent ozonation on EfOM fractions [22–31]. However, in some of these works the employed ozone doses were either not properly quantified [22,23] or too high to be considered for practical applications [24]. Moreover, changes in EfOM fractions are often available in a very qualitatively way [25–27], or expressed as variations in the average molecular size but not quantified in terms of organic carbon concentrations [28,29]. In other few works, changes in EfOM fractions were not related to or discussed together with micropollutants oxidation or the reduction of any other general parameters typically monitored in wastewater treatment [30,31]. None of these studies discuss the fate of EfOM for various wastewater sources presenting different water qualities.

EfOM contained in reclaimed wastewater treated by ozonation can cause some technical and environmental problems if further treatments are planned next. For instance, residual OM could contribute to the formation of harmful disinfection by-products in a subsequent disinfection step, or be partly responsible for membrane fouling in a filtration unit [32,33]. Also, EfOM can compete with target pollutants for adsorption sites in activated carbon systems or avoid the separation of these chemicals from the water matrix if these are bound to the organic matter surface [32,33]. Moreover, since prior to be used this water need to be redirected to its final destination, EfOM can be a perfect substrate for bacterial growth in distribution systems, or cause eutrophication in receiving water compartments if the final use is related to surface or groundwater recharge [32].

This work aimed to contribute to the –still– scarce knowledge regarding the variation of EfOM fractions during ozonation of wastewater effluents. Concretely, the objective of the study was to assess changes taking place when ozone doses required for the effective abatement of micropollutants are applied. To do so, ozonation experiments in semi-continuous mode where performed for six different wastewater effluents presenting a wide range of water qualities and spiked with an ozone-resistant organic micropollutant as internal reference. The evolution of distinguishable dissolved EfOM fractions was then followed by means of the SEC-OCD technique, together with variations observed for other parameters typically discussed in practice, such as UVA_{254}, COD and DOC. Finally, some relationships between EfOM changes and some effluent quality and ozonation parameters were discussed.

2. Materials and methods

2.1. Wastewater effluents

Six wastewater effluents coming from five wastewater treatment plants (WWTPs) in the province of Barcelona (Spain) were employed in this work. Three of these effluents (M1, M2 and M3) were collected from the outlet of membrane biological reactor (MBR) systems, whereas the rest (C1, C2 and C3) came from the outlet of conventional activated sludge (CAS) treatment units. Their main quality parameters are gathered in Table 2. The raw CAS effluents were filtered through conventional filter paper to remove the largest particles. All the effluent samples were kept at 4 ºC until they were used.

Differences observed in the main quality parameters of tested effluents were attributed to particular WWTPs technologies and operational conditions, especially those regarding biological processes. They covered a relatively broad range of effluent qualities and therefore represented the diverse range of wastewaters that currently can be found in practice.

Table 2. Effluent quality parameters. M and C stands for MBR and CAS effluents, respectively.

Sample ID	pH	UVA_{254} [m^{-1}]	TOC [mg C L^{-1}]	DOC [mg C L^{-1}]	COD [mg O_2 L^{-1}]	Turbidity [NTU]	IC [mg C L^{-1}]	NO_2^- [mg N L^{-1}]
M1	7.9	17.9	6.7	6.6	14.9	0.6	87.4	0.9
M2	7.4	16.3	10.5	10.3	20.7	0.9	42.7	< 0.1
M3	7.7	14.9	12.4	12.1	16.6	0.3	53.0	0.1
C1	7.5	22.9	14.0	13.6	29.7	1.1	63.6	0.1
C2	7.8	67.2	42.1	27.6	93.5	28.6	114.7	0.1
C3	7.7	66.4	25.6	21.3	53.0	20.1	98.3	< 0.1

2.2. *Ozonation experiments*

Wastewater ozonation experiments were performed in a 750 mL semi-batch reactor, at a temperature of 20 ºC and without pH adjustment. A mechanical stirrer was used to provide a proper contact between liquid and gas phases. The gas flow rate and the ozone inlet concentration were maintained at 0.1 L min^{-1} and 0.63 mmol L^{-1}, respectively. The transferred ozone dose (TOD), which represents the ozone consumption, was determined through continuous evaluation of the O_3 mass balance in the gas phase. Further details of the experimental setup and ozone dose calculations can be found elsewhere [34].

Each wastewater effluent was spiked with 0.45 µM of the pesticide acetamiprid (ACMP), here employed as reference micropollutant, and then ozonized for 30 min under the mentioned operational conditions. Samples were withdrawn at known time intervals and kept at room conditions until complete consumption of dissolved ozone was achieved. Then, analyses for ACMP, typical physicochemical parameters (namely UVA_{254}, DOC and COD) and EfOM fractions were conducted.

2.3. *Analytical methods*

ACMP concentration was determined through HPLC-UV, following the method described elsewhere. UV absorbance at 254 nm, TOC-DOC and COD were determined according to Standard Methods procedures 5910B, 5310B and 5220D, respectively [35]. In order to characterize EfOM fractions after applying particular ozone doses, the SEC-OCD technique from DOC-Labor was employed. As mentioned, this procedure consists of size exclusion chromatography (SEC) followed by organic carbon detection. Other detectors, such as an UV absorbance or an organic nitrogen detector (UVD and OND, respectively) are also typically added and used to identify and quantify EfOM fractions. Additional information regarding this technique can be found elsewhere [21,36].

3. Results and discussion

3.1. Ozone demand, radical scavenging and removal of the reference compound ACMP

Immediate ozone demand (IOD) of each wastewater sample was estimated in this work as the minimum TOD required to detect dissolved ozone in the reaction medium [37]. The initial hydroxyl radical (•OH) consumption rates, which provide information about the amount of •OH available in the reaction medium for micropollutant oxidation [38], were here estimated considering the sum of contributions by dissolved EfOM and alkalinity. For EfOM contribution, a mean rate constant value between dissolved EfOM and •OH of $2.1 \cdot 10^5$ $(\text{mg C L})^{-1}\text{s}^{-1}$ was used according to the work by Lee et al. [10], together with the DOC values in Table 2. Consumption rate due to alkalinity was calculated according to the known rate constant of bicarbonate ion reaction with •OH ($8.5 \cdot 10^6$ $\text{M}^{-1}\text{s}^{-1}$ [39]) and the IC values in Table 2. Estimated values of IOD and •OH consumption rates are presented in Table 3.

Table 3. Estimated IOD and •OH consumption rates of tested effluent samples. EfOM contributions in samples C2 and C3 may have been underestimated, as only dissolved EfOM was taken into account.

Effluent sample ID	**M1**	**M2**	**M3**	**C1**	**C2**	**C3**
IOD [mmol O_3 L^{-1}]	0.29	0.19	0.23	0.3	0.6	0.4
•OH consumption rate [s^{-1}]	$2.0 \cdot 10^5$	$2.5 \cdot 10^5$	$2.9 \cdot 10^5$	$3.3 \cdot 10^5$	$6.6 \cdot 10^5$	$5.2 \cdot 10^5$

Although relatively low O_3 doses (*e.g.,* 0.1-0.3 mmol L^{-1} or 5-15 mg L^{-1}) should be enough to meet the removal of organic compounds with medium or high reactivity to ozone [10,11,14,40], this criteria could get gradually stricter as is likely to occur in view of the increasing water scarcity and concern on micropollutants presence in water resources. Then, the abatement of even those MPs recalcitrant to ozone may be also required in a near future. In this study, we selected ACMP as reference compound on the basis of this hypothesis. ACMP reacts very slowly with ozone [41], and therefore only hydroxyl radicals generated through O_3 decay contribute to its degradation during ozonation. If ozone-resistant MPs such as this pesticide are significantly removed from wastewater effluents, a higher abatement of any other compound with higher sensitivity towards ozone attack would be guaranteed. Furthermore, O_3 doses necessary for disinfection purposes are generally lower than that for micropollutant oxidation [9,42].

Measurements of the reference compound ACMP at regular reaction times allowed the obtaining of the degradation profiles presented in Fig. 1. Ozone doses required to reach 80% abatement of ACMP differed significantly between samples. These were approximately between 0.4 and 0.8 mM (~19-38 mg L^{-1}) for effluents M1-M3 and C1, whereas for effluents C2 and C3 such doses were about 1 mM (48 mg/L) or even higher. If a less ambitious goal is established, let us say a minimum abatement of 50%, doses between 0.3 and 0.5 mM (14-24 mg L^{-1}) would instead be required for the cleanest effluents and between 0.6 and 0.8 Mm (29-38 mg L^{-1}) for samples C2 and C3.

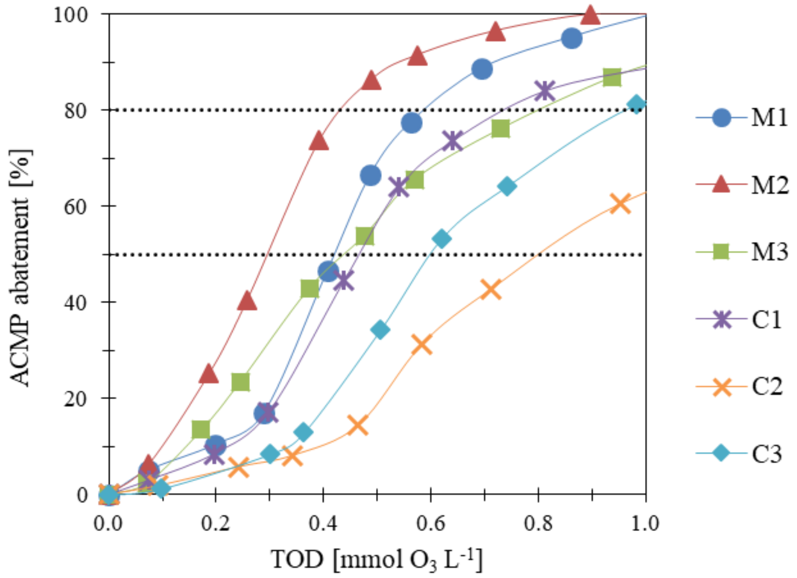

Figure 1. Abatement of the reference compound ACMP during semi-batch ozonation experiments with different wastewater effluent samples.

The feasibility of ozonation steps implementation for MPs abatement (including ozone-resistant compounds) should be individually assessed for each wastewater source by means of more comprehensive procedures [43], especially for those effluents presenting a higher O_3 demand and •OH scavenging rate (*e.g.*, C2 and C3). In any case, in this study we considered maximum ozone doses of about 1 mM as potentially practical for ozone applications to enhanced wastewater treatment and reclamation goals, and explored the fate of EfOM when subjected to these treatment conditions.

3.2. Changes of general EfOM descriptors (UVA, COD and DOC) during ozonation

Changes in UV absorbance at 254 nm (UVA_{254}) during ozonation experiments are shown in Fig. 2. Ozone typically reacts with electron-rich moieties of EfOM [38] –responsible for sample aromaticity–, resulting this in a sustained decrease of the wastewater UV absorption along the process. Differences observed between effluents regarding UVA_{254} decrease can be related to their respective water characteristics, which led to different availabilities of oxidants in the reaction medium (see estimated IOD and •OH consumption rate values in Table 3). Thus, for C2 and C3 effluents, both containing important amounts of O_3-consuming [20] particulate/colloidal matter (see TOC-DOC content and turbidity, Table 2) and alkalinity (IC), the UVA_{254} decrease at 30 min (TOD: 0.9-1.0 mM) ranged between 40 and 50%, whereas for MBR effluents (M1-M3) this value was determined to be considerably higher (70-80%) for a lower ozone consumption. In the particular case of C1, its lower content in solid and colloidal matter (TOC-DOC: 0.4 mg C L^{-1}; turbidity = 1.1 NTU) compared with C2 and C3 allowed a larger aromaticity reduction, more similar to that accounted for membrane bioreactor effluents.

Fig. 3 shows the COD/COD_0 profiles obtained for each water source, as a function of the TOD. COD removals at the end of the treatment (TOD: 0.6-1.0 mM) ranged from 10 to 45%, depending on the tested sample. Again, clear differences were observed between effluents, together with a consistent trend for this bulk parameter with respect to the UVA_{254} evolution, previously described. According to this, for instance, the M2 effluent –with relatively low content in organic matter and the lowest alkalinity among the studied wastewaters– was the one for which the largest COD removal was observed, whereas C2 and C3 samples (highest content in both organic and inorganic carbon as well as in colloidal and particulate matter) exhibited the lowest –and also the slowest– reduction for this parameter. In general, lower overall reductions of COD (max. 45%) in comparison to UVA_{254} (up to 80%) were observed. It seems that the provided oxidation conditions were not strong enough in order to achieve comparable levels of organic matter transformation in terms aromaticity depletion and COD reduction.

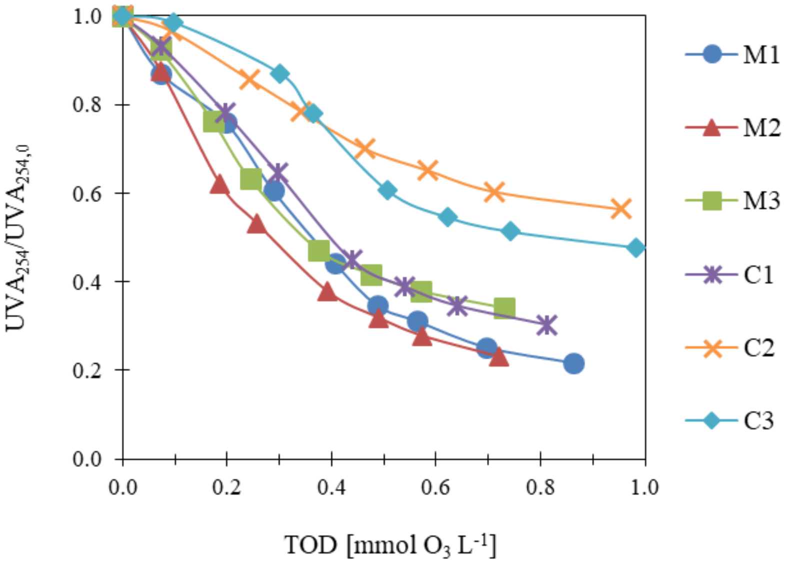

Figure 2. UV absorbance evolution during ozonation of wastewater effluents.

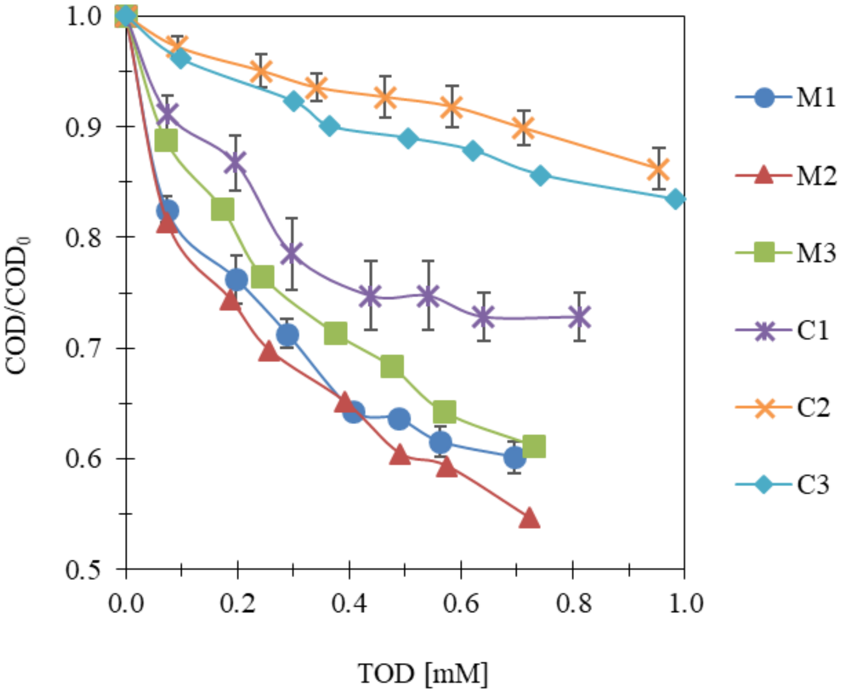

Figure 3. COD removal versus transferred ozone dose during semi-batch effluent ozonation experiments.

Fig. 4 shows the percentage of DOC removal during effluent ozonation experiments, determined at three different ozone doses (TOD values of 0.2-0.3, 0.3-0.5 and 0.6-1.0 mM). For effluents M1, M2 and M3, all of them coming from MBR systems, the DOC concentrations after 30 min of treatment (TOD: 0.6-0.7 mM) were reduced by 26.8%, 22.1% and 21.4%, respectively, which are in comparison lower removal levels than those reached for COD or aromaticity at the same consumed ozone doses. In wastewater ozonation, the degree of mineralization is typically low, and other water quality parameters related to the organic content –such as COD and UVA_{254}– are in general more affected during the process. This is reasonable, as DOC concentration only is reduced when decarboxylation reactions are produced, that is, when the maximum possible level of organic matter oxidation takes place [38].

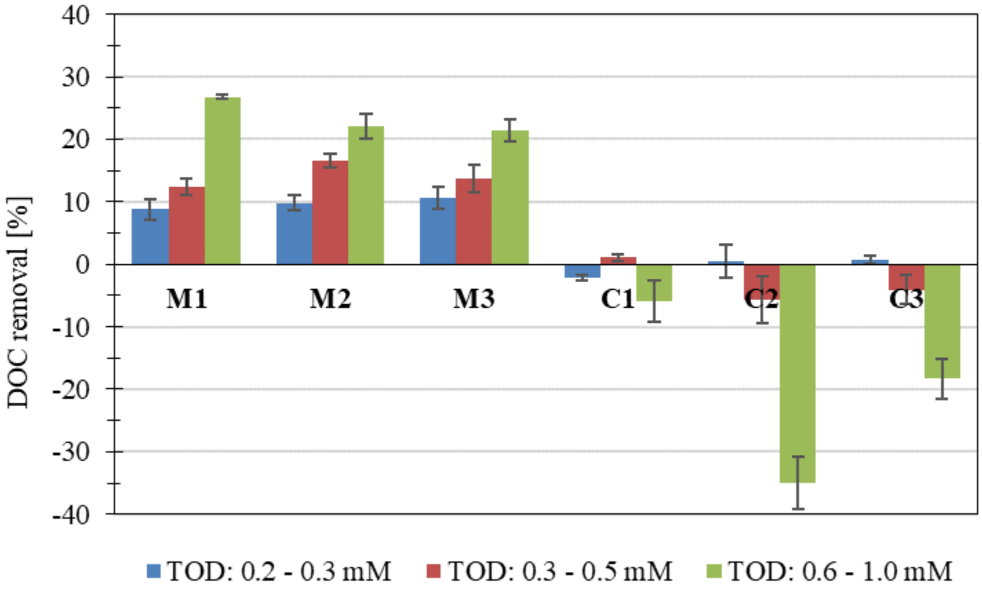

Figure 4. DOC concentration removal in wastewater ozonation experiments at various transferred ozone doses (TOD).

Concerning effluents C1, C2 and C3, the observed DOC removals at the end of ozonation experiments were negative in all cases. Water effluents coming from CAS systems usually contain residual amounts of suspended solids and colloids (see TOC, DOC and turbidity values of Table 2). Therefore, and in agreement with literature [44,45], it is possible that part of this non-dissolved material could be solubilized upon oxidation. For the CAS effluents tested in the present study, this phenomenon was observed after consumption of relatively high ozone doses (*i.e.*, 0.7-1.0 mM), rather than at low TOD values. In fact, at O_3 doses between 0.2 and 0.5 mM only small changes in the DOC concentration where registered, which could be indicative of a simultaneous oxidation-solubilization of, respectively, the dissolved and undissolved EfOM.

3.3. Evolution of EfOM fractions

Figs. 5 and 6 show the evolution of (dissolved) EfOM fractions and their relative contribution to DOC during ozonation of wastewater effluents. Samples coming from CAS processes presented larger percentages of biopolymers than MBR effluents (6.9-24.9% vs 0.8-1.7%, respectively), which was already expected given that ultrafiltration membranes employed in MBR units are able to retain extracellular polymeric substances (EPSs). Differences were also observed in the humic contents (2697-3319 and 3335-5217 µg C L^{-1} for MBR and CAS, respectively) which, in agreement with previous related studies concerning membrane fouling in MBR units, suggests that a part of the largest constituents of this EfOM fraction could also be retained during the separation process [24,46].

Regarding CAS effluents (Fig. 5), biopolymers were not significantly removed until higher doses of ozone were consumed [from 6.9 to 4.2% (C1), from 23.9 to 15.3% (C2) and from 13.8 to 7.5% (C3) of dissolved EfOM content for O_3 doses of 0.7-1.0 mM]. Especially remarkable is the case of humic substances, which noticeably increased from the beginning of the treatment, especially for C2 and C3 samples. The observed accumulation of humic acids during the entire C2 and C3 ozonation time, together with the fact that these two waters contain the highest fraction of suspended solids among all the studied effluents may be linked. Thus, the non-soluble fraction of the humic matter could be solubilized when oxidized [24,36]. This affirmation would be experimentally supported by the DOC measurements made at different ozone doses and early seen in this study, which revealed significant increases in this parameter (35% and 18% for C2 and C3 samples, respectively) for consumed ozone doses of 0.9-1.0 mM. Significantly higher doses applied in related works for effluents containing suspended EfOM [24] could have hinder a possible initial increase of this fraction followed by subsequent depletion for higher oxidant dosages. This was in fact observed for sample C1, a CAS effluent containing a lesser amount of suspended solids. Moreover, the continuous solubilization of humic species would provide an additional explanation to the low rates of UVA_{254}

depletion found for C2 and C3 waters. BB remained almost unaltered until higher ozone doses were applied, which means that humic substances were not being destroyed at those oxidation extents. Only at O_3 doses of 0.7-1.0 mM, an enrichment in the BB contents [from 15.3 to 21.7% (C1), from 11.4 to 17.4% (C2) and from 14.6 to 19.8% (C3)] was noticeable in all EfOMs. Regarding LMWN, the concentration of this fraction slightly increased at the end of the treatment for samples C2 and C3, but only after an initial –and also slight– reduction at the first stages of the process took place. On the contrary, for effluent C1 a sustained decrease in this fraction concentration was observed during the entire ozonation time. Again, differences between effluents C2 and C3, on one hand, and effluent C1, on the other, appear to be well explained by the solubilization process taking place in the first ones: the continuous introduction of humic substances to the system would hypothetically lead to an accumulation of degradation intermediates (*i.e.*, LMWN), contrarily to what typically happens in water matrices in which this re-dissolution of OM does not significantly take place (*e.g.*, MBR effluents and also sample C1). Despite the slightly increase in LMWN observed for C2 and C3, a gradual impoverishment and accumulation of this fraction in all the tested CAS effluents was registered [overall changes in EfOM composition for consumed O_3 doses of 0.7-1.0 mM: from 28.3 to 18.9% (C1), from 22.5 to 18.9% (C2), from 28.4 to 22.15 (C3)]. Finally, a continuous accumulation of LMWA was observed for all three samples, leading to the enrichment in this component of the corresponding EfOM compositions [from 5.2 to 18.9% (C1), from 5.5 to 10.7% (C2) and from 9.8 to 19% (C3)]. This evolution was predictable, as carboxylic acids present low reactivity towards ozone and the contribution of hydroxyl radical oxidation in complex water matrices is usually expected to be low [38,47].

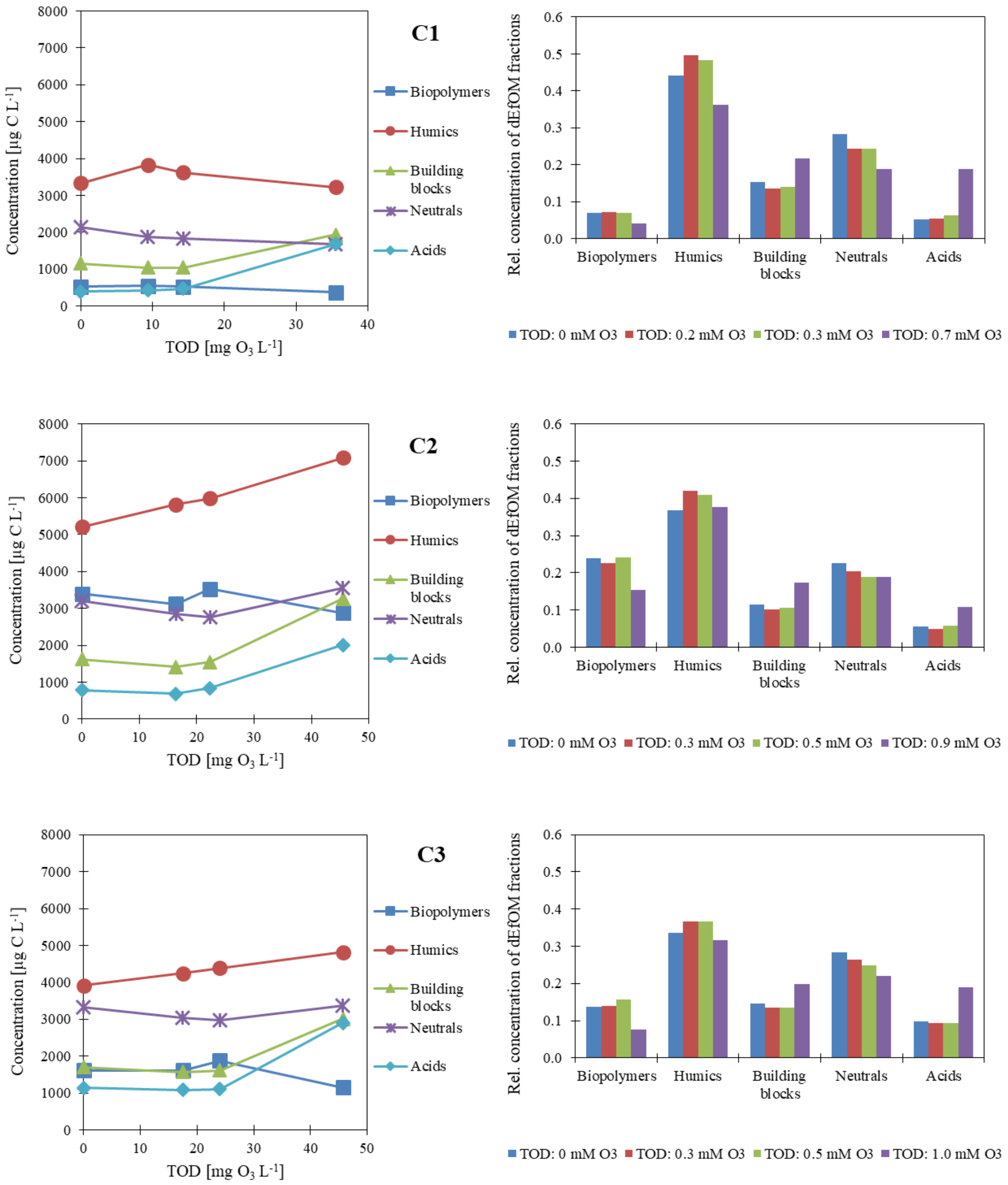

Figure 5. Evolution of dissolved EfOM fractions and contribution to DOC for ozonized CAS effluents.

The evolution of EfOM fractions during ozonation of MBR effluents is shown in Fig. 6. With no biopolymers nor suspended solids present in wastewater matrices, ozone primarily attacked humic substances and LMWN, leading this to the gradual accumulation of BB but particularly LMWA (from 4.1 to 17.55% (M1), from 3.3 to 20.2% (M2) and from 5.4 to 8.2% (M3), for consumed ozone doses of 0.6-0.7 mM). The overall increase of humic substances concentration observed for the M3 dissolved EfOM was the result of the small changes that took place in the rest of fractions, together with a DOC reduction of *ca.* 21% at the end of the treatment.

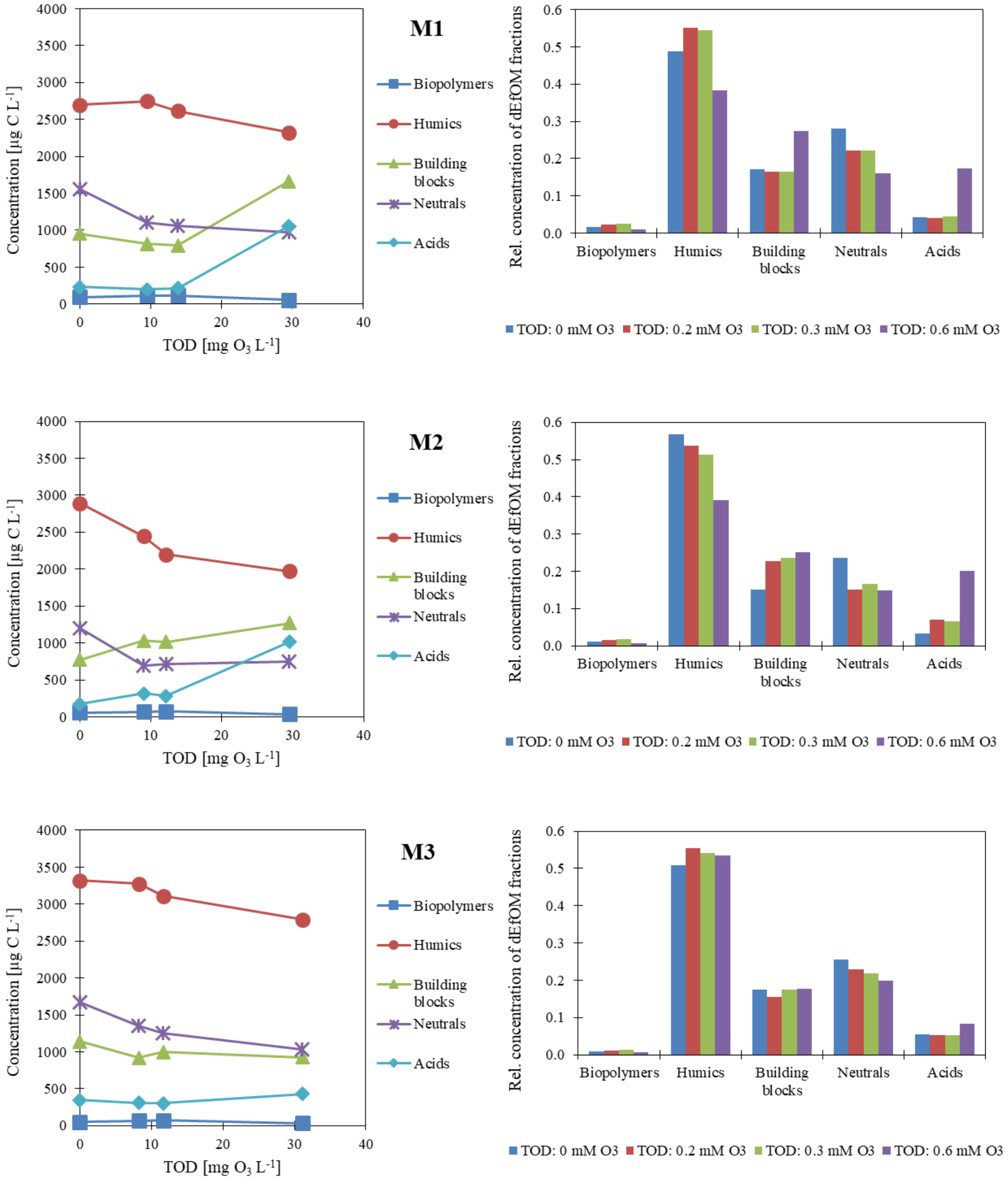

Figure 6. Evolution of dissolved EfOM fractions and contribution to DOC for ozonized MBR effluents.

Concerning the negative impacts that EfOM changes produced through ozonation could cause, some of them require special mention: in first place, the cleavage of macromolecules and medium-size structures to yield LMWA (which are not effectively mineralized by ozone) is known for leading to the enhancement of water biodegradability

[20,48]. Although this could be interesting if further biological treatments are wanted to be applied, it could be also detrimental if this water is discharged or reused: biodegradable EfOM is a perfect substrate for bacterial growth in pipes, membranes or receiving water compartments. On its part, and although biopolymers were partly removed during the process, this reduction was in any of the cases higher than *ca.* 45%. For CAS effluents, containing a significantly higher concentration of these components, the reduction percentage was still lower. This means that the greatest part of biopolymers, partly responsible for membrane fouling, for instance, remained unaltered in the water matrix. With respect to particulate matter solubilization during the treatment, ozonizing secondary effluents containing suspended solids seems to be not recommended. In addition to the mentioned problems related to biodegradability enhancement, increasing the dissolved organic matter content in an already treated wastewater can lead to other problems such as the generation of disinfection by-products, not to mention the complete treatment inefficiency this implies.

3.4. Relationship between process parameters and EfOM changes

Although UVA_{254} is typically used as an estimate of to the humic fraction content in EfOM [19,49–52], a strict correlation between these two factors has not been observed during ozonation experiments. Oxidation of humic substances initially occurs at the external part of the coil formed by these molecules, which in turn prevents its inner part to be destroyed by ozone and hydroxyl radicals [53]. According to the aromaticity model for humic substances proposed by Del Vecchio and Blough [54], the attack on the peripheral part of humic structures, potentially leading to the oxidation of those electron-donating or -accepting subunits responsible for charge transfer transitions –and therefore, also for UV absorption–, would be enough to reduce the sample UVA_{254}. Similar observations reported by studies employing chlorine as oxidizing agent [55], instead of ozone, support this hypothesis. Likewise, the observed mismatch between COD and UVA_{254} reduction during ozonation experiments (see Figs. 1 and 2) could be partly related to the steric impediment caused by the spatial configuration of humic substances.

Recent works have shown how the measurement of spectroscopic parameters (UVA and fluorescence removal) could be potentially used as on-line proxies for biodegradable DOC generation during ozonation and other advanced tertiary treatments [56,57]. This biodegradable fraction of EfOM corresponds to the presence of medium-weight BB, as well as to LMWN and LMWA. Since all these species have their origin in the cleavage of larger humic molecules, it seems logical to put the focus on the relationship between this fraction and some common effluent quality and process parameters in order to anticipate potential changes during ozonation.

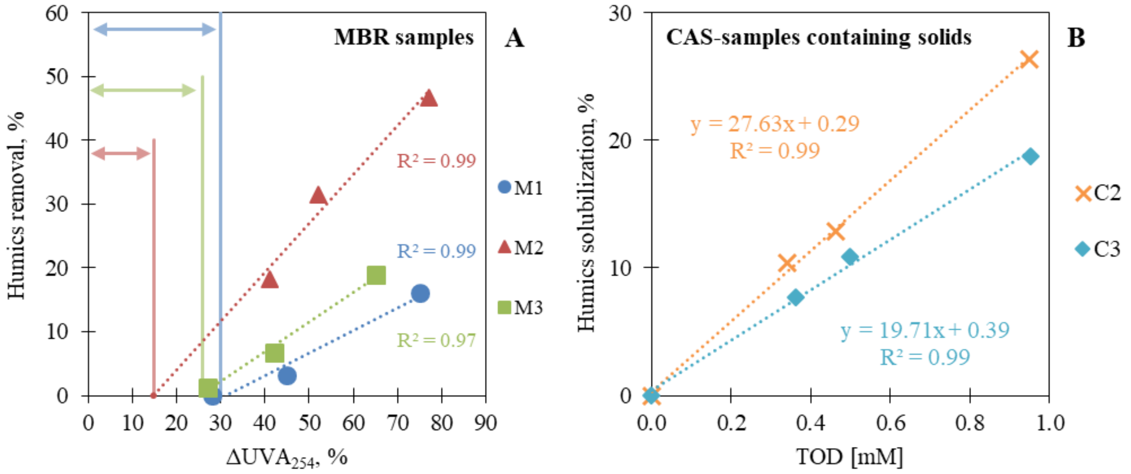

Figure 7. Relationship between effluent quality and process parameters with humic substances concentration in wastewater effluents ozonation. A) Humics removal in MBR effluent samples versus % UVA reduction; B) Humics solubilization versus transferred ozone dose in CAS effluent samples containing significant amounts of suspended organic matter.

Fig. 7A shows a plot of the percentage of humics removal versus the UVA_{254} depletion, for samples coming from MBR units. As seen, a good relationship between them appears to be possible after an initial lag stage in which any abatement of humic substances is observed. In other words, a degree of UV absorbance reduction is observed before measuring any depletion in the concentration of humic substances. This is also indicated in Fig. 7A. The magnitude of this lag can be related with the oxidizing conditions of the media, since a higher availability of oxidant species in the medium favors a more severe oxidation of humic species. As known, O_3 and •OH availability during ozonation will depend on the effluent characteristics, being the main contributors to that the contents in organic and inorganic matter that readily consume these oxidants. Interestingly, the observed trend for IOD (*i.e.*, 0.29, 0.19 and 0.23 mmol O_3 L^{-1} for samples M1, M2 and M3, respectively) agreed well with the trend observed for the lag values represented in Fig. 7A, which resulted to be: M2 > M3 > M1 (corresponding to 14.5, 25.5 and 31.1 % of UVA depletion, respectively). The slope of the humics-UVA_{254} removal correlation for these waters, which would give an idea about the process kinetics, also followed the same trend (0.35, 0.76 and 0.47 for M1, M2 and M3, respectively).

Contrarily, this agreement was not observed also for the initial •OH consumption rate values estimated for MBR effluents. In fact, the presence of •OH in the reaction medium not only depends on the consumption rate of these species by the water matrix but also on the capacity of consumed ozone to generate it. Therefore, a better indicator of •OH availability to react with humic substances during the first stages of ozonation process should also consider ozone consumption. A good option can be the use of the ratio between •OH exposure (*i.e.*, $\int[\bullet[OH]\,\mathrm{d}t$) and IOD. Hydroxyl radical exposure for an ozone consumption corresponding to the IOD value could be estimated in this work through ACMP degradation data presented in Fig. 1, according to the calculation procedure described elsewhere [34]. The obtained $\int[\bullet[OH]\,\mathrm{d}t$/IOD values were $3.1\cdot10^{-7}$, $7.3\cdot10^{-7}$ and $4.9\cdot10^{-7}$ s for samples M1, M2 and M3, respectively. As can be checked, the trend followed by these values now match with the lag and slope values in Fig. 7A: the higher the amount of hydroxyl radicals available per ozone dose, the stronger the oxidation conditions, thus allowing a more significant (and faster) degradation of humic substances by this transient species during the initial stages of ozonation.

Finally, if it was the case that ozonation was applied to a CAS effluent containing significant amounts of suspended matter, the percentage of humics solubilization in the water matrix seems to be well correlated with the transferred ozone dose. This is shown in Fig. 7B: the higher the oxidation extent, the higher the number of hydrophilic moieties generated in the non-soluble fractions of EfOM. In addition, larger concentrations of solid matter, which also contribute to a higher IOD value, seem to favor faster solubilization kinetics, as shown in the correlation parameters obtained in experiments with samples C2 and C3.

Conclusions

Ozone application for the effective removal of micropollutants from wastewater produced significant changes in EfOM concentration and quality in all effluents tested. The extent of COD and UVA_{254} reduction agreed well with the water quality of each effluent, being the most influencing factors the concentration of both dissolved and particulate/colloidal matter and alkalinity. For CAS samples containing relatively large amounts of suspended solids, an increase in the DOC concentration was observed. This was attributed to the solubilization of non-dissolved humic substances. The continuous introduction of this fraction (humic substances) in the reaction medium resulted in the net accumulation of this component. Only for samples coming from MBR systems, the sequential reduction of the largest fractions leading to an accumulation of some of the lightest components, namely BB and LMWA, could be clearly observed. Also for these waters, a net level of OM mineralization took place. In general, an accumulation of low molecular weight acids at the end of the treatment was registered. Potentially useful relationships between some observed changes (variation in humic species content), water quality (UVA_{254}) and process parameters (IOD, $\int[\bullet OH]\mathrm{d}t$/IOD, TOD) were established. Changes in organic matter concentration and characteristics derived from ozone application could be detrimental for water reuse purposes, depending on the final application of the treated water. Thus, a careful consideration of this factor together with the water properties of the effluent to treat and the quality requirements to achieve throughout the process (*i.e.*, micropollutants removal and disinfection) should be properly assessed during the planning stage of an ozonation unit.

Acknowledgements

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4.3 Application, intensification and modelling of peroxone process for enhanced oxidation of ozone-refractory micropollutants in wastewater effluents (Appendix VI)

In view of the high ozone doses required for the effective abatement of ozone-refractory MPs during wastewater ozonation, the combination of ozone with hydrogen peroxide (*i.e.*, peroxone process) was tested in municipal wastewater effluents as potential strategy to increase the availability of hydroxyl radicals in the reaction medium. Different operational conditions (*i.e.*, H_2O_2/O_3 ratios) and H_2O_2 dosing strategies were examined and compared with the aim of improving the process efficiency. Finally, simple methods allowing the performance description and kinetic modelling of the process were suggested and validated. Three different effluents were employed in this work: two coming from MBR systems (MBR-1 and MBR-2) and another one treated in a CAS bioreactor (CAS-3).

After initially checking the low abatement of ACMP (employed as model/•OH probe compound) at typical oxidant doses during single ozonation (see corresponding data in Figure 1, Appendix VI), experiments with continuous dosing of hydrogen peroxide at different H_2O_2/O_3 molar ratios (0.25, 0.5 and 1) were conducted. Further details of H_2O_2 dosing conditions can be found in Table 2, Appendix VI. The obtained degradation profiles are represented in Figure 2 of the same appendix. The process efficiency improved with respect to experiments without H_2O_2 addition, even at the lowest ratio of oxidants. In fact, only modest enhancements in ACMP oxidation were observed for higher H_2O_2/O_3 relationships, compared to a value of 0.25. For that particular condition, the overall needs for 80% abatement of the model compound decreased 36% in average (from 37 to 24 mg L^{-1}, from 43 to 26 mg L^{-1} and from 51 to 34 mg L^{-1} for MBR-1, MBR-2 and CAS-3 effluents, respectively). Considering energetic expenses for ozone and hydrogen peroxide production (*i.e.*, 15 kWh/kg and 10 kWh/kg, respectively [194]), that supposed an average reduction of energy requirements of about 30%. The observed improvements were in contrast to that reported in previous related literature, in which only slight enhancements in ozone-refractory compounds oxidation were observed in experiments with H_2O_2 addition, with respect to single ozonation [194]. A key difference of this work with other related studies testing the O_3/H_2O_2 combination to enhance MPs oxidation, which also explained the observed differences in performance improvement, is that ozone was applied at higher doses than those corresponding to IOD completion. In most studies dealing with ozone or peroxone application for MPs oxidation in wastewater effluents, sub-IOD (*i.e.*, low) ozone doses are typically applied [136,144,145]. During the first ozonation stage, EfOM and alkalinity but also other matrix components such as nitrite, exert a strong oxidant demand/scavenging [107]. Ozone is thus very unstable and cannot react with the hydroperoxide anion (H_2O^-), which as mentioned (section 1.3.2) is the real precursor of the peroxone process. Once IOD is satisfied, however, more ozone is available to react with H_2O^-, leading to an enhancement in hydroxyl radical generation.

For a better comparison of the process efficiency at different operational conditions, the $R_{OH,O3}$ parameter was determined in all experiments. This concept, which gives an idea about the •OH availability per consumed ozone, had already been successfully applied to describe and compare ozonation process in effluents showing a broad range of effluent qualities (see section 4.2.1 and/or Appendix IV). Thus, its use was also tested for O_3/H_2O_2 process characterization. Similarly to what happened in the single ozonation study, each peroxone experiment yielded two $R_{OH,O3}$ values, one per process stage (primary or IOD and secondary). $R_{OH,O3}$ plots and corresponding values can be found in Figures 2 and 3 of Appendix VI, respectively.

As already advanced, the enhancement in oxidation efficiency was more noticeable after IOD completion. Moreover, it was observed that H_2O_2/O_3 ratios of 0.25 allowed the highest efficiency in all tested effluents during the secondary ozonation stage. Indeed, larger relationships appeared to result in a slight decrease in the process performance, probably due to some •OH scavenging exerted by an excess of hydrogen peroxide. Concerning the initial stage of the process, this was little affected compared to single ozonation, which leaves the door opened to potential peroxone application with H_2O_2 addition only during the secondary ozonation stage. In any case, oxidant ratios required to observe any improvement in this stage, with respect to single ozonation, were higher than that needed in the secondary ozonation stage.

After investigations on the optimal oxidant ratios required to optimize the oxidation efficiency throughout the entire peroxone process, only achievable through implementation of continuous addition of hydrogen peroxide, the use of this strategy was compared to a classical dosing approach by means of which H_2O_2 was added just before starting ozone bubbling. As shown in Figure 4 of Appendix VI, additional experiments following this methodology at a H_2O_2/O_3 ratio of 0.25 revealed that continuous addition of hydrogen peroxide led to better oxidation efficiencies than initial dosing of this reagent. However, those differences were only significant in the case of MBR effluent samples. Energy savings (to reach 80% abatement of ACMP) observed in peroxone experiments with MBR-1 and MBR-2 effluents were, in average and compared to single ozonation, about 30% and 9% when employing continuous or initial H_2O_2 addition. In contrast, these extra savings were only about 5% in the case of effluent CAS-3.

Finally, the abatement of ozone-recalcitrant MPs in peroxone application with continuous H_2O_2 addition was modelled through two different approaches, similarly to that done with single ozonation process in the work presented in Appendix IV. Thus, the strategy based on the use of $R_{\mathrm{OH,O3}}$ values and TOD assessment (Eq. 35), on one hand, and the method based on the monitoring of UVA_{254} absorbance and $k_{\mathrm{UVA,OH}}$ determination (Eq. 34), on the other, were both tested. Good agreements ($R^2 > 0.96$) between measured and predicted abatements were observed for different compounds (IBU and ATZ), tested effluents (three in total, two from MBR systems and another one from a CAS bioreactor) and prediction models (based on $R_{\mathrm{OH,O3}}$ and TOD monitoring, on one hand, and on $k_{\mathrm{UVA,OH}}$ and UVA_{254} monitoring, on the other). Corresponding data can be found represented in Figure 6 (Appendix VI).

Appendix VI

Continuous H_2O_2 addition in peroxone process: performance improvement and modelling in wastewater effluents

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ABSTRACT

The extension of ozonation up to ozone (O_3) doses beyond immediate ozone demand (IOD) completion combined with continuous addition of hydrogen peroxide (H_2O_2) was studied as potential strategy of treatment aimed to the effective abatement of ozone-resistant micropollutants (MPs) from wastewater effluents. Through experiments involving the continuous addition of H_2O_2 in a semi-continuous ozone contactor, it was demonstrated that this new approach could lead to a 36% reduction of the overall O_3 needs for a constant H_2O_2/O_3 molar ratio of 0.25 compared with single ozonation, representing a 28% reduction in the energy consumption. This improvement, however, was mainly attributed to H_2O_2 addition during the secondary ozonation stage, where the direct ozone demand becomes less important. The •OH-exposure per consumed ozone (R_{OHO3}) calculation demonstrated that larger H_2O_2/O_3 ratios (0.5-1) lead to a better but little oxidation performance during the IOD stage, whereas relationships of 0.25 work markedly better during the secondary stage of the process. Moreover, continuous versus total initial addition of H_2O_2 were compared and the first one showed better performance, with differences in estimated energy costs up to 21%. Finally, and since monitoring the fate of O_3-recalcitrant MPs during the process is essential, two different strategies for the real-time control of the O_3-recalcitrant MPs fate during the process were tested, one based on the R_{OHO3} concept and the other on continuous measurements of ultraviolet absorbance at 254 nm (UVA_{254}). They both showed accurate predictions ($R^2 > 0.96$) for different compounds, effluents and processes.

KEYWORDS

Wastewater, O_3/H_2O_2 process, Micropollutants, Oxidation efficiency, Oxidant dosing, Kinetic modelling

1. Introduction

Even though ozonation is nowadays stablished as one of the most effective end-of-pipe solutions for micropollutants (MPs) abatement in municipal wastewater effluents [1–5], this process still presents some drawbacks that limit its widespread application. As a consequence of the low reactivity with ozone (O_3) exhibited by some of the MPs typically present in wastewater effluents, as well as the relatively low availability of hydroxyl radicals (•OH) in the system, some of these compounds are not effectively removed when applying this technology [5]. These species are known as ozone-resistant micropollutants, and they typically present second-order rate constants with O_3 lower than 10 $M^{-1}s^{-1}$ [1]. Although current ozone applications do not focus on the complete abatement of these recalcitrant chemicals, water resources stress in some parts of the world may eventually trigger the need for producing high-quality reclaimed wastewater. In this situation, the monitoring and removal of ozone-resistant micropollutants –especially if these represent potential risks to human and environmental health– during ozonation may become necessary [6–8]. Increasing the oxidant exposure required to effectively remove these species from wastewater effluents would involve the application of larger ozone doses, which can make the process unaffordable, as well as potentially lead to significant generation of harmful oxidation byproducts, such as bromate [9,10]. Combining ozone with hydrogen peroxide (H_2O_2) can be a practical alternative to improve single ozonation performance. By means of this process application, hydroxyl radical (•OH) production is increased with respect to single ozonation, thus allowing larger removals of ozone refractory MPs for equivalent ozone doses [11]. In addition, bromate formation during ozonation of water matrices containing significant amounts of bromide can be significantly reduced in the presence of H_2O_2 [5,12].

A number of previous studies have reported experimental evidence on the benefits –in terms of micropollutants abatement– of employing the O_3/H_2O_2 combination (also known as peroxone process) for drinking water applications [13–15]. However, this enhancement in micropollutants abatement appears to be minimal for water matrices presenting a higher pollution load (*i.e.*, wastewater effluents) [15–17]. Furthermore, interesting aspects of the process –such as the employed H_2O_2 dosing strategy– remain barely explored. In most of the lab-scale studies dealing with the peroxone process, hydrogen peroxide at known H_2O_2/O_3 ratios is dosed before ozone addition from a concentrated ozone stock solution [1,13,18,19]. Similarly, in semi-batch or continuous ozone applications this reagent is added before ozone bubbling or injection [15].

Moreover, the currently employed ozone doses in lab- pilot- and full-scale ozone applications are, in general, not higher than 20 mg L^{-1}. Under these conditions, the immediate ozone demand (IOD) of secondary effluents is usually not exceeded and no ozone residual is detected in the reaction medium [20,21]. Therefore, the ozone demand can be considered constant during the whole process and, consequently, there is a single optimal H_2O_2/O_3 ratio for each application. However, as previously stated, the final quality demands for the treated effluent can be more restrictive, requiring the employment of ozone doses beyond IOD completion. In this situation –which would involve a change in the ozone mass transfer regime from gas to liquid phase [21]–, it must be explored if independent H_2O_2/O_3 ratios during each one of the two stages of the process could be required in order to optimize the overall process performance in terms of oxidation efficiency.

Another aspect of the peroxone process that requires to be further investigated in its application is the monitoring and control of ozone-resistant micropollutants abatement. In most related works, a prediction based in the use of the time-integrated concentration of hydroxyl radicals in the reaction medium (*i.e.*, the hydroxyl radical exposure $\int[\bullet OH]\,\mathrm{d}t$) has proven to be feasible and accurate [17,22,23]. However, this term needs to be previously calculated by means of experiments involving the use of a probe compound [24], fact that hinders the full-scale application of this control strategy for real-time monitoring. In this sense, the use of easily measurable parameters such as the transferred ozone dose (TOD) or the evolution of ultraviolet absorbance at 254 nm (UVA_{254}) as surrogates for hydroxyl radical exposure could be a practical option. Recently, it has been shown that these two parameters were highly correlated during single ozonation process

[25,26]. Thus, they could also be helpful for the kinetic modelling of peroxone process with continuous H_2O_2 addition.

In summary, this work aimed to evaluate the use of continuous hydrogen peroxide addition as new strategy in peroxone process applied for the enhancement of micropollutants abatement in a semi-batch ozone contactor. The main objective was describing the process performance in terms of oxidation efficiency under different operational conditions (*i.e.*, H_2O_2/O_3 ratios), stablishing comparisons between continuous and initial addition of H_2O_2. The concluding objective was testing practical modelling strategies potentially allowing the real-time monitoring and control of ozone-resistant MPs removal during this process application.

2. Materials and methods

2.1. Chemicals and reagents

Acetamiprid (ACMP), atrazine (ATZ) and ibuprofen (IBU) analytical standards were acquired from Sigma-Aldrich (Germany). Ammonium metavanadate (99.0%) was supplied by Fluka. Ultrapure water was produced by a filtration system (Millipore, USA). Pure oxygen ($\geq$ 99.999%) for ozone production was supplied by Abelló Linde (Spain). The rest of reagents, including hydrogen peroxide solution (30% w/v), were acquired from Panreac (Spain).

2.2. Wastewater effluents

Three wastewater effluents were collected from WWTPs in the Metropolitan Area of Barcelona (Spain) were employed in this work. Two of them (MBR-1, MBR-2) came from membrane biological reactor (MBR) systems, whereas sample CAS-3 was collected from a conventional activated sludge (CAS) unit. Their quality parameters are summarized in Table 1. Total organic carbon (TOC) and dissolved organic carbon (DOC, previous filtration through 0.45 µm PTFE filters) were determined by means of a TOC-VCSN analyzer (Shimadzu, Japan). UVA_{254} was measured by means of a DR6000 spectrophotometer (Hach, USA). Turbidity was determined by means of a 2100Q turbidimeter (Hach, USA). Alkalinity was measured employing an automatic titrator

(Hach, Spain). Nitrite (NO_2^-) concentration was measured by ion-exchange chromatography with UV detection. All samples were refrigerated at 4 ºC until use.

Table 1. Effluent quality parameters. All measurements were carried out per triplicate, being discrepancies between obtained values lower than 5% in all cases.

WWTP ID	**Location**	**pH**	**TOC [mg C L^{-1}]**	**DOC [mg C L^{-1}]**	**UV_{254} [m^{-1}]**	**Turbidity [NTU]**	**Alkalinity [mg $CaCO_3$ L^{-1}]**	**NO_2^- [mg N L^{-1}]**
MBR-1	Vallvidrera	7.8	7.2	7.1	9.1	0.3	448.1	0.03
MBR-2	Gavà-Viladecans	7.7	13.6	13.3	17.4	0.5	208.3	0.19
CAS-3	Gavà-Viladecans	7.8	51.1	21.7	50.3	18.5	469.4	0.16

Main differences in water quality presented by effluents were, in summary: the relative content in both, organic and inorganic carbon (the latter expressed as alkalinity) and the presence of solid and colloidal matter of the CAS-3 sample, compared with the MBR effluents. These marked variations in water properties were expected to illustrate the matrix effect on the process performance for a wide range of effluent qualities.

2.3. *Ozonation of wastewater effluents*

Ozonation experiments were performed in a semi-continuous, jacketed contactor with a working volume of 750 mL. Ozone was produced by a 301.19 lab ozonizer (Sander, Germany) and injected at the bottom of the reactor by means of a fritted glass diffuser (pore size: 150-250 µm). A proper contact between gas and liquid phases was ensured by means of a mechanical mixing system. Experiments were performed at a temperature of 20±1 ºC, without pH adjustment. The gas flow rate and the inlet ozone concentration were set at 0.1 NL min^{-1} and 30 mg NL^{-1}, respectively. The ozone concentrations at the inlet and the outlet gas streams were continuously measured by means of two BMT 964 ozone analyzers (BMT Messtechnik, Germany). A Q45H/64 dissolved O_3 probe (Analytical Technology, USA) was placed in a liquid recirculation stream (flow rate: 0.2 L min^{-1}) and allowed the measurement of the ozone concentration in the reaction medium. A detailed scheme of the ozonation setup can be found elsewhere [25].

The transferred ozone dose (TOD), which represents the accumulated amount of ozone that is transferred to the water sample per unit of volume and time, was determined according to Eq. 1. F_g, V_{liq} stand for, respectively, the gas flow and the volume of the liquid phase; t is the contact time; and $[O_3]_{in}$ and $[O_3]_{out}$ represent the inlet and outlet ozone concentrations in the gas phase, respectively.

$$TOD = \int_0^t \frac{F_g}{V_{liq}} \cdot ([O_3]_{in} - [O_3]_{out}) \cdot \mathrm{d}t \qquad (1)$$

Each wastewater effluent was spiked with 100 µg L^{-1} of ACMP, which was employed as •OH probe compound according to the methodology explained in detail by Elovitz and von Gunten [24]. Then, the solution was homogenized by the mechanical stirring prior to the treatment. Subsequently, the wastewater was ozonized for 60 min under the operational conditions before described. At specific reaction times, sample aliquots were withdrawn from the reactor and stored at room conditions until dissolved ozone was completely consumed. Then, residual concentrations of ACMP, H_2O_2 and UV absorbance at 254 nm were determined as required.

Additional experiments were performed in order to illustrate the usefulness of R_{OHO3} concept in the prediction of ozone-recalcitrant micropollutants removal during peroxone process application. In this case, the pesticide atrazine (ATZ) and the drug ibuprofen (IBU) were selected because both are typical ozone-resistant compounds. Thus, each wastewater effluent was spiked with low concentrations (50 µg L^{-1}) of ATZ and IBU.

MPs, including ACMP, ATZ and IBU are typically found in wastewater effluents at concentrations not higher than the µg/L level. Being so, we selected these concentrations (100 µg/L for ACMP and 50 µg/L for ATZ and IBU) because they did not represent a high oxidant scavenging during the process and allowed us to monitor their residual concentrations by HPLC-DAD.

During ozonation, samples were taken at known reaction times, stored at room conditions until complete ozone consumption was achieved and kept for subsequent micropollutants quantification. All experiments were performed at least in duplicate.

2.4. Hydrogen peroxide dosing

During O_3/H_2O_2 experiments, hydrogen peroxide addition was performed by means of two different methods: a) continuous dosing through a metering pump; or b) direct spiking from the commercial solution, before ozone injection. For O_3/H_2O_2 experiments with continuous hydrogen peroxide dosing, an Ismatec 829 metering pump (Cole-Parmer, Germany) connecting the contactor and a reservoir tank containing the H_2O_2 solution was employed. The flow-rate was set at the lowest possible value (0.33 mL min^{-1}) to minimize the medium dilution. In order to apply H_2O_2/O_3 molar ratios of 0.25, 0.5 and 1 when working in continuous dosing mode, the transferred ozone dose per unit time (TOD/t, mg O_3 L^{-1} min^{-1}) was employed as reference for H_2O_2 addition. As ozonation typically exhibits a two-stage –one fast, one slow– behavior regarding the ozone transfer to the liquid phase [21], two TOD/t values determined in single ozonation experiments were employed as reference in each experiment to calculate the H_2O_2 flow-rate required to meet the working H_2O_2/O_3 ratios during the whole treatment. Two fresh H_2O_2 solutions –one per process stage– were prepared just before starting the peroxone experiments (concentrations of stock solutions included in Table S1 in the Supplementary Information). Hydrogen peroxide was initially supplied from the first solution –more concentrated, due to a faster ozone consumption at the beginning of the process–, until the characteristic transition between fast and slow ozone transfer regimes was reached. From this point, and until the end of the experiment, H_2O_2 was pumped from the second –and more diluted– stock solution. In experiments with initial H_2O_2 dosing, a dose equivalent to the total amount of peroxide added in continuous addition experiments was transferred to the reaction medium shortly before ozone bubbling. Details regarding particular dosing conditions for all the experiments performed are gathered in Section 3.2 (Table 2).

2.5. Analytical procedures

The UV absorbance data was determined with a DR6000 UV VIS spectrophotometer (Hach, USA). H_2O_2 residual concentration was determined after complete O_3 consumption through the metavanadate spectrophotometric procedure [27]. The concentrations of ACMP, ATZ and IBU were quantified by means of a high performance liquid chromatograph (HPLC) equipped with a diode array detector (DAD), all supplied by Agilent (1260 Infinity). The column employed was a Teknokroma Mediterranea Sea18 (250 mm x 4.6 mm and 5µm size packing). The flow rate and injection volume were set, respectively, at 1.0 mL min^{-1} and 100 µL in all determinations. For ACMP analyses, the mobile phase consisted of 30:70 volumetric mixtures of acetonitrile and Milli-Q water acidified at pH 3 by the addition of H_3PO_4. The detection wavelength was set to 250 nm. For ATZ and IBU quantification, the mobile phase consisted of 70:30 volumetric mixtures of acetonitrile and pH 3 Milli-Q water, and the UV detection was performed at 225 nm. The limits of quantitation were 3.3 µg L^{-1}, 0.9 µg L^{-1} and 2.1 µg L^{-1} for ACMP, ATZ and IBU, respectively.

3. Results and discussion

3.1. Fate of ACMP as a model O_3-resistant compound during wastewater single ozonation

Fig. 1 shows the evolution of ACMP as a function of the TOD in single ozonation experiments extended to ozone doses up to 60 mg L^{-1}. ACMP is a neonicotinoid pesticide which barely reacts with ozone (k_{O3} = 0.25 $M^{-1}s^{-1}$) and presents a second-order rate constant for its reaction with hydroxyl radicals ($k_{\bullet OH}$) of $2.1 \cdot 10^9$ $M^{-1}s^{-1}$ [28]. Because of these properties, this chemical was selected in the present study as model ozone-recalcitrant micropollutant. In the view of the obtained ACMP degradation profiles, it is quite clear that typically employed ozone doses (according to multiple lab-, pilot- and full-scale studies found in literature, ranging from 5 to 20 mg L^{-1}), represented by a shaded area in Fig. 1, do not provide enough •OH-exposure to achieve important removal levels for this compound (between 20% and 40% depending on the effluent). Similar conclusions can be drawn from results reported over the last years in ozonation studies focused in the abatement of selected micropollutants that also included in their list some compounds with low ozone reactivity [1,2,4,13,29]. However, the ozone doses required to achieve acceptable degradation levels (*e.g.*, > 80%) for these species were insufficiently discussed in those reports, probably because ozonation of wastewater effluents was not extended beyond typically employed O_3 dosages. For the three wastewater effluents that were selected in the present study, and depending on their different contents in organic matter and alkalinity (that is, the water matrix components considered to be mainly responsible for •OH scavenging during ozonation [5]) the applied doses to achieve an 80% degradation level should be 37 mg L^{-1}, 43 mg L^{-1} and 51 mg L^{-1} for MBR-1, MBR-2 and CAS-3, respectively. This represents an increment, compared to the considered maximum dose of 20 mg L^{-1}, between 46% and 61%. Another interesting information drawn from these results is the fact that the IOD (represented in Fig. 1 by dashed lines) needs to be completed –and indeed exceeded– in order to reach the transferred ozone doses required for O_3-recalcitrant MPs abatement.

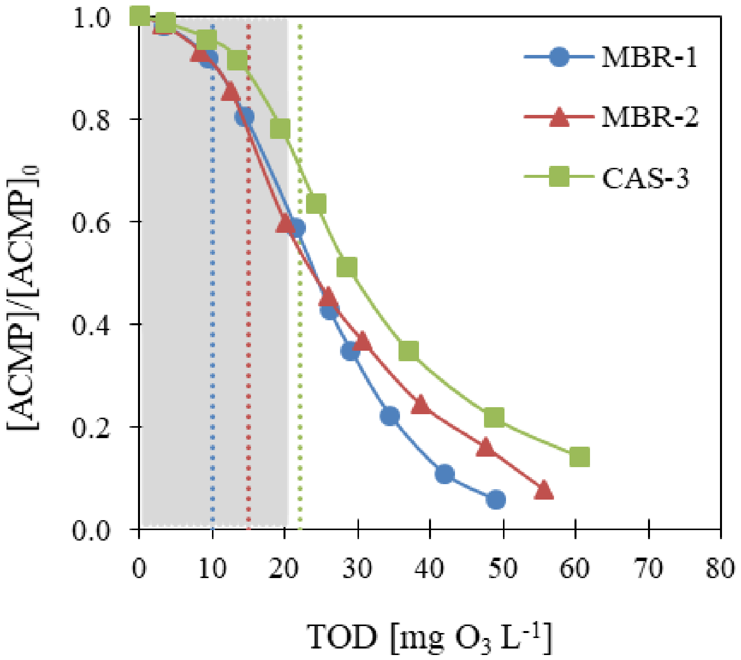

Figure 1. Removal of ACMP from wastewater effluents by means of single ozonation: C/C_0 profiles versus TOD. The shaded area indicates the currently applied range of O_3 doses in full- pilot- and lab scale applications, and the dashed lines represent the IOD values of the tested effluents. Experimental conditions: $[ACMP]_0$: 100 µg L^{-1}; F_g: 0.1 NL min^{-1}; $[O_3]_{in}$: 30 mg NL^{-1}; T: 20 ºC.

Fig. S1 (see the Supplementary Information) illustrate changes taking place in the ozone transfer efficiencies during single ozonation experiments extended up to transferred ozone doses (TOD) of 60 mg L^{-1}. Approximately after IOD completion –which according to the results obtained took place for TOD values between 10 mg L^{-1} and 22 mg O_3 L^{-1}, depending on the water source (see Fig. S1, right column plots) – the ozone transfer efficiency from gaseous to liquid phase notably decreases (before IOD, η_{tr1}: 0.69-0.74; after IOD, η_{tr2}: 0.12-0.19). This two-stage behavior in ozone transfer is a consequence of two different O_3 demands exerted by the water matrix components at different oxidation extents [21]. As above mentioned, if ozone demand is different during the two regimes of the process, the optimal H_2O_2/O_3 ratios to enhance the •OH production are expected to vary from primary to secondary ozonation stages. This is explored in the next section.

3.2. Peroxone with H_2O_2 continuous addition for enhanced abatement of ozone-recalcitrant ACMP

Peroxone process extended beyond IOD with continuous H_2O_2 addition were conducted in semi-batch ozonation mode. Table 2 gathers particular H_2O_2 dosing conditions for each one of the experiments carried out. First, the process is described in terms of oxidation performance and then comparisons between continuous or initial addition of hydrogen peroxide are presented. In experiments with initial H_2O_2 addition, the dose of this oxidant was selected according to the total H_2O_2 dose in continuous addition experiments (Table 2, last column).

Table 2. Hydrogen peroxide dosing conditions during peroxone experiments. Total H_2O_2 dose values presented in the last column represent the total amount of hydrogen peroxide dosed in continuous addition experiments, and was also the dose of this reagent applied in experiments with total initial addition.

Effluent	**H_2O_2/O_3 ratio (molar)**	**H_2O_2 dose, Stage 1 [mg L^{-1}]**	**H_2O_2 dose, Stage 2 [mg L^{-1}]**	**Total H_2O_2 dose [mg L^{-1}]**
MBR-1	0	-	-	-
	0.25	4.00	8.15	12.15
	0.5	6.95	17.35	24.30
	1	14.65	33.95	48.60
MBR-2	0	-	-	-
	0.25	3.97	8.38	12.35
	0.5	6.95	17.74	24.69
	1	14.35	35.03	49.38
CAS-3	0	-	-	-
	0.25	3.81	11.05	14.86
	0.5	7.28	22.50	29.78
	1	17.52	42.00	59.52

3.2.1. *Removal of ACMP at different H_2O_2/O_3 ratios: process efficiency*

Although peroxone process has proven to be effective for enhanced •OH production from O_3 decomposition, some studies dealing with the use of this combination in wastewater effluents have reported that only a little improvement in O_3-resistant MPs abatement is observed, compared to single ozonation [15–17]. All previous works were performed with total H_2O_2 addition at the beginning of the ozonation process. Fig. 2 (left column) show ACMP degradation profiles during continuous hydrogen peroxide dosage in peroxone application in wastewater effluents MBR-1, MBR-2 and CAS-3 at different H_2O_2/O_3 constant ratios. As it can be observed, addition of hydrogen peroxide improves the overall degradation efficiency, even at the lowest employed H_2O_2/O_3 ratio (*i.e.*, 0.25). For that particular condition, ozone doses required to eliminate 80% of the initial ACMP were reduced from 37 mg L^{-1} to 24 mg L^{-1} for MBR-1, from 43 mg L^{-1} to 26 mg L^{-1} for MBR-2 and from 51 mg L^{-1} to 34 mg L^{-1} for CAS-3. Those changes represent a 36% decrease in the overall O_3 needs. Of course, the use of hydrogen peroxide involves additional costs that need to be considered when performing the corresponding economic assessment. However, if we consider typical energy costs of 15 kWh/kg and 10 kWh/kg for O_3 and H_2O_2 production [30], respectively, the overall energy consumption is reduced in this particular case by 28%, pointing out the global benefit of peroxone process on recalcitrant micropollutant removal in municipal effluents. This is in contrast with previous results from literature in which the power consumption was incremented by 25% [30]. This can be attributed to the fact that ozone was always dosed at sub-IOD concentrations, that is, when O_3 demand exerted by the water matrix was high. In this situation, ozone is very unstable and its decomposition in water is controlled by radical-type chain reactions with effluent organic matter (EfOM) [5]. In addition, •OH generation may be hindered by ozone reactions not conducting to hydroxyl radical formation (e.g., reaction between O_3 and nitrite [31]).

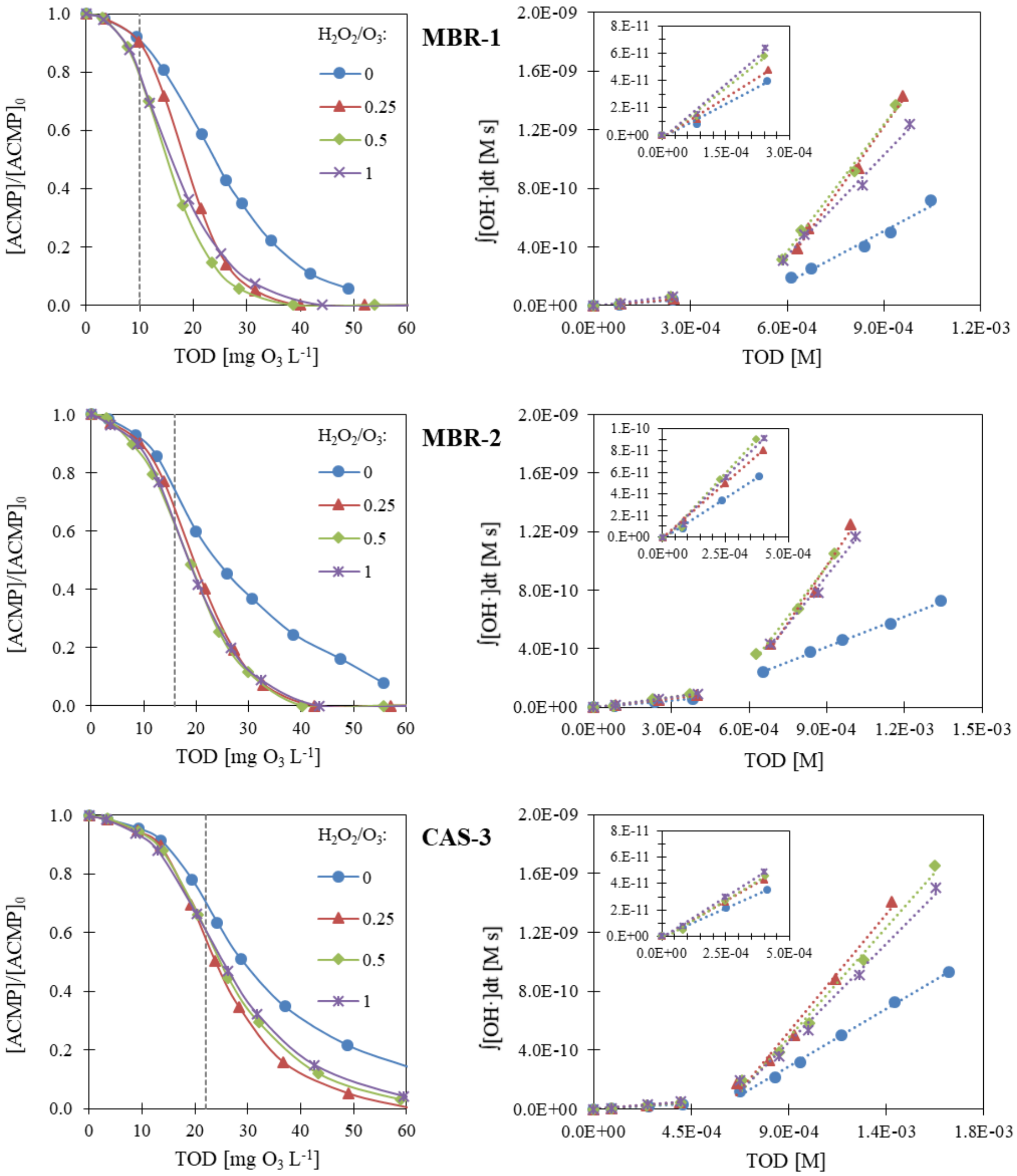

Figure 2. Removal of ACMP by O_3 and O_3/H_2O_2 processes from effluents MBR-1, MBR-2 and CAS-3 with continuous H_2O_2 addition at different oxidant ratios (left column); and ∫[•OH]dt vs TOD plot for each experiment (right column). Dashed lines in the first plot indicate the IOD values. Insets in the latter are a zoom of the plot region corresponding to the initial reaction stage. Experimental conditions: $[ACMP]_0$: 100 µg L^{-1}; F_g: 0.1 NL min^{-1}; $[O_3]_{in}$: 30 mg NL^{-1}; T: 20 °C.

From the degradation profiles of ACMP, it is clear that the effect of continuous H_2O_2 addition on the oxidation efficiency becomes more significant after IOD completion. During the initial stage, however, the process is mainly controlled by ozone reactions with EfOM and little enhancement in the pesticide removal is observed. Nevertheless, during the secondary stage (*i.e.*, after IOD has been satisfied), more O_3 is available to react with the deprotonated form of hydrogen peroxide (HO_2^-), leading to an enhancement in •OH production compared to single ozonation (Eqs. 2-7) [32–34].

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \tag{2}$$

$$O_3 + HO_2^- \rightarrow O_3^{\bullet -} + HO_2^{\bullet} \tag{3}$$

$$HO_2^{\bullet} \leftrightarrow O_2^{\bullet -} + H^+ \tag{4}$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \tag{5}$$

$$O_3^{\bullet -} + H^+ \leftrightarrow HO_3^{\bullet} \tag{6}$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \tag{7}$$

In addition, carbonate radicals ($CO_3^{\bullet -}$) usually formed during the O_3/H_2O_2 treatment are expected to promote ozone decomposition (Eq. 8, [35]) to finally yield hydroxyl radicals by some of the aforementioned mechanisms. This effect may become more significant during the second stage of the process, as selective $CO_3^{\bullet -}$ reactivity with EfOM –which contributes to the inhibition of ozone decomposition (Eq. 9, [36])– may be lower after IOD completion [37–39].

$$CO_3^{\bullet -} + H_2O_2 \rightarrow HCO_3^- + HO_2^{\bullet} \tag{8}$$

$$CO_3^{\bullet -} + EfOM \leftrightarrow CO_3^{2-} + products \tag{9}$$

Variations between effluents or operational conditions in the peroxone process performance, in terms of oxidation efficiency, can be well reflected by the R_{OHO3} concept. This parameter, recently proposed as an absolute measure of the oxidation efficiency during ozonation, is calculated as the •OH-exposure per consumed ozone [40]. In the present work, its value has been calculated according to Eq. 10.

$$R_{OHO_3} = \frac{\int [\bullet OH]\, \mathrm{d}t}{TOD} \qquad (10)$$

Fig. 2 (right column) show the R_{OHO3} plots for each wastewater. Data fitted well a two-stage linear model, each one of these stages corresponding to the two ozone transfer regimes observed during the process. For the initial stage, characterized by a strong oxidant demand, R_{OHO3} values were between $0.11 \cdot 10^{-6}$ s and $0.39 \cdot 10^{-6}$ s for different wastewaters and experimental conditions (*i.e.*, H_2O_2/O_3 ratios). After IOD, however, significantly larger values (between $0.96 \cdot 10^{-6}$ s and $4.2 \cdot 10^{-6}$ s) were registered. Like single ozonation processes, differences observed between effluents can be attributed to water properties, mainly organic matter content and alkalinity. Both components, organic species and carbonates, exert a scavenging effect over hydroxyl radicals that reduces their availability in the reaction medium and decreases the MPs oxidation efficiency. Detailed explanations regarding the influence of these parameters in the value of R_{OHO3} during ozonation can be found elsewhere [25,40].

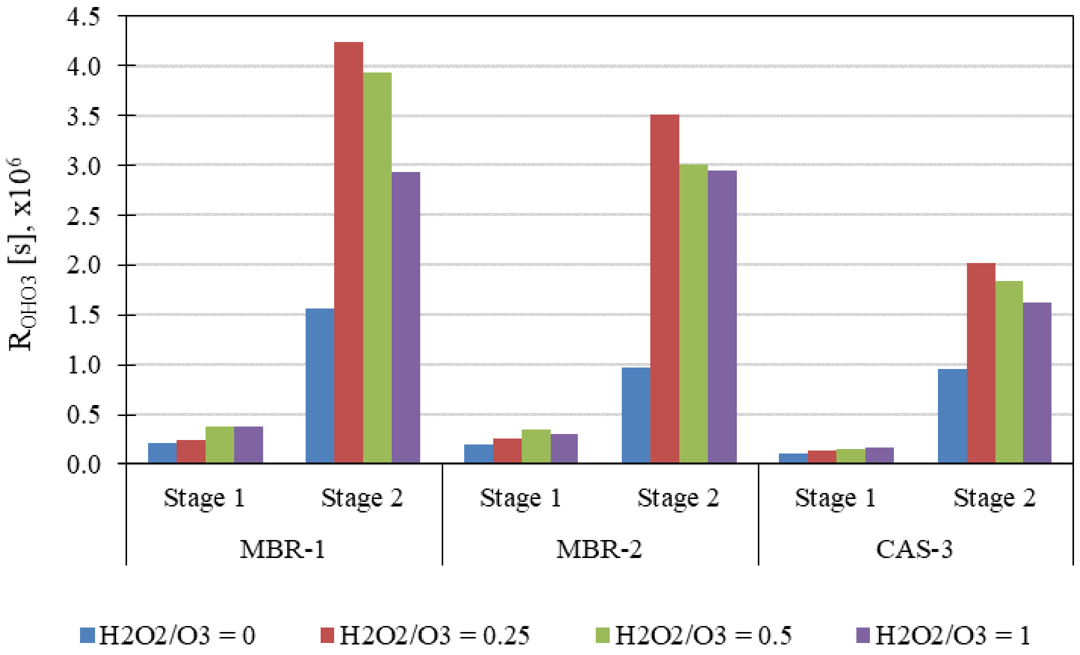

Figure 3. Comparison of R_{OHO3} values obtained from ACMP degradation experiments from effluents MBR-1, MBR-2 and CAS-3 employing O_3 and the combination O_3/H_2O_2 at different oxidant ratios (data represented in Fig. 1), before (Stage 1) and after (Stage 2) IOD. Experimental conditions: $[ACMP]_0$: 100 µg L^{-1}; F_g: 0.1 NL min^{-1}; $[O_3]_{in}$: 30 mg NL^{-1}; T: 20 ºC.

The R_{OHO3} concept can be also useful to investigate the optimal conditions (*i.e.*, H_2O_2/O_3 ratios) for extended peroxone application with continuous H_2O_2 addition. Fig. 3 shows the R_{OHO3} variation for effluents MBR-1, MBR-2 and CAS-3 at different H_2O_2/O_3 ratios, before (Stage 1) and after (Stage 2) IOD. One can readily notice that the effect of H_2O_2 addition is much more significant after the IOD, as already advanced in the view of the ACMP degradation profiles. On the contrary, the oxidation efficiency during the initial stage of the process is little afected. The above mentioned differences in the scale of values from initial to secondary regimes are also noticed in the view of this graph. It is also interesting here the observed fact that for all three effluents, regardless of their water properties, the H_2O_2/O_3 ratios showing best performances for pre- and post-IOD stages are different. Larger relationships (and therefore, larger amounts of H_2O_2) are required during the initial stage of the process, compared to the post-IOD phase. Concretely, H_2O_2/O_3 ratios between 0.5 and 1 showed better perfomances for initial process stage, whereas for post-IOD step the best oxidant relationship was 0.25. This fact may be attributed to the strong O_3 demand exerted by the water matrix during the initial steps of the treatment, which control the ozone decomposition process. In this situation, higher H_2O_2/O_3 ratios are required if some enhancing effect by H_2O_2 (*i.e.*, •OH-exposure increase) is wanted to be observed. On the contrary, after IOD completion the oxidant demand exerted by the water matrix is much lower, which allows a larger ozone availability in the reaction medium compared to the first stage. Therefore, the amount of hydrogen peroxide required to initiate ozone decomposition to •OH (Eq. 3) is also lower. Dosing H_2O_2 during the secondary stage at H_2O_2/O_3 ratios larger than 0.25 may conduct to an extra •OH-scavenging effect exerted by an excess of this reagent [5,41]. This most likely caused the decrease in the oxidation efficiency observed in Fig. 3 for all three effluents.

From the above results, the optimal point to start the addition of hydrogen peroxide during the ozonation process for an improvement on ozone recalcitrant MP removal appears to be after IOD completion. The scarce enhancement in the model compound removal observed at the initial stage, especially compared with the good performance observed once IOD is completed, constitutes a strong argument to make this decision. Moreover, ozone doses applied at the initial stage are relatively low, and this oxidant is instantaneously consumed by high organic and inorganic compounds content during that period. Therefore, the potential formation of significant amounts of bromate is an unlikely risk. Nevertheless, this last statement should be experimentally corroborated.

3.2.2. Continuous versus initial H_2O_2 dosing

During the application of extended peroxone process, and according to the results presented so far in this work, it seems clear that two different H_2O_2/O_3 ratios individually optimized for each one of the process stages should be employed if the best possible overall treatment performance is wanted to be achieved. In order to further prove the necessity of optimizing the H_2O_2 addition strategy, continuous versus initial dosing of H_2O_2 was compared in additional experiments. Fig. 4 (a-c) shows ACMP degradation profiles for peroxone experiments applied to effluents MBR-1, MBR-2 and CAS-3 at a H_2O_2/O_3 ratio of 0.25 and continuous or initial hydrogen peroxide dosing. In Fig. 4d, R_{OHO3} variations corresponding to those experiments are also represented. As it can be seen, the overall process efficiency for all effluents was better when operating with continuous peroxide addition. These differences, however, were more significant in the case of experiments with effluents MBR-1 and MBR-2. In those cases, the addition of H_2O_2 continuous and initial mode resulted in mean decreases of the ozone requirements to abate ACMP by 80% of 37% and 18 %, respectively, compared to single ozonation process. These reductions in the ozone dose correspond to overall energy savings of around 30% and 9%, respectively. The potential benefits of continuous H_2O_2 implementation instead of total initial dosing, therefore, become evident in the view of these data. On the other hand, overall differences observed in the oxidation performance when employing one or other operational modes were less obvious in the case of effluent CAS-3. For that particular scenario, the reduction in the O_3 needs only represented an extra 5% of energy savings when comparing continuous to initial addition (26% vs 21%, respectively).

According to Figure 4, it seems that the excess of hydrogen peroxide at the beginning of the reaction in experiments with initial H_2O_2 addition slightly favored the process performance during its first stage, but negatively affected it after IOD completion. The latter can be probably attributed to a lack of hydrogen peroxide during the secondary stage of the process due to the consumption of this reagent during the initial moments of reaction. Overall, this resulted in a clearly lower performance of ACMP oxidation. The initial enhancement followed by a decrease in the oxidation efficiency was more evident for the cleanest waters (*i.e.*, MBR-1 and MBR-2), as illustrated in Figs. 4(a-c) and especially in Fig. 4d. The latter clearly show how the R_{OHO3} parameter, which indicates the •OH availability per ozone dose, is between 2 and 10% higher during the initial stage of experiments with initial H_2O_2 addition compared with experiments carried out with continuous dosing. The contrary happened during stage 2, for which this value was significantly lower (up to 24%, depending o the effluent) compared to continuous addition experiments.

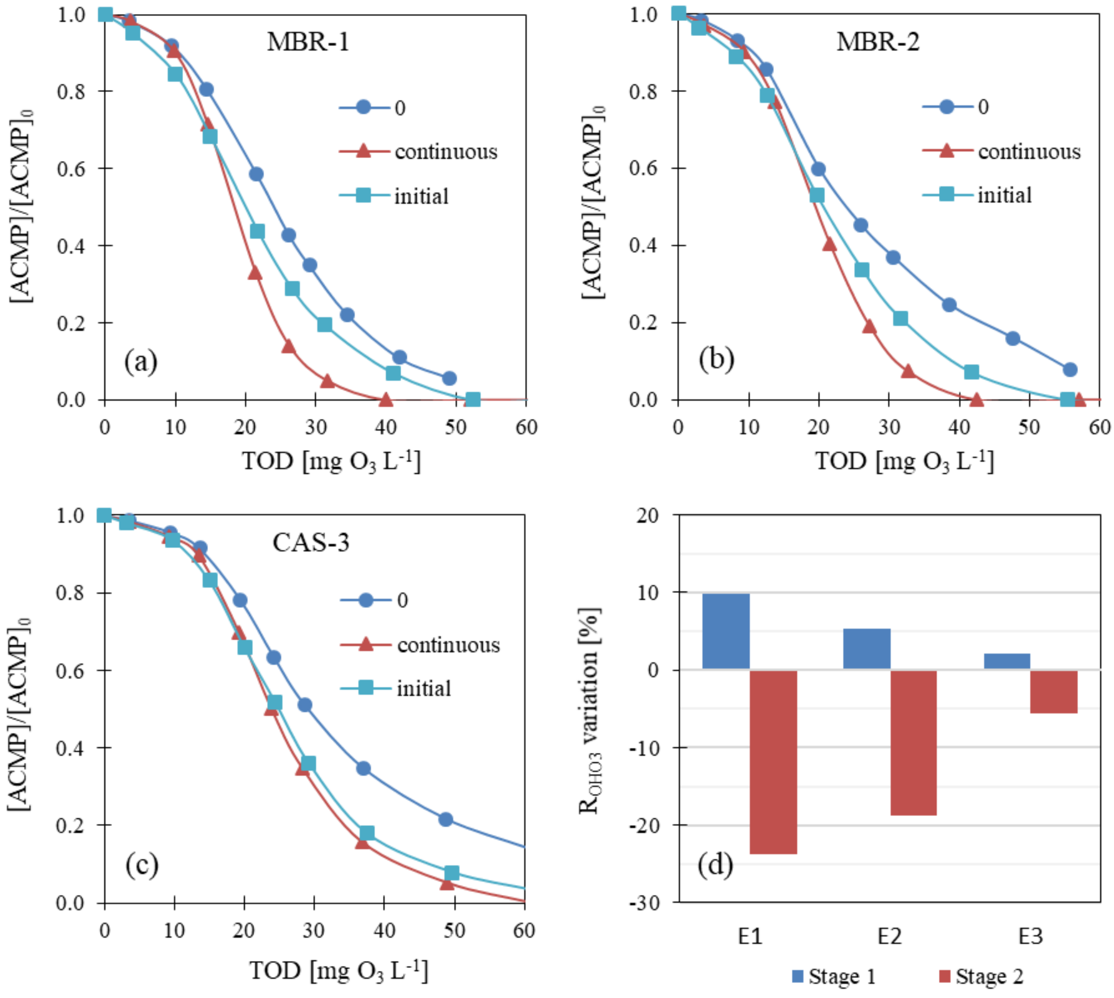

Figure 4. Removal of ACMP from effluents MBR-1, MBR-2 and CAS-3 by O_3 and O_3/H_2O_2 combination: comparison between continuous and initial addition of H_2O_2 (H_2O_2/O_3 ratio = 0.25). Figs. a) - c): ACMP evolution with TOD; Fig. d): R_{OHO3} percent variation for experiments with initial addition compared to experiments with continuous dosing. Experimental conditions: $[ACMP]_0$: 100 µg L^{-1}; F_g: 0.1 NL min^{-1}; $[O_3]_{in}$: 30 mg NL^{-1}; T: 20 °C.

It is important to mention that the reduction in the overall O_3 needs required for ACMP oxidation observed in continuous versus initial H_2O_2 experiments at a H_2O_2/O_3 ratio of 0.25 was also noticed in experiments performed at larger H_2O_2/O_3 relationships (*i.e.*, 0.5 and 1). These results can be found in the SI (Fig. S2). Differences in the O_3 savings observed when comparing continuous to initial addition slightly increased for the particular case of effluent CAS-3 to 8% and 12% for H_2O_2/O_3 ratios of 0.5 and 1, respectively. However, these extra savings, compared to the one obtained with a H_2O_2/O_3 ratio of 0.25, would probably not justify the application of higher amounts of hydrogen peroxide, which would increase the absolute costs of the treatment.

In the view of the results presented in this section, adding hydrogen peroxide simultaneously to ozone could be useful to maximize the oxidation efficiency during the peroxone process application. This novel strategy also involves the change of H_2O_2 dosing between the primary and secondary stages of the process, or even the decission of starting the addition of this reagent once IOD has been completed, as H_2O_2 dosing at the first stage does not contribute in a significant way to the overall improvement of ozone-recalcitrant micropollutant depletion.

3.3. Monitoring of O_3-resistant micropollutants removal

For a reliable, cost-effective real-time monitoring and control of the fate of O_3-recalcitrant MPs during the application of O_3 and O_3/H_2O_2 processes, it may be necessary the use of surrogate parameters whose evolution along the treatment is closely correlated with the abatement of these species. Moreover, the continuous measurement of the selected surrogate along the wastewater treatment should be technically feasible in order to represent a potentially implementable option in full-scale applications. In this sense, the use of UVA_{254} seems to be one of the most practical choices [42–46]. In our previous contribution, it was experimentally demonstrated how the decay of this parameter during extended ozonation of six different wastewater effluents is perfectly correlated to hydroxyl radical exposure [25]. In that work, that correlation was also theoretically demonstrated (see Eq. 11). Only Chys and coworkers reported similar findings by presenting relatively good agreements for exponential correlations between •OH-exposure and spectroscopic measurements, UVA_{254} between them [42]. In addition, the potential use of this prediction strategy during the application of peroxone process has not been explored yet. As an example, Fig. 5 shows the natural logarithm of UVA_{254} residual versus hydroxyl radical exposure for O_3/H_2O_2 experiments with effluent MBR-1 and continuous addition of hydrogen peroxide. Data obtained for effluents MBR-2 and CAS-3 can be found in the SI (Fig. S3). Linear correlation coefficients (R^2) higher than 0.95 were obtained in all cases. In accordance with results, two different linear regressions were observed for each experiment, corresponding to the fast and slow kinetic regimes of the process. Since hydrogen peroxide can absorb radiation at 254 nm [47], residual H_2O_2 concentrations measured during peroxone experiments with initial peroxide addition should be taken into account for potential corrections. However, the poor molar absorptivity of this oxidant and the relatively low residual concentrations detected during experiments with continuous addition of H_2O_2 resulted in minor impacts on $\int[\bullet OH]dt$-UVA_{254} correlations. Thus, data without further corrections was employed this time.

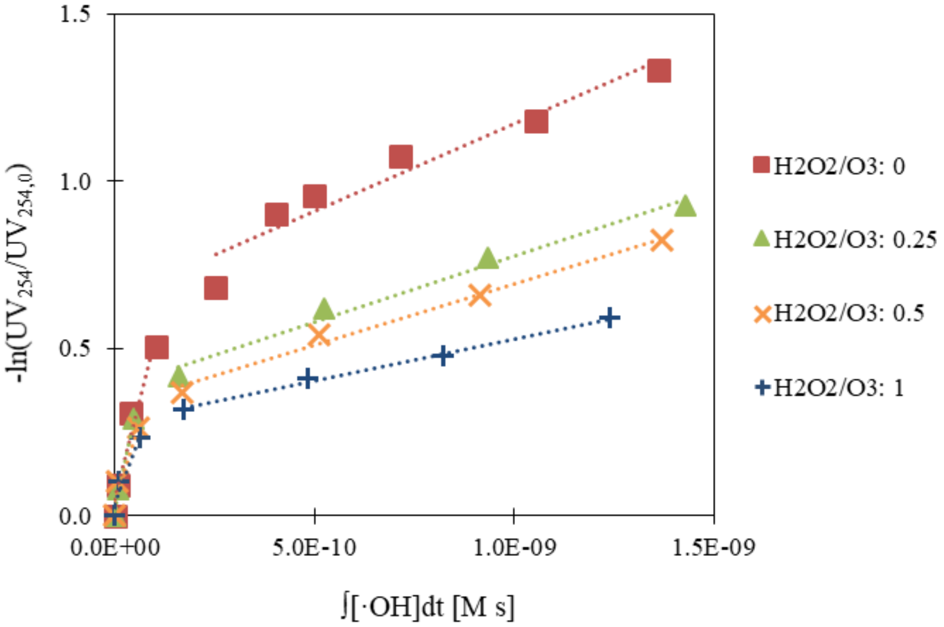

Figure 5. Correlation between UVA_{254} abatement and hydroxyl radical exposure during continuous H_2O_2 addition peroxone experiments with effluent MBR-1 and different H_2O_2/O_3 ratios. Experimental conditions: $[ACMP]_0$: 100 µg L^{-1}; F_g: 0.1 NL min^{-1}; $[O_3]_{in}$: 30 mg NL^{-1}; T: 20 ºC.

Predictions in •OH-exposure based on the use of UVA_{254} monitoring (Eq. 11) allow the estimation of O_3-resistant MPs abatement, according to second-order kinetics (Eq. 12, [5]). In addition, the R_{OHO3} concept (Eq. 10) can be used to estimate the $\int[\bullet OH]dt$ term if the TOD is known at any time interval, which was the case of the present work.

$$-ln\left(\frac{UVA_{254}}{UVA_{254,0}}\right) = k_{UVA,OH}\cdot\int[\bullet\, OH]\,\mathrm{d}t \tag{11}$$

$$-ln\left(\frac{[MP]}{[MP]_0}\right) = k_{\bullet OH}\int[\bullet\, OH]\,\mathrm{d}t \tag{12}$$

Fig. 6 shows predicted and experimental data obtained for single ozonation and peroxone experiments (continuous peroxide addition and H_2O_2/O_3 ratios of 0.25) in the studied effluents regarding the abatement during this process of two typical O_3-resistant micropollutants: the drug ibuprofen (IBU, k_{O3}: 9.6 $M^{-1}s^{-1}$ and $k_{\bullet OH}$: $7.4\cdot10^9$ $M^{-1}s^{-1}$ [48]) and the pesticide atrazine (ATZ, k_{O3}: 6.0 $M^{-1}s^{-1}$ and $k_{\bullet OH}$: $3.0\cdot10^9$ $M^{-1}s^{-1}$ [22]). The predicted fate of these chemicals during the process was estimated by means of both UVA_{254}- and R_{OHO3}-based models. Good agreements between model predictions and measured data was observed in all cases (R^2 of 0.97 and 0.96 for data predicted through R_{OHO3}- and UVA_{254}-based models, respectively), with apparent independence from effluents, oxidation processes or micropollutants employed.

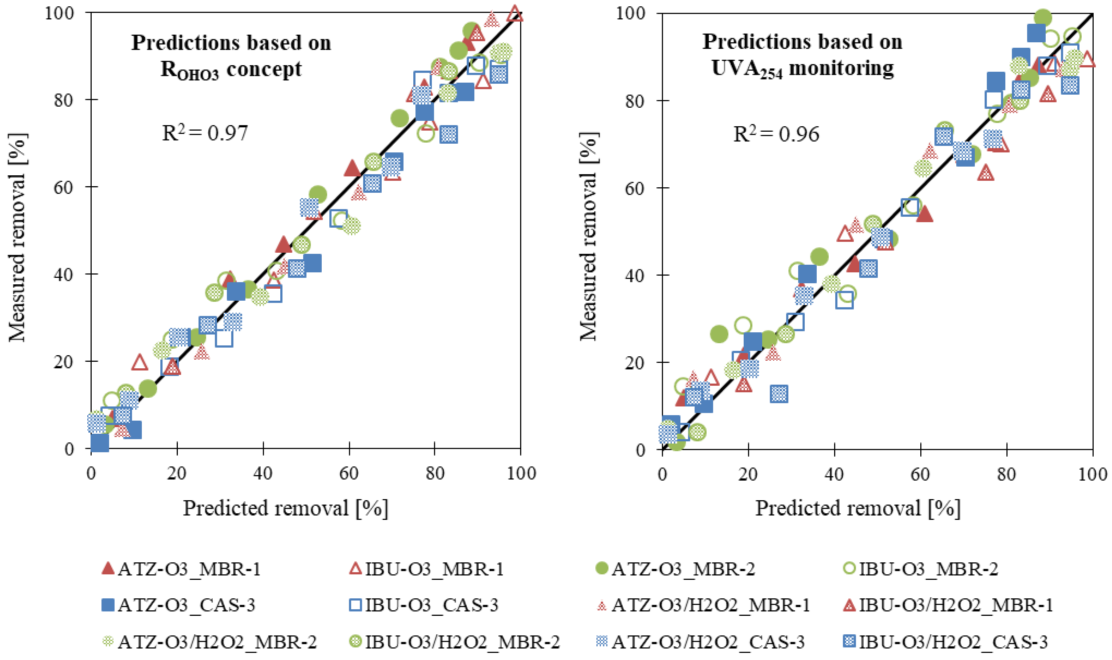

Figure 6. Measured versus predicted removals for atrazine and ibuprofen in effluents MBR-1, MBR-2 and CAS-3 in single ozonation and peroxone experiments (H_2O_2/O_3 ratio = 0.25, continuous addition). Predictions were performed employing two different models: one based on the R_{OHO3} concept (left figure) and the other on the existing correlation between •OH-exposure and the UVA_{254} decay during the treatment. Experimental conditions: $[ACMP]_0$: 100 µg L^{-1}; F_g: 0.1 NL min^{-1}; $[O_3]_{in}$: 30 mg NL^{-1}; T: 20 ºC.

Conclusions

This work demonstrates that the optimization of the H_2O_2 addition strategy is essential to improve the oxidation performance of peroxone process. Continuous dosing of H_2O_2 during ozonation significantly enhanced both •OH availability and MP abatement, for all studied wastewaters. Larger relationships (from 0.5 to 1) worked better during the initial or IOD stage, whereas H_2O_2/O_3 ratio of 0.25 was optimal during the secondary ozonation stage. By following this strategy, overall ozone needs could be reduced by 36% (employed H_2O_2/O_3 ratio: 0.25) with respect to single ozonation, which approximately corresponded to 28% savings in the overall energy costs associated to oxidants use. In addition, continuous H_2O_2 dosing was demonstrated to perform better than total initial addition of this reagent, estimating energy requirements to be up to 21% lower in the first case and for the cleanest effluents. The observed improvement in the oxidation efficiency, however, was generally little during the initial stage and became especially important after IOD. This work also demonstrated that UV absorbance of the water matrix, as surrogate for •OH-exposure estimation, can be used to control fate of organic species with low ozone reactivity. This strategy has proven to be useful for the accurate abatement prediction of different O_3-recalcitrant MPs from water matrices presenting a wide range of quality, employing single ozonation or the peroxone process as oxidative treatment.

Acknowledgements

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Supplementary Information for

Continuous H_2O_2 addition in peroxone process: performance improvement and modelling in wastewater effluents

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The SI includes the following additional figures (3) and tables (1):

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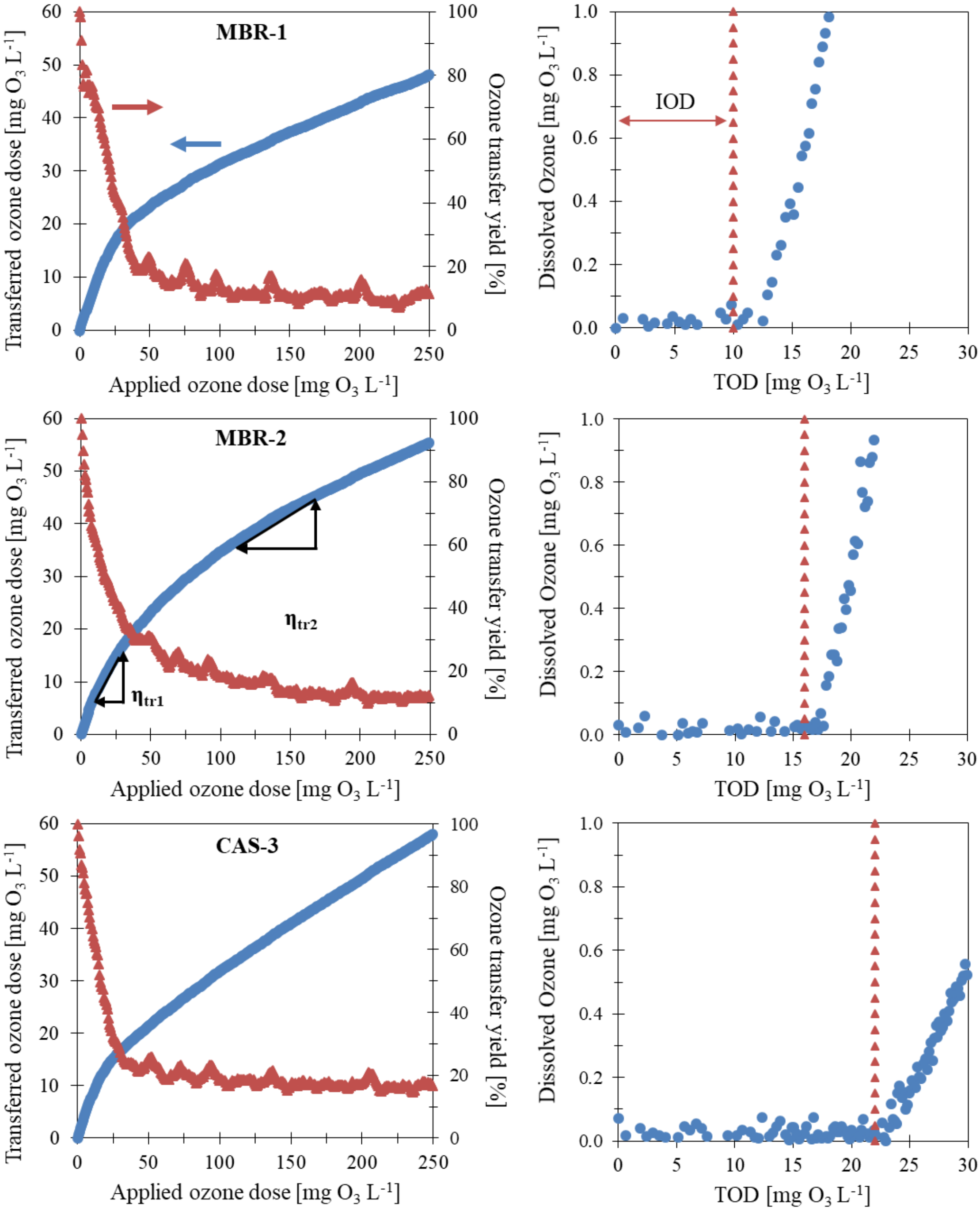

Figure S1. Ozone mass transfer (left) and immediate demand (right) during ozonation of wastewater effluent samples. Experimental conditions: F_g: 0.1 L min^{-1}; $[O_3]_{in}$: 30 mg L^{-1}; T: 20 ºC.

Table S1. Hydrogen peroxide dosing conditions during peroxone experiments with continuous addition of H_2O_2. $[H_2O_2]_{SS1}$ and $[H_2O_2]_{SS2}$ stand for the concentration of H_2O_2 stock solutions for primary and secondary ozonation stages, respectively. In all cases, the H_2O_2 dosing flow-rate was set at the lowest possible value (0.33 mL min^{-1}).

Effluent	**H_2O_2/O_3 ratio (molar)**	**$[H_2O_2]_{SS1}$ [mg L^{-1}]**	**$[H_2O_2]_{SS2}$ [mg L^{-1}]**
MBR-1	0	-	-
	0.25	1407	205
	0.5	2814	411
	1	5628	822
MBR-2	0	-	-
	0.25	1342	241
	0.5	2684	483
	1	5367	966
CAS-3	0	-	-
	0.25	1471	338
	0.5	2942	677
	1	5883	1354

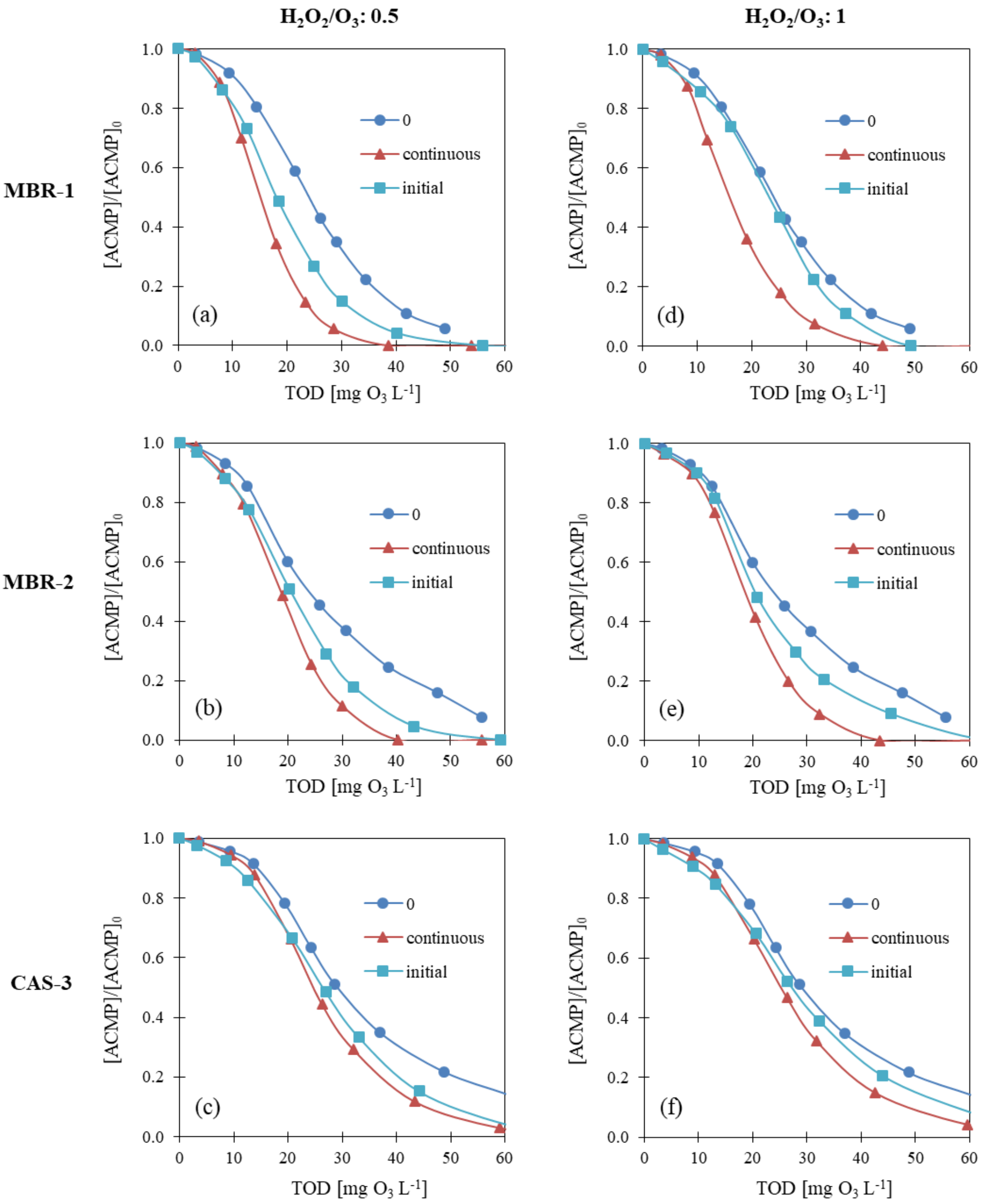

Figure S2. Removal of ACMP from effluents MBR-1, MBR-2 and CAS-3 by O_3 and O_3/H_2O_2 combination: comparison between continuous and initial addition of H_2O_2 for H_2O_2/O_3 molar ratios of 0.5 (a-c) and 1 (d-f). Plots corresponding to experiments performed with a molar ratio of 0.25 are included in the main text. Experimental conditions: $[ACMP]_0$: 100 µg L^{-1}; F_g: 0.1 NL min^{-1}; $[O_3]_{in}$: 30 mg NL^{-1}; T: 20 ºC.

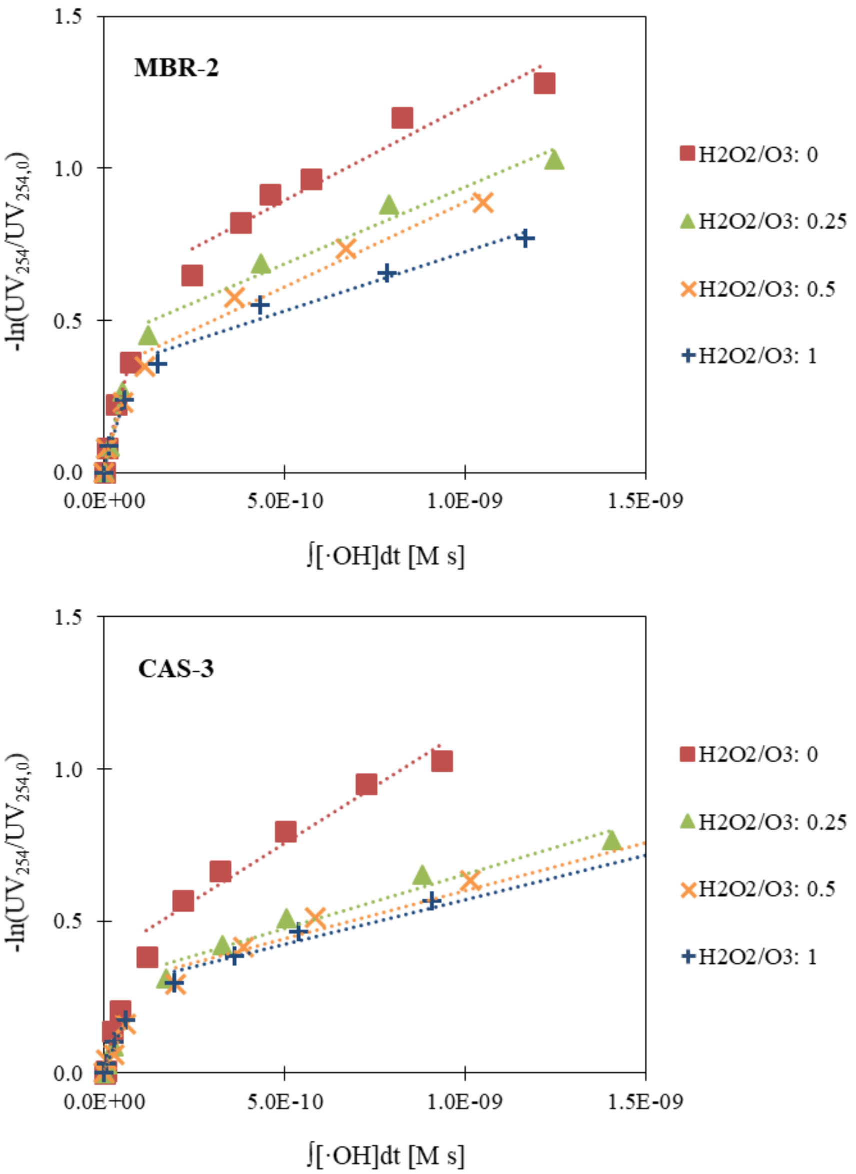

Figure S3. Correlation between UVA_{254} abatement and hydroxyl radical exposure during continuous H_2O_2 addition peroxone experiments with effluents MBR-2 and CAS-3 at different H_2O_2/O_3 ratios. Experimental conditions: $[ACMP]_0$: 100 µg L^{-1}; F_g: 0.1 NL min^{-1}; $[O_3]_{in}$: 30 mg NL^{-1}; T: 20 ºC.

5 Conclusions and recommendations

5.1 Conclusions

The following conclusions are organized according to the specific objectives initially set for this thesis and the results obtained.

Regarding **individual degradation studies of selected priority/emerging concern pesticides (MC, ACMP and DDVP) (Appendices I-III)**, it could be concluded that:

- MC and DDVP are prone to ozone attack, which means that both pesticides would be probably effectively abated in ozone applications. ACMP, on its part, reacts very slowly with O_3, which hinders its removal through ozonation.
- Despite the observed differences in their second-order rate constants, all three pesticides react very quickly with •OH formed through ozone decomposition.
- Although MC is readily oxidized by ozone, some toxic transformation products are formed. Especially remarkable is the case of methiocarb sulfoxide, which appears to be even more toxic than MC. In addition, formed TPs do not apparently react as quickly with ozone as MC, and therefore are poorly abated.
- Intermediates detected for ACMP and DDVP should apparently be less toxic than the parent compound. However, a toxicity enhancement is observed during ozonation, which is less significant or readily disappear when •OH oxidation occurs.
- The role of hydroxyl radicals in ozonation process is decisive in the effective abatement of all pesticides, potentially formed TPs and associated toxicity. Even though ozone can effectively oxidize some of the tested compounds, the radical route should be –as far as possible– enhanced.

From the study on the **abatement of ozone-refractory compounds during ozonation, including the assessment of potential strategies for the kinetic modelling and control of this process (Appendix IV)**, the following points could be highlighted:

- The effective removal (*i.e.*, > 80%) of ozone-refractory compounds, in general, requires the employment of higher ozone doses than the currently employed ones.

Concretely, it appears to be that TOD values higher than the effluents IOD should be overpassed.

- Ozonation of wastewater effluents can be well described, in terms of oxidation efficiency (*i.e.*, •OH availability per consumed ozone) through the application of a two-stage model based on the recently defined $R_{OH,O3}$ concept.
- $R_{OH,O3}$ values, especially those corresponding to the initial stage of the process, are markedly affected by the effluent characteristics, mainly organic matter content and alkalinity.
- Coupling chemical kinetics and the $R_{OH,O3}$ concept allow good predictions of ozone-resistant MPs abatement for a broad range of effluent properties.
- UVA_{254} decrease measured during ozonation correlates well with the availability of hydroxyl radicals in the medium (*i.e.*, •OH exposure). Thus, UVA_{254} measurements can be used for •OH exposure online estimation and (consequently) prediction of ozone-refractory MPs abatement during ozonation of wastewater effluents.

In view of the results obtained in the **assessment of EfOM fractions during ozonation of wastewater effluents applied for micropollutants removal, including ozone-refractory compounds (Appendix V)**, it is concluded that:

- DOC is reduced in MBR effluents, whereas for effluents coming from CAS treatments a significant increase in this parameter was observed for the highest consumed dose of ozone. This was attributed to the solubilization of suspended solids contained in the original effluent.
- In MBR effluents, the humic substances fraction is gradually oxidized and transformed into smaller components such as the so-called building blocks and low molecular weight acids.
- In CAS samples with significant amounts of suspended solids, accumulation of smaller fractions with increasing ozone doses also occur, but a net increase in the humic fraction content is observed. It appears to be that the observed DOC gain in these effluents is due to the solubilization of humic substances.
- Contrarily to what is typically assumed, the abatement of humic substances appears to be not so well correlated with aromaticity reduction, being only observed after a certain abatement of UVA_{254}.

- The lag in humic substances abatement observed with respect to aromaticity reduction, as well as the kinetics of the process, appear to correlate well with the initial oxidant demands of the effluents.

Concerning the study of the **application, intensification and modelling of peroxone process for enhanced oxidation of ozone-refractory micropollutants in wastewater effluents (Appendix VI)**, the main conclusions are:

- Addition of hydrogen peroxide at low molar relationships (*i.e.*, H_2O_2/O_3 of 0.25) significantly improve the abatement of ozone recalcitrant compounds with respect to single ozonation, regardless of the effluent properties. This enhancement leads to a reduction in the ozone needs, resulting in turn in important energy savings.
- The enhancement in oxidation efficiency (*i.e.*, hydroxyl radicals availability per consumed ozone) mainly occurs during the secondary ozonation stage, that is, after IOD completion, and it appears to be directly related to a lower oxidant demand of the effluent after this point of the process.
- Increasing the H_2O_2/O_3 ratio does not lead to en enhancement after IOD. In fact, lower $R_{OH,O3}$ values are obtained for oxidation ratios of 0.5 and 1, compared to the process using a relationship equal to 0.25.
- Continuous addition of H_2O_2 works lead to a more efficient oxidation process than total initial addition of this oxidant.
- Modelling strategies based on the use of the $R_{OH,O3}$ concept –which is also useful to describe the peroxone process– and UVA_{254} monitoring are useful for accurate prediction of different ozone-refractory MPs abatement in different effluent samples.

5.2 Recommendations

Some recommendations are also provided, according to the potential for improvement, continuation and practical application of the research carried out in this thesis.

In first place, the author encourages the expansion of kinetic, mechanistic and toxicological studies of individual compounds to more priority/emerging concern pesticides and other families of chemicals included in Directive 2013/39/EU and the watch list of Decision

2018/840/EU. According to these regulations, the study of alternative technologies for the abatement of these substances from water and wastewater should be a research priority, and ozonation is a mature and suitable technology for that purpose. If possible, a wider battery of bioassays should be included in the toxicity assessment, considering specific and unspecific toxicity tests and the potential negative impacts over different trophic levels.

Concerning the study of the abatement of ozone-refractory compounds including modelling and control strategies for this process, further research on this topic is also required, including testing the use of the $R_{\mathrm{OH,O3}}$ concept to describe other ozone-based processes or the application of this strategy, if possible, at pilot- and full-scale. The use of UVA_{254} as surrogate parameter is quite interesting regarding its potential application in online control systems. Thus, testing this approach in larger scales is strongly recommended. Finally, research should in addition focus on somehow including ozone-reactive micropollutants on abatement modelling strategies, which should allow the monitoring and control of any chemical removal during ozonation.

Regarding the fate of EfOM during ozonation, and depending on the final destination of the treated effluent, potential impacts of residual EfOM should be properly assessed through bacterial growth tests or estimations of eutrophication potential. If disinfectant addition is planned after ozonation, the potential formation of disinfection byproducts should be also evaluated. A good approach would be the use of a biological post-treatment to remove the newly generated biodegradable matter. However, not all EfOM would be eliminated, and in any case the feasibility of this process should be carefully investigated.

Finally, and since the peroxone process is nowadays mostly employed for bromate control during ozonation, studies on the formation of this harmful product through this process application should be conducted in the next stage of this research. Also, potential implementation of H_2O_2 continuous dosing mode at larger scales should be assessed.

Other contributions by the author

In addition to the journal publications presented in this PhD thesis, the author also collaborated in other research studies during his predoctoral stage, mainly with visiting scholars and students, from which some journal publications were ultimately derived. Moreover, he contributed to several conferences and scientific meetings, presenting part of the research in which he took part, whether included in his thesis or not. References for both journal articles and congress contributions are provided below. The author also participated in a research study during a short stay at the University of Alberta, in Canada, where he temporarily joined Dr. Mohammed Gamal El-Din's laboratory. For three months, his work was focused on ozone-based catalytic processes applied for enhanced treatment of combined sewer overflows (CSOs), which are suspected to cause significant negative impacts when discharged to Canadian water bodies. Interesting data were obtained from this collaborative study and a journal publication is currently in preparation.

Journal articles

Bustos, N., Cruz-Alcalde, A., Iriel, A., Fernández Cirelli, A., Sans, C. (2019). Sunlight and UVC-254 irradiation induced photodegradation of organophosphorus pesticide dichlorvos in aqueous matrices, *Science of the Total Environment* 649, 592-600.

Villota, N., Lombraña, J.I., Cruz-Alcalde, A., Marcé, M., Esplugas, S. (2019). Kinetic study of colored species formation during paracetamol removal from water in a semicontinuous ozonation contactor, *Science of the Total Environment* 649, 1434-1442.

Bertagna Silva, D., Cruz-Alcalde, A., Sans, C., Giménez, J., Esplugas, S. (2019). Performance and kinetic modelling of photolytic and photocatalytic ozonation for enhanced micropollutants removal in municipal wastewaters, submitted to *Applied Catalysis B: Environmental* and currently under 2nd review.

Malvestiti, J.A., Cruz-Alcalde, A., López-Vinent, N., Dantas, R.F., Sans, C. (2019). Catalytic ozonation by metal ions for municipal wastewater disinfection and simultaneous micropollutants removal, submitted to *Chemical Engineering Journal*.

Congress communications

Oral presentations

Cruz-Alcalde, A., Esplugas, S., Sans, C. A practical approach for the control of micropollutants removal during wastewater ozonation using kinetic and water quality parameters, in: *International Ozone Association Conference on Ozone and Advanced Oxidation. Solutions for Emerging Pollutants of Concern to the Water and the Environment (IOA-EA3G2018)*, Lausanne (Switzerland), September 2018.

Cruz-Alcalde, A., Esplugas, S., Sans, C. Formación de radicales hidroxilo y predicción de la eliminación de microcontaminantes durante la ozonización de efluentes de depuradora, in: *XIII Congreso Español de Tratamiento de Aguas (META 2018)*, León (Spain), June 2018.

López, N.; Cruz-Alcalde, A.; Romero, L.; Chávez, M.; Marco, P.; Giménez, J.; Esplugas, S. Assessment of different reactor configurations for a Diphenhydramine Removal by UV-A LED Photo-Fenton Process, in: *10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA10)*, Almeria (Spain), June 2018. ISBN: 978-84-17261-27-6.

Cruz-Alcalde, A. Hydroxyl radical formation and prediction of micropollutants abatement during ozonation of municipal wastewater effluents, in: *3rd IdRA Young Researchers Seminar*, Barcelona (Spain), May 2018.

Sans, C., Bustos, N., Cruz-Alcalde, A., Iriel, A., Fernández Cirelli, A. Effect of sunlight and UV-C disinfection dose irradiation on the degradation of organophosphorus pesticide dichlorvos, in: *18th European Meeting on Environmental Chemistry (EMEC18)*, Porto (Portugal), November 2017. ISBN: 978-972-752-228-6.

Cruz-Alcalde, A., Sans, C., Esplugas, S. First assessment of water ozonation applied to highly toxic methiocarb removal, in: *10th World Congress of Chemical Engineering (WCCE10)*, Barcelona (Spain), October 2017. ISBN: 978-84-697-8629-1.

Sans, C., Cruz-Alcalde, A., Esplugas, S. Priority pesticides abatement from water and wastewater by ozonation, in: *23th International Ozone Association World Congress and Exhibition (IOA WC17)*, Washington D.C. (USA), August 2017.

Cruz-Alcalde, A., Sans, C., Esplugas, S. Assessing the application of ozonation process to priority pesticide dichlorvos removal from water, in*: 2nd Summer School on Environmental Applications of Advanced Oxidation Processes and Training School on Advanced Treatment Technologies and Contaminants of Emerging Concern*, Porto (Portugal), July 2017.

Cruz-Alcalde, A., Sans, C., Esplugas, S. Assessing the application of ozone-based processes to priority pesticides removal from water and wastewater, in: *5th European Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP5),* Prague (Czech Republic), June 2017: p. 37. ISBN: 978-80-7080-991-4.

Cruz-Alcalde, A., López-Vinent, N. Removal of contaminants of emerging concern by means of Advanced Oxidation Processes, in: *2nd IdRA Young Researchers Seminar,* Barcelona (Spain), May 2017.

Poster presentations

Cruz-Alcalde, A., Esplugas, S., Sans, C. Simultaneous dosing of ozone and hydrogen peroxide for advanced oxidation treatment of municipal wastewater effluents, in: *International Ozone Association Conference on Ozone and Advanced Oxidation. Solutions for Emerging Pollutants of Concern to the Water and the Environment (IOA-EA3G2018)*, Lausanne (Switzerland), September 2018.

Cruz-Alcalde, A., Esplugas, S., Sans, C., Evolución de las fracciones de la materia orgánica contenida en efluentes de depuradoras municipales durante el proceso de ozonización, in: *XIII Congreso Español de Tratamiento de Aguas (META 2018)*, León (Spain), June 2018.

Silva, D.B., Cruz-Alcalde, A., Esplugas, S., Sans, C. Application of UV radiation for enhanced micropollutant removal in water and wastewater ozonation, in: *10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA10)*, Almeria (Spain), June 2018. ISBN: 978-84-17261-27-6.

López, N.; Cruz-Alcalde, A.; Romero, L.; Chávez, M.; Marco, P.; Giménez, J.; Esplugas, S. Application of UV-A LED Photo-Fenton in a Batch Reactor Evaluating Different Wavelengths, in: *10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA10)*, Almeria (Spain), June 2018. ISBN: 978-84-17261-27-6.

López, N.; Cruz-Alcalde, A.; Romero, L.; Chávez, M.; Marco, P.; Giménez, J.; Esplugas, S. Photo-Fenton treatment of Histamine 1 with UV-A LED and BLB radiation: energetic efficiency comparison, in: *10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA10)*, Almeria (Spain), June 2018. ISBN: 978-84-17261-27-6.

Cunha, R.F.; Cavalcante, R.P.; Cruz-Alcalde, A.; Giménez, J.; Marco, P.; Esplugas, S.; Wender, H.; Martines, M.A.U.; de Oliveira, L.C.S.; Casagrande, G.A.; Machulek Jr., A.; de Oliveira, S.C. Synthesis of pure and N-modified Anatase titania and their photocatalytic activity in degradation of metoprolol, in: *10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA10)*, Almeria (Spain), June 2018. ISBN: 978-84-17261-27-6.

Cruz-Alcalde, A., Sans, C., Esplugas, S. Elimination of priority pesticides during wastewater ozonation: reaction characterization and application in real matrices, in: *18th European Meeting on Environmental Chemistry (EMEC18)*, Porto (Portugal), November 2017. ISBN: 978-972-752-228-6.

Cruz-Alcalde, A., Sans, C., Esplugas, S. Is ozonation a suitable treatment option for waters contaminated by the highly toxic pesticide methiocarb? in: *IOA Ozone Symposium at Wasser Berlin 2017*, Berlin (Germany), March 2017.

Resumen en castellano

Introducción

El aumento de la población, junto a otros factores como el crecimiento industrial y el progreso constante de regiones del mundo aún en desarrollo contribuyen hoy en día al aumento de la demanda mundial de agua [1,4]. Por otro lado, los recursos hídricos existentes no son indefinidos ni están uniformemente repartidos [6], por lo que un número de países cada vez mayor sufre, en un grado u otro, escasez de agua [3,6]. En vista de este gran problema que afecta cada vez a más personas, la reutilización del agua va ganando terreno como una de las soluciones con mayor potencial.

La actividad humana genera de manera continua grandes cantidades de agua residual. Cerca del 20% de estas aguas se tratan antes de ser descargadas al medio ambiente [3], y una parte de estas últimas se vuelve a emplear en agricultura, industria, actividades recreativas o aplicaciones medioambientales, entre otros usos minoritarios [11]. A pesar de que el potencial de reutilización del agua es elevado [16], el coste económico asociado a esta práctica junto con la falta de regulaciones y la mala percepción por parte de la sociedad hacen que hoy en día el agua residual se vea como un recurso sólo en algunos lugares del planeta [17]. Además de todos estos factores, algunos tipos de contaminación del agua continúan siendo indebidamente considerados por las autoridades y en los proyectos de tratamiento y reutilización de aguas residuales. Un buen ejemplo es el de los microcontaminantes orgánicos, y concretamente de los contaminantes de preocupación emergente y las sustancias definidas como prioritarias.

El continuo desarrollo, producción, uso y eliminación de toda clase de compuestos orgánicos empleados a diario en las distintas actividades humanas, está provocando la presencia de estas sustancias en los compartimentos acuáticos [19–21]. Fármacos, productos de cuidado personal, hormonas, tensoactivos, aditivos industriales, pesticidas…la mayoría de estos compuestos resisten los tratamientos de aguas convencionales y son descargados al medio acuático desde las plantas de tratamiento [23]. A pesar de que en general se encuentran en bajas concentraciones, se sospecha que su presencia en las aguas implica riesgos para salud humana y la seguridad ambiental [19,24]. Pese a ello, el conocimiento en relación a la peligrosidad de muchas de estas sustancias es aún muy limitado [25,26].

A aquellos compuestos de conocida peligrosidad se les conoce como sustancias prioritarias, y en regiones como Europa su presencia en las aguas está regulada por la Directiva 2013/39/UE [35]. Aquellas otras sustancias bajo sospecha o estudio por los riesgos que pueden comportar reciben comúnmente el nombre de contaminantes de preocupación emergente [29,30]. En Europa, se establecen programas de monitoreo y estudio para algunas de estas sustancias, con el fin de determinar si deben pasar a ser categorizadas como prioritarias o no. La Decisión 2018/840/UE recoge la última lista de contaminantes de preocupación emergente que actualmente se encuentran en estudio [37].

Uno de los grupos de microcontaminantes que más preocupan a la sociedad son los pesticidas. Aproximadamente la mitad de las sustancias recogidas en las listas de sustancias prioritarias o contaminantes de preocupación emergente pertenecen a esta categoría [35,37]. Los pesticidas son sustancias diseñadas con la finalidad última de disuadir, incapacitar o simplemente matar seres vivos considerados perjudiciales. Se emplean sobre todo para la protección de los cultivos en agricultura, aunque también en otras aplicaciones como el control de enfermedades animales y humanas [41,42]. Su uso se hizo especialmente popular a partir de la segunda mitad del siglo XX y, debido a la peligrosidad de estos compuestos [40,47,48], las regulaciones al respecto han seguido un patrón de descubrimiento-restricción-prohibición que llega hasta nuestros días [46]. De este modo, los primeros pesticidas en aparecer fueron los organoclorados, que fueron prohibidos y remplazados por familias menos peligrosas como los organofosforados, los carbamatos, los piretroides y, unas décadas después, los neonicotinoides. Con el tiempo, varios compuestos de estas familias han demostrado los riesgos que conllevan para la salud humana y el medio ambiente, por lo que su uso se ha ido restringiendo poco a poco [46]. Otros muchos, al ser necesarios, se encuentran bajo sospecha, pero se siguen empleando, lo que sigue provocando que se encuentren trazas de los mismos en el medio acuático [55]. Dada esta situación, y de acuerdo a lo que la –aún escasa– legislación en materia de microcontaminantes intenta promover, se deben encontrar soluciones para la mitigación de la presencia en el agua de este tipo de compuestos. Una buena parte de este objetivo pasa por el estudio y aplicación de procesos de tratamiento avanzado en las plantas de depuración de aguas residuales, que constituyen una de las principales fuentes de introducción de microcontaminantes en el medio acuático [23].

La creciente preocupación de la sociedad por la presencia de microcontaminantes en las aguas motivó hace ya algunas décadas el estudio del uso del ozono como agente para eliminar estas sustancias [104]. Hoy en día, los procesos de tratamiento basados en ozono constituyen una de las mejores opciones a tal fin [104–107]. Su aplicación a escala real es costosa y no existen leyes claras que obliguen a eliminar los microcontaminantes de las aguas, aunque en algunos países del mundo, la preocupación por esta problemática ha conducido al establecimiento de iniciativas basadas en la mejora de las estaciones depuradoras de aguas residuales mediante esta tecnología [104].

El proceso de ozonización se basa en la introducción y disolución de ozono en fase gas en el agua a tratar, seguida de la oxidación de los contaminantes debida a reacciones directas y selectivas de la molécula de ozono (O_3), o al ataque no selectivo y de mayor poder destructivo por parte del radical hidroxilo (•OH), formado como subproducto de las reacciones del ozono con los constituyentes del agua [107]. La primera vía es efectiva en la degradación muchas sustancias, aunque no para todas ellas, pues algunos contaminantes son resistentes al ozono y sólo el radical hidroxilo es capaz de destruirlas [107,136]. En un intento de incrementar la presencia de •OH durante la ozonización, se emplean los Procesos de Oxidación Avanzada (POA) basados en ozono.

Existen muchas variedades que combinan ozono con catalizadores metálicos y no metálicos, sólidos o en disolución, además de otros agentes como la radiación ultravioleta (UV) [107,124,126,129]. Pero sin duda, el proceso de oxidación basado en ozono con mayor efectividad y potencial de aplicación es el que combina O_3 y peróxido de hidrógeno (H_2O_2) [107]. El proceso se basa en la reacción entre la molécula de ozono y la forma disociada del H_2O_2, o anión hidroperóxido (HO_2^-) [111,117]. Dicha reacción da lugar a la formación radicales hidroxilos con un rendimiento del 50%, es decir, por cada dos moléculas de ozono consumidas se genera un •OH [130]. Superar este rendimiento mediante la combinación del ozono con otros agentes (por ejemplo, catalizadores) es complicado y, en cualquier caso, los inconvenientes técnicos que presentan dichas combinaciones (necesidad de separación de los catalizadores y el efluente tratado, inactivación del catalizador, entre otros) dificultan su aplicación a escala real, limitando su uso –al menos de momento– a su estudio en el laboratorio.

En lo que a los procesos de ozonización se refiere, además del coste económico, se deben tener en cuenta varios aspectos técnicos a la hora de valorar la factibilidad de su aplicación en aguas residuales. La efectividad del proceso, por ejemplo, está directamente ligada a la cinética de las reacciones de oxidación de los compuestos objetivo con los dos oxidantes involucrados: ozono y radical hidroxilo [104]. Además, conocer la cinética de las reacciones es extremadamente útil para la predicción de la eliminación de los microcontaminantes durante la ozonización [136].

Hoy en día, los contaminantes resistentes al ataque del ozono suponen una limitación de esta tecnología [135]. Eliminarlos de manera efectiva o al menos monitorizar o controlar su eliminación durante el proceso resulta fundamental. La degradación de estas sustancias mediante el proceso de ozonización simple es generalmente pobre, y parece requerir de dosis más elevadas de ozono [136,138,140,141]. El uso de la combinación O_3/H_2O_2, por su parte, generalmente ofrece márgenes de mejora muy modestos cuando se aplica a dosis de ozono bajas [136,144,145]. La aplicación de dosis de oxidante algo más elevadas en ambos procesos parece no haberse contemplado, y además el proceso O_3/H_2O_2 parece poder ofrecer aún cierto potencial de mejora.

A fin de describir la eliminación de un compuesto recalcitrante al ozono durante un proceso de tratamiento basado en el uso de este oxidante, la Ec. (I) puede ser de utilidad.

$$-\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = k_{\bullet\mathrm{OH}} \cdot \int [\bullet\,\mathrm{OH}]\mathrm{d}t \tag{I}$$

El factor $k_{\bullet\mathrm{OH}}$ es la constante cinética de reacción entre el radical hidroxilo y el microcontaminante (M), mientras que $\int[\bullet\mathrm{OH}]\mathrm{d}t$ es la concentración del oxidante integrada en el tiempo, que representan de manera sencilla su disponibilidad durante el proceso [150]. Conocer ambos factores es esencial para poder predecir con precisión la eliminación de los compuestos en un proceso dado [136]. La constante cinética se puede determinar en experimentos de laboratorio [107], además de existir amplias bases de datos [107,146] y algoritmos para la predicción de su valor en base a la aplicación de un conjunto de reglas químicas [147–149]. En cuanto al término integral, su determinación también puede llevarse a cabo para cada tipo de agua en pruebas de laboratorio [107,150]. No obstante, esta metodología impide el uso de las predicciones realizadas para el establecimiento de sistemas de control a tiempo real. Una solución puede ser el uso de parámetros de calidad del agua sensibles al proceso de ozonización que, fácilmente monitorizados a tiempo real, puedan servir para predecir la disponibilidad de radicales hidroxilos durante el proceso.

Un aspecto relacionado con la eficiencia del proceso que queda aún por cubrir es la falta de un parámetro que describa la eficiencia del mismo en términos de oxidación y que pueda servir para comparar el rendimiento de distintos procesos llevados a cabo a diferentes condiciones de operación en diferentes aguas residuales. En este sentido, el uso del parámetro $R_{\mathrm{OH,O3}}$, recientemente definido como la concentración integrada en el tiempo de radicales hidroxilo entre la dosis de ozono consumida [159], puede ser interesante. Su empleo en la caracterización y modelización cinética de la degradación de microcontaminantes en aguas residuales aún no ha sido investigado.

$$R_{\mathrm{OH,O3}} = \frac{\int [\bullet\, OH]\mathrm{d}t}{\mathrm{Ozono\ consumido}} \tag{II}$$

Además de los aspectos relacionados con la cinética del proceso, otro factor a tener en cuenta al aplicar ozono en el tratamiento de aguas reales es la formación de subproductos de degradación, ya sea a partir de transformaciones de los microcontaminantes o a través de reacciones del ozono con otros componentes de la matriz acuosa [104]. Para el primer caso, el conocimiento de los mecanismos de reacción del ozono y el radical hidroxilo junto con técnicas analíticas avanzadas es suficiente para saber qué nuevos compuestos se están formando [107,133,146]. Además, deben estudiarse los posibles efectos adversos de los intermedios de reacción ya que, aunque en general unas pocas transformaciones químicas de la molécula de partida sean suficientes para reducir su actividad biológica, en ocasiones estos productos pueden presentar una mayor toxicidad [104,107]. Otro grupo de productos de transformación a tener en cuenta es aquel producto de las reacciones del ozono y los radicales hidroxilos con la materia orgánica de efluente [104,170]. Los compuestos resultantes pueden contribuir a un buen número de problemas técnicos y ambientales, como por ejemplo ensuciamiento y saturación de membranas y otros procesos de separación posteriores, el crecimiento bacteriano en sistemas de distribución (en caso de reutilización del agua tratada) y la eutrofización de las aguas que reciban el efluente [170].

Objetivos

Considerando como objetivo principal de esta tesis la contribución al conocimiento relacionado con la caracterización del rendimiento y el modelado cinético de procesos de oxidación basados en el uso de ozono para la eliminación de microcontaminantes de matrices acuosas, se definieron los siguientes objetivos específicos a llevar a cabo en cada una de las partes en las que se dividió el trabajo de investigación:

- El estudio cinético, mecanístico y toxicológico del proceso de degradación de pesticidas considerados prioritarios o de preocupación emergente.
- La evaluación del rendimiento y el modelado cinético de la eliminación de microcontaminantes resistentes al ozono durante la aplicación del proceso de ozonización en efluentes de depuradora.
- El estudio de la evolución de la materia orgánica de los efluentes sometidos al proceso de ozonización para la eliminación de microcontaminantes, incluyendo compuestos resistentes al ozono.
- La evaluación de la combinación del ozono con peróxido de hidrógeno con el fin de mejorar el rendimiento de la oxidación de microcontaminantes en efluentes de depuradora, así como la valoración de alternativas en relación a la dosificación de oxidantes para la mejora del proceso en sí y el modelado cinético de las mismas.

Materiales y métodos

Los pesticidas prioritarios (o de preocupación emergente) empleados en el trabajo experimental de esta tesis fueron: metiocarb (MC), acetamiprid (ACMP) y diclorvos (DDVP). Los siguientes contaminantes modelo y sustancias de referencia fueron asimismo utilizados: atrazina (ATZ), *p*-benzoquinona (pBZQ), ácido *p*-clorobenzoico (pCBA), ibuprofeno (IBU), metoprolol (MPL), fenol (PH) y sulfametoxazol (SMX).

Además de los estudios con agua pura como matriz, en esta tesis se trabajó en la ozonización de efluentes secundarios. Se emplearon a tal propósito muestras de efluente procedentes de las siguientes cinco estaciones depuradoras de aguas residuales (EDAR) de la provincia de Barcelona: El Prat de Llobregat, Gavà-Viladecans, La Llagosta, Vacarisses y Vallvidrera. Para los trabajos presentados en los Apéndices IV y V, se tomaron efluentes procedentes de reactores biológicos convencionales de fangos activos (CAS) de las EDAR de El Prat de Llobregat, Gavà-Viladecans y La Llagosta (muestras codificadas como C-PRA [o C1], C-GAV [o C2] y C-LLA [o C3], respectivamente), y también muestras procedentes de biorreactores de membrana (MBR) de las estaciones de Vacarisses, Vallvidrera y Gavà-Viladecans (efluentes M-VAC [o M1], M-VAL [o M2] y M-GAV [o M3], respectivamente). Para el trabajo presentado en el apéndice VI, se utilizaron tres muestras de efluentes: dos procedentes de procesos MBR de las EDAR de Vacarisses (MBR-1) y Gavà-Viladecans (MBR-2) y un efluente de la línea convencional de la depuradora de Gavà-Viladecans (CAS-3). Las propiedades fisicoquímicas de cada uno de los efluentes se recogen en la Tabla 11 (sección 3.2).

Los experimentos de ozonización se llevaron a cabo siguiendo dos metodologías distintas: ensayos en discontinuo y ensayos en un reactor operado en modo semicontinuo.

Para el estudio cinético, mecanístico y toxicológico de las reacciones del ozono y el radical hidroxilo con los pesticidas MC, ACMP y DDVP (publicaciones presentadas en los Apéndices I-III), el método de trabajo escogido fue el ensayo de ozonización en discontinuo. Este tipo de experimento permite un control total de la dosis de oxidante aplicada, algo fundamental cuando se requiere la determinación de las constantes cinéticas de reacción de segundo orden que rigen la degradación de los contaminantes orgánicos durante la ozonización. El procedimiento se basa en la adición de alícuotas de una disolución acuosa saturada de ozono a una disolución acuosa modelo que contiene los pesticidas en estudio. La mezcla se deja entonces reaccionar hasta que el ozono es completamente consumido. Finalmente, se llevan a cabo las determinaciones analíticas necesarias. La disolución *stock* de ozono se prepara mediante el burbujeo en agua ultrapura de una corriente gaseosa de oxígeno con un cierto contenido en O_3. Para la determinación de las constantes cinéticas de reacción de los pesticidas MC y DDVP, se llevaron a cabo experimentos de competición a pH 7. Se aplicaron distintas dosis de ozono a una serie de viales que contenían mezclas acuosas del pesticida en estudio y una (para cinéticas de reacción del MC [SMX] y el DDVP

[MPL] con ozono) o dos (para cinéticas de reacción del MC [SMX y PH] y el DDVP [MPL y pBZQ] con •OH) sustancias de referencia. Además, para las cinéticas de reacción con ozono, se suprimió la oxidación del radical hidroxilo mediante la adición de un exceso de *tert*-butanol (tBuOH). Para cada dosis de ozono, se analiza mediante HPLC la concentración del pesticida y los competidores. El compuesto ACMP es poco reactivo con el ozono, por lo que, en lugar de experimentos de competición, se llevó a cabo un ensayo de ozonización en una solución individual de este compuesto a pH 2 (mediante adición de ácido fosfórico), empleando un gran exceso molar (50:1) de O_3. En este caso, se siguieron en el tiempo las concentraciones del pesticida (mediante Cromatografía Líquida de Alta Eficacia [HPLC] con detección UV) y el ozono (mediante el método índigo). Por su parte, en la determinación de la constante de reacción entre ACMP y •OH, llevada a cabo mediante un experimento de competición, se empleó únicamente una sustancia de referencia (pCBA). La elucidación de los intermedios de reacción, por otro lado, se llevó a cabo mediante experimentos de ozonización con disoluciones individuales de cada compuesto a diferentes dosis de ozono, con y sin la presencia de tBuOH. Las muestras oxidadas se analizaron mediante HPLC combinada con Espectrometría de Masas (HPLC-MS), en busca de intermedios de reacción. Las mismas muestras se emplearon posteriormente en ensayos de toxicidad aguda con la bacteria marina *Vibrio fischeri*. Todos los experimentos anteriormente citados se realizaron por triplicado, a pH 7 y a una temperatura de 20 ± 2 ºC.

Para el estudio de la ozonización con efluentes de depuradora (publicaciones presentadas en los Apéndices IV-VI), los ensayos se llevaron a cabo en un reactor de vidrio operado en modo semicontinuo. Este tipo de experimento permite trabajar a mayores dosis de ozono evitando al mismo tiempo una dilución significativa de la solución modelo, el principal inconveniente de los ensayos en discontinuo anteriormente descritos. La solución modelo –típicamente formada por una matriz de efluente de depuradora que contiene uno o más compuestos modelo en bajas concentraciones– se carga en la vasija de reacción. Mediante un difusor de vidrio poroso instalado en el fondo del reactor, dicha solución se pone en contacto con una mezcla gaseosa de oxígeno y ozono, durante un tiempo determinado en el cual se mantiene la homogeneidad del medio mediante un sistema de agitación mecánica. A diferentes tiempos de contacto, se extraen muestras del medio de reacción y se llevan a cabo las determinaciones analíticas necesarias. En esta tesis, el compuesto ACMP (100 µg L^{-1}) se utilizó como compuesto "sonda" para la cuantificación de la disponibilidad del radical hidroxilo en el medio [150], en los estudios presentados en los Apéndices IV-VI. Otros compuestos como ATZ o IBU, resistentes al ozono, se utilizaron como compuestos modelo (25 y 50 µg L^{-1}, respectivamente) en la validación de los modelos cinéticos propuestos en los estudios de los Apéndices IV y VI. Finalmente, los pesticidas MC y DDVP también se emplearon como compuestos modelo (50 µg L^{-1}) en algunos experimentos de ozonización de efluentes de depuradora (Apéndice IV). En todos los experimentos en semicontinuo se aplicó un caudal de gas de 0.1 NL min^{-1} y una concentración de entrada de ozono de 30 mg NL^{-1}. En general, se siguieron las concentraciones de los microcontaminantes, así como algunos parámetros de calidad del agua como la absorbancia UV, el carbono orgánico total o disuelto (TOC o DOC) o la demanda química de oxígeno (DQO). Para el estudio presentado en el Apéndice V, además, se evaluaron las distintas fracciones de la materia orgánica disuelta mediante la Cromatografía de Exclusión por Tamaños con Detección de Carbono Orgánico (SEC-OCD) [182].

En los experimentos de ozonización en semicontinuo, la dosis de ozono transferida (TOD) a la disolución a cada tiempo de contacto se estimó mediante la medición del caudal de gas que atraviesa el sistema y de las concentraciones de ozono en la corriente de entrada y de salida del reactor [143]. La demanda instantánea de ozono (IOD), un parámetro de diseño importante en el proceso de ozonización, se estimó como aquel valor de TOD a partir del cual se detecta ozono disuelto en el medio de reacción [142,143]. La concentración de ozono en el medio se monitorizó mediante un sensor amperométrico. Todos los experimentos se llevaron a cabo a una temperatura de 20 ± 1 ºC, sin ajuste de pH y al menos por duplicado.

La dosificación del peróxido de hidrógeno en los experimentos con el proceso *peroxone* (O_3/H_2O_2, ver Apéndice VI) se realizó de dos formas: mediante dosificación continúa usando una bomba dosificadora, o en una única adición al inicio del experimento. En el primer caso, la dosificación se realizó desde un depósito de vidrio que contenía una dilución de la solución comercial de H_2O_2. El caudal de la bomba dosificadora se fijó al mínimo posible para evitar una dilución significativa del medio de reacción. Se empleó la velocidad de transferencia de ozono determinada en experimentos de ozonización simple, TOD/*t*, como parámetro de referencia para establecer la concentración de H_2O_2 en el depósito de reserva, con el objetivo final de aplicar ratios molares H_2O_2/O_3 de 0.25, 0.5 y 1. En el proceso de ozonización se dan típicamente dos regímenes de transferencia de ozono (primero uno rápido y, después de completarse la IOD, uno más lento [142,143]), por lo que en cada experimento fueron necesarias dos disoluciones de H_2O_2 de distinta concentración (primero una más concentrada y luego una más diluida), una para cada valor de TOD/*t* observado. En cuanto a los experimentos con dosificación inicial única, la cantidad adicionada de H_2O_2 se correspondió con la dosis total añadida en los experimentos con dosificación continua.

Una imagen real y un esquema de la planta de ozonización a pequeña escala, especialmente diseñada y puesta a punto por el autor de esta tesis para la realización de una parte de la misma, pueden observarse en las Figuras 14 y 15 (sección 3.3.3).

Resultados y discusión

En lo que respecta al estudio cinético con disoluciones modelo de los pesticidas MC, ACMP y DDVP, los valores obtenidos para las constantes de reacción de segundo orden fueron: $1.7\cdot10^{6}$ $M^{-1}s^{-1}$ (MC), 0.25 $M^{-1}s^{-1}$ (ACMP) y 590 $M^{-1}s^{-1}$ (DDVP), para reacciones con ozono, y $8.2\cdot10^{9}$ $M^{-1}s^{-1}$ (MC), $2.1\cdot10^{9}$ $M^{-1}s^{-1}$ (ACMP) y $2.2\cdot10^{9}$ $M^{-1}s^{-1}$ (DDVP), para reacciones con •OH.

En cuanto a los mecanismos de degradación, en el caso del pesticida metiocarb se pudieron distinguir tres compuestos de transformación, fruto de la oxidación secuencial del grupo sulfuro contenido en la molécula de MC, en combinación con procesos de hidrólisis de las estructuras resultantes (ver Tabla 2 y Figura 3 en el Apéndice I). Destacó la identificación del metiocarb sulfóxido, un compuesto conocido por ser potencialmente más tóxico que su compuesto de partida. En lo que respecta a los mecanismos de degradación del ACMP, se distinguieron dos posibles rutas oxidativas, ambas iniciadas mediante abstracción de hidrógeno por parte del radical hidroxilo, pero dando lugar a diferentes productos de transformación (ácido 6-cloronicotínico, *N’*-ciano-*N*-metil acetamidina y *N’*-ciano acetamidina, por un lado, y N-ACMP-desmetilo, por el otro) según si la oxidación fue iniciada en el grupo metileno o metilo, ambos enlazados a la amina terciaria comprendida en la molécula de ACMP. Más detalles acerca de los compuestos de transformación detectados y los mecanismos de degradación propuestos para el ACMP pueden ser consultados en la Tabla 1 y la Figura 4 del Apéndice II). Respecto a la degradación del insecticida DDVP, y en base a los compuestos de transformación detectados en experimentos con y sin adición de tBuOH (ver Tabla 2 del Apéndice III), se pudieron proponer varias rutas de oxidación debidas a reacciones radicalarias o de oxidación directa por parte del ozono.

Estas se esquematizan en la Figura 4 del Apéndice III. La oxidación mediante el radical hidroxilo pudo iniciarse de tres formas distintas: mediante abstracción de hidrógeno de uno de los grupos metilo enlazados al grupo fosfato y por adición de •OH al átomo de fósforo o al doble enlace del grupo diclorovinilo. Estos mecanismos, en combinación con reacciones de oxidación e hidrólisis, habrían llevado a la detección de los compuestos DDVP-desmetilo, dimetil fosfato y ácido dicloroacético como productos de transformación. Por su parte, la degradación por oxidación directa del ozono probablemente tuvo lugar mediante la adición de este oxidante al doble enlace de la molécula de DDVP. El único intermedio detectado en este caso, fruto del mecanismo de ozonólisis combinado con una descarbonatación de la molécula resultante, fue el dimetil fosfato.

El análisis toxicológico de las soluciones modelo de MC antes y después de ser ozonizadas reveló variaciones importantes en la toxicidad según la dosis de ozono aplicada, incluyendo un aumento significativo de este parámetro que pudo relacionarse con una mayor concentración del intermedio metiocarb sulfóxido, y viceversa. Esta información se recoge en la Figura 4 del Apéndice I. El estudio de toxicidad de los pesticidas ACMP y DDVP (ver datos en la Figura 5 de los Apéndices II y III, respectivamente) reveló variaciones en la toxicidad que no pudieron ser atribuidas a la presencia de un único producto de transformación. El efecto sinérgico de varios compuestos coexistentes en las disoluciones pareció ser responsable de las variaciones observadas en la toxicidad. En cualquier caso, para los ensayos con los tres pesticidas se observó una disminución o aumento menos significativo de la toxicidad de las muestras oxidadas respecto a la solución no oxidada en experimentos sin adición de tBuOH, es decir, cuando los radicales hidroxilos contribuyeron a la oxidación de los compuestos de partida y productos de transformación.

En el estudio de ozonización de efluentes de depuradora para la eliminación de contaminantes resistentes al ozono, el seguimiento del pesticida ACMP como sustancia modelo (Apéndice IV, Figura 2) reveló que el empleo de dosis de ozono por encima de la IOD sería necesario para la eliminación significativa de compuestos resistentes. La dosis a aplicar, según los resultados obtenidos, parecería depender de manera evidente de dos características principales del efluente: el contenido en materia orgánica y la alcalinidad. El proceso de ozonización de los efluentes de depuradora pudo ser descrito con éxito mediante el uso de un modelo bifásico basado en el uso del concepto $R_{\mathrm{OH,O3}}$, permitiendo esto comparar entre distintos efluentes la eficiencia del proceso en términos de disponibilidad de radicales por ozono consumido. La Figura 3 (Apéndice IV) permite apreciar el cambio de pendiente en el gráfico de $\int[\bullet OH]dt$ frente a TOD, para valores de TOD correspondientes al valor de IOD. Los valores de $R_{OH,O3}$ obtenidos en la fase inicial del proceso, recogidos en la Tabla 3 del Apéndice IV, fueron (1.53-7.60)·10^{-7} s, mientras que para la etapa de la ozonización posterior a la IOD se hallaron en el rango (0.61-2.95))·10^{-6} s. El uso de un modelo de predicción basado en el parámetro $R_{OH,O3}$ y en la medida de la TOD, por un lado, y de otro modelo basado en la monitorización de la absorbancia ultravioleta medida a 254 nm (UVA_{254}) como parámetro sustituto, por otra parte, fueron propuestos y puestos a prueba en la predicción y el control a tiempo real de la eliminación de compuestos recalcitrantes al ozono durante el proceso de ozonización. Se obtuvieron excelentes correlaciones ($R^2 > 0.98$) entre los datos de eliminación predichos y medidos experimentalmente empleando distintos contaminantes, efluentes y modelos de predicción. La explicación detallada de estos modelos de predicción, así como la representación gráfica de los resultados obtenidos se recogen en las secciones 3.3-3.5 del Apéndice IV.

En lo que respecta al estudio de la evolución de la materia orgánica de los efluentes tratados mediante ozonización, se observaron en general reducciones significativas de la aromaticidad (hasta un 80%) y no tanto (hasta un 45%) en la DQO. En efluentes procedentes de sistemas MBR, la observó una mineralización de la materia orgánica disuelta de hasta un 25%. Todo lo contrario ocurrió en los efluentes procedentes de tratamientos convencionales por fangos activos, para los que se observó un aumento considerable del contenido en materia orgánica disuelta (hasta un 35%) atribuido a la solubilización de materia orgánica suspendida presente en las muestras de efluente originales. Los datos de evolución de los parámetros generales de calidad del agua (UVA_{254}, DQO y TOC) durante los experimentos de ozonización con los diferentes efluentes se recogen en las Figuras 2, 3 y 4 del Apéndice V.

Los análisis mediante la técnica SEC-OCD permitieron evaluar los cambios en la composición de la materia orgánica durante el proceso de ozonización. La Figura 5 del Apéndice V recoge los resultados correspondientes a los efluentes CAS, mientras que en la Figura 6 del mismo se muestran los datos correspondientes a la ozonización de efluentes procedentes de sistemas MBR. Se pudo comprobar experimentalmente que la materia orgánica mineralizada o solubilizada respectivamente en los efluentes MBR y CAS consistió principalmente en sustancias húmicas, y que al final del proceso, independientemente de las propiedades del efluente, se produjo una acumulación de compuestos orgánicos de bajo peso molecular, principalmente ácidos carboxílicos. Finalmente, la evolución de algunas de las fracciones de la materia orgánica en distintos efluentes se pudo correlacionar con parámetros de calidad del agua y propios del proceso de ozonización. Esta información se muestra en la Figura 7 del Apéndice V.

En el estudio de la aplicación del proceso O_3/H_2O_2 en efluentes de depuradora con fin de incrementar la eficiencia en la oxidación de contaminantes resistentes al ozono, se comprobó cómo la adición de peróxido de hidrógeno de manera simultánea al burbujeo de O_3 (relación molar H_2O_2/O_3 de 0.25) pudo permitir reducciones de hasta el 36% en la dosis de ozono requerida, en comparación con el proceso de ozonización simple. Esto se puede ver de manera clara en los datos representados en la Figura 2 (Apéndice VI). Teniendo en cuenta costes operacionales estimados para la producción a escala real de ambos oxidantes, dicha reducción en las necesidades de ozono supondría un ahorro energético del 28%. La mejora en la eficiencia que podría potencialmente permitir dicho ahorro energético se atribuyó sobre todo al aumento de la disponibilidad de radicales hidroxilo en la segunda fase del proceso de ozonización una vez completada la IOD, para la cual también se observó que la relación molar óptima entre H_2O_2 y O_3 fue 0.25, independientemente de las propiedades del efluente. Esto pudo comprobarse fácilmente gracias a la estimación de los correspondientes valores de $R_{\mathrm{OH,O3}}$ para cada una de las condiciones de operación ensayadas (ver Figura 3 del Apéndice VI). Experimentos adicionales, comparando el rendimiento del proceso al añadir el peróxido de hidrógeno de manera continua o al inicio en forma de dosificación única, revelaron que la adición simultánea al burbujeo de ozono funciona mejor, observándose ahorros energéticos del 30% y el 9% (respecto a la ozonización simple) en cada una de las alternativas, respectivamente. Los datos correspondientes a esta comparativa se recogen en la Figura 4 del Apéndice VI.

Finalmente, y de manera similar a lo llevado a cabo en el estudio de ozonización simple (trabajo presentado en el Apéndice IV), se ensayaron dos estrategias de modelización distintas para la predicción de la eliminación de contaminantes resistentes al ozono durante la aplicación del proceso *peroxone*. De nuevo, se observaron buenas correlaciones ($R^2 > 0.96$) entre los datos de degradación predichos y obtenidos experimentalmente para distintos contaminantes, procesos y efluentes (ver Figura 6, Apéndice VI).

Conclusiones

Las siguientes constituyen las principales conclusiones del trabajo de investigación llevado a cabo en esta tesis. Se ordenan según la estructura definida para la consecución de los objetivos inicialmente establecidos para la misma.

En relación a los estudios cinéticos, mecanísticos y toxicológicos de la degradación de los pesticidas seleccionados (Apéndices I-III), se pudo concluir que:

- Los insecticidas MC y DDVP reaccionan con el ozono, pudiéndose llegar a degradar de manera efectiva durante la aplicación de este oxidante al tratamiento de matrices acuosas reales. El ACMP, por su parte, es resistente al O_3. Todos ellos, sin embargo, son oxidados de manera eficiente por parte de los radicales hidroxilos formados al descomponerse el ozono.
- El pesticida MC, al degradarse, forma el metiocarb sulfóxido, de mayor toxicidad que el compuesto de partida. Este producto también presenta menor reactividad al ozono que el MC. Los compuestos de degradación de ACMP y DDVP son aparentemente menos tóxicos que los compuestos de partida, aunque la sinergia entre los mismos podría llegar a causar efectos tóxicos.
- La presencia de radicales hidroxilos parece garantizar una eliminación efectiva de los compuestos de partida, así como de los intermedios de reacción formados y la toxicidad asociada a los mismos. Promover la vía de oxidación radicalaria durante la ozonización, por tanto, parece ser fundamental.

En cuanto a los estudios del proceso de ozonización simple y la combinación O_3/H_2O_2 llevados a cabo en efluentes de depuradora, se destacan las siguientes conclusiones:

- Las dosis de ozono aplicadas actualmente no son suficientes para la eliminación efectiva de aquellos contaminantes resistentes al ozono.
- El aumento de las dosis de oxidante por encima del valor correspondiente a la IOD parece ser necesario para una reducción significativa de la presencia de microcontaminantes resistentes al ozono en los efluentes.

- La aplicación del proceso de ozonización en efluentes de depuradora a las dosis de ozono necesarias para la eliminación efectiva de compuestos recalcitrantes al O_3, conlleva la transformación de la materia orgánica del efluente. En efluentes más “limpios” o libres de sólidos suspendidos, se produce la oxidación y rotura de sustancias húmicas en compuestos de peso molecular menor, tales como ácidos orgánicos. En efluentes que contienen sólidos en suspensión, la aplicación del ozono parece provocar una solubilización de dichas partículas.
- El uso del proceso O_3/H_2O_2 puede ser empleado con el fin de aumentar la eficiencia de la oxidación, es decir, para tener mayor disponibilidad de radicales hidroxilo por ozono consumido. En este sentido, la adición de peróxido de manera continua en lugar de al inicio del proceso junto con el uso de relaciones molares bajas (H_2O_2/O_3 de 0.25), parece ser la mejor estrategia para mejorar la eficiencia del proceso y conseguir ahorros energéticos significativos asociados a un menor consumo de oxidantes.
- Tanto el proceso de ozonización simple como el proceso *peroxone*, pueden describirse mediante modelos de dos etapas basados en el concepto $R_{\mathrm{OH,O3}}$. Este parámetro, además, puede ser útil para estimar de forma precisa la eliminación durante el proceso de ozonización de aquellos contaminantes resistentes al ozono.
- Gracias a la relación entre la reducción de la aromaticidad durante el proceso de ozonización y la disponibilidad de radicales hidroxilos en el medio, esta puede estimarse en tiempo real mediante el seguimiento in situ del parámetro UVA_{254}. Esto resulta extremadamente útil para el control de la eliminación de contaminantes orgánicos en efluentes de depuradora mediante el uso de procesos basados en ozono.

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