



UNIVERSITAT DE
BARCELONA

Ozonation of Municipal Wastewater for Water Reuse

Mireia Marcé Escalé

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UNIVERSITAT DE
BARCELONA

Programa de Doctorat de Ciència i Tecnologia dels Materials

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CERTIFICA QUE:

El treball d'investigació amb el títol " OZONATION OF MUNICIPAL WASTEWATER FOR WATER REUSE" constitueix la memòria que presenta la Llicenciada en Química, Mireia Marcé Escalé, per aspirar al grau de Doctor de la Universitat de Barcelona. Aquesta tesi doctoral ha estat realitzada en el marc del programa de doctorat " Ciència i Tecnologia dels Materials" al Departament d' Enginyeria Química i Química Analítica de la Universitat de Barcelona.

I perquè així consti als efectes oportuns, signen el present escrit a Barcelona, 16 de Febrer de 2017.

Dr. Santiago Esplugas Vidal

Director de la tesi doctoral

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“If there is magic on this planet, it is contained in water.”
— Loren Eiseley

“Difficulty is the lure of desire. Those who share difficulties put the other at the same level and make it into a game of dialogue: Let’s think that ... together. Any human being has the capacity to relate to knowledge, feelings, ideas and proposals that have generated other human beings. Are they difficult indeed? They will awake in us and refine new skills, new sensibilities and forms of intelligence. Equality is not a result, it is a premise and it has a single slogan: share the desire and never treat a mate as an ignorant.”

Marina Garcés, 2015

Curiosity is one of the virtues that I most appreciate. That genuine curiosity that generates interest and goes deeply, widening, leading you to look and ask. And which usually blows up in the form of enthusiasm. Manzoni sings "there is not enough with happiness, we demand euphoria" and I often adapt it, mentally, as "there is not enough with interest, I love the enthusiasm". It is a slogan, a wish.

Carles Capdevila, 2015

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Abstract

Water is essential for life in all the levels: humans, animals and plants depend on it for their existence. The unsustainable growth, the changes in the consumption pattern and the climate change have positioned water resources under pressure. In this scenario where the water quality and quantity are a worldwide concern, research and development have analyzed and generated various emerging technologies that can promote the use of alternative sources of water.

In the problematic water pollution scenario mentioned before, advanced oxidation processes (AOPs) emerge as a possible alternative to treat the biologically persistent wastewater improving water quality and therefore restoring the aquatic environment. These processes degrade organic pollutants by forming hydroxyl radicals (OH·) which are highly reactive and non-selective. Nowadays, AOPs include also the processes that involve other radicals as sulfate radicals (SO₄²⁻·).

Ozone application is used in wastewater, disinfection and air treatment to minimize the pollution. This process has two main strengths: on one hand, the strong oxidant potential and secondly, the lack of residues after its application. Ozone can react directly, via molecular pathway or indirectly via hydroxyl radical.

In this work, ozone has been applied to different non-conventional points of the treatment line, to check if its action could promote the enhancement of the whole treatment. Thus, it has been applied at the outlet of the primary effluent leading us to an improvement in the water quality parameters and in the removal of micropollutants. Moreover, other significant parameters for ozone application as the ozone demand and mass transfer have been studied.

Afterwards, the study was focus in the application of ozone on the activated sludge matrix. In this case, ozone showed good performance too, improving the settleability, increasing the solubility of sludge and eliminating micropollutants in both phases (sludge and supernatant).

Finally, the combination of ozone application with biological treatments was tested. Thus, ozone was applied to the primary effluent which was lately treated by an aerobic biological treatment. In this case, good performances were observed at the level of micropollutants. Lately, ozone was applied to the conventional activated sludge matrix which was subsequently introduced in an anaerobic process to check the enhancement of biogas production. In this case, only two ozone doses showed better performances than the initial sludge without ozone pretreatment. Biodegradability and acute toxicity was studied for the primary effluent before and after ozonation, showing an improvement when the transfer ozone dose increased.

List of contents

Acknowledgements.....	V
Abstract	vii
List of Figures	xiii
List of Tables.....	xvii
List of abbreviations, acronyms and symbols	xxiii
1. BRIEF INTRODUCTION AND THESIS OBJECTIVES	1
1.1 Brief Introduction.....	1
1.2 EU Water Framework Directive	1
1.3 TRIUMPH Project.	2
1.4 Design factors for the combined system	2
1.5 Structure of the PhD Thesis	3
2. STATE OF ART.....	5
2.1 Water Role: Importance, perspectives and sustainable development.	5
2.2 Wastewater Reuse	6
2.3 Wastewater characteristics	8
2.4 Effluent Organic Matter	8
2.4.1 <i>Natural Organic Matter</i>	9
2.4.2 <i>From Organic Pollutants to Emerging micropollutants</i>	10
2.4.3 <i>Soluble microbial products and extracellular polymeric substances</i>	10
2.5 General Legal Framework	11
2.6 Conventional Municipal Wastewater treatment.....	13
2.6.1 <i>Micropollutant occurrence and fate in WWTPs</i>	15
2.7 Advanced Oxidation Processes - State of art.....	22
2.7.1 <i>Removal of Micropollutants by AOP's in wastewater</i>	23
2.8 Ozonation.....	25
2.8.1 <i>Ozone physico-chemical properties</i>	26
2.8.2 <i>Ozone Generation</i>	27
2.8.3 <i>Ozone Solubility in Water and Mass Transfer</i>	28
2.8.4 <i>Ozone reactivity</i>	29
2.8.5 <i>Formation of byproducts as a result of Ozonation</i>	32
2.8.6 <i>Ozone applications in water</i>	34
3. MATERIALS AND METHODS	36

3.1	Experimental Set Ups.....	36
3.1.1	<i>Ozone set up</i>	36
3.1.2	<i>Biological Set Up- Aerobic Experiments</i>	38
3.1.3	<i>Biological Set Up- Biomethane potential test</i>	39
3.2	Main analytical techniques and instruments.....	39
3.2.1	<i>Determination of Dissolved Organic Carbon (DOC), Inorganic Carbon (IC) and Total Nitrogen (TN)</i>	39
3.2.2	<i>Determination of Chemical Oxygen Demand (COD)</i>	40
3.2.3	<i>Determination of Biochemical Oxygen Demand (BOD)</i>	40
3.2.4	<i>Measurement Residual oxidants (Bromine)</i>	42
3.2.5	<i>Measurement of aromaticity</i>	42
3.2.6	<i>Ion- Exchange Chromatography (IEC)</i>	42
3.2.7	<i>Alkalinity</i>	42
3.2.8	<i>Acute toxicity - Microtox®</i>	43
3.2.9	<i>Determination of Solid content: Suspended Solids (SS), Volatile Suspended Solids (VSS), Volatile Solids (VS) and Total Solids (TS)</i>	43
3.2.10	<i>Analysis of micropollutants</i>	43
3.2.11	<i>Liquid Chromatography with size exclusion (LC-OCD-OND)</i>	47
3.3	Origin and type of wastewater samples	49
4.	APPLICATION OF OZONE ON PRIMARY EFFLUENT: MODELING, CHANGES ON ORGANIC MATTER DISTRIBUTION AND MICROPOLLUTANT REMOVAL	51
4.1	Introduction	51
4.2	Materials and methods.....	52
4.2.1	<i>Wastewater Characterization</i>	52
4.2.2	<i>Operating Conditions</i>	53
4.2.3	<i>Definitions</i>	54
4.3	Results and Discussion	55
4.3.1	<i>Ozone mass transfer</i>	55
4.3.2	<i>Organic matter removal: ozone needs, kinetics and organic matter transformation</i>	60
4.3.3	<i>Ozone impact in micropollutants present in primary effluents</i>	67
4.3.4	<i>Removal of AOX in primary effluent</i>	68
4.3.5	<i>Removal of Pharmaceuticals in primary effluent</i>	69
4.3.6	<i>Removal of Surfactants and PBDEs in primary effluent</i>	71
4.3.7	<i>Removal of PAHs and Pesticides contained in primary effluent</i>	72
4.3.8	<i>Micropollutant removal overview depending on ozone reactivity</i>	73
4.4	<i>Conclusions</i>	75
4.5	Supplementary Information	¡Error! Marcador no definido.
4.6	<i>Appendix</i>	80
5.	APPLICATION OF OZONE ON ACTIVATED SLUDGE: MICROPOLLUTANT REMOVAL AND SLUDGE QUALITY	81
5.1	Introduction	81
5.2	Materials and Methods.....	82

5.2.1	<i>Sampling at the Wastewater Treatment Plant</i>	82
5.2.2	<i>Ozone Treatment</i>	82
5.2.3	<i>Analysis of micropollutants</i>	83
5.2.4	<i>Further Analysis</i>	84
5.3	Results and Discussion	84
5.2.5	<i>Ozone impact on organic matter solubilization</i>	84
5.2.6	<i>Impact on the sludge quality</i>	88
5.2.7	<i>Occurrence of selected compounds and elimination overall treatment</i>	89
5.2.8	<i>Removal of pharmaceuticals contained in sludge</i>	90
5.2.9	<i>Non- ionic and anionic Surfactant Degradation by ozone application</i>	94
5.2.10	<i>PAHs and PBDEs removal efficiencies and ozone dosage in CAS effluents</i>	95
5.2.11	<i>Ozone impact on Pesticides</i>	97
5.4	Conclusions	98
5.5	Supplementary Information	98
6.	PROCESS COMBINATION: OZONE AND BIOLOGICAL PROCESSES.	114
6.1	Introduction	114
6.2	Materials and methods	115
6.2.1	<i>Wastewater and sludge characterization</i>	115
6.2.2	<i>Operating Conditions</i>	116
6.2.3	<i>Specific analysis and measurements during biological tests.</i>	116
6.2.4	<i>Definitions</i>	116
6.3	Results and Discussion	117
6.3.1	<i>Ozone treatment coupled to aerobic biological treatment- impact to organic matter. ...</i>	117
6.3.2	<i>Ozone treatment coupled to aerobic biological treatment – impact on micropollutants.</i>	122
6.3.3	<i>Acute Toxicity and Biodegradability</i>	128
6.3.4	<i>Anaerobic digestion of Ozone pre-treated Sludge</i>	131
6.4	Conclusions	135
6.5	Supplementary Information	¡Error! Marcador no definido.
7.	CONCLUSIONS AND RECOMMENDATIONS	142
8.	RESUM EN CATALÀ	147
8.1.	Breu introducció i objectius	147
8.2.	Introducció	149
8.3.	Materials i Mètodes	151
8.4.	Resultats	155
8.5.	Conclusions i recomanacions	166
9.	REFERENCES	171

List of Figures

Figure 1.1 Work package (WP) breakdown of the TRIUMPH project.....	2
Figure 1.2 Ozone application strategy.....	3
Figure 2.1 Global Physical and Economic Water Scarcity (WWAP 2016).	6
Figure 2.2 Organic constituents of EfOM divided by dEfOM and particulate EfOM (POC)Organic constituents of EfOM divided by dEfOM and particulate EfOM (POC)	9
Figure 2.3 Conventional Wastewater Treatment with an additional tertiary treatment	14
Figure 2.4 Schematic diagrams of current (left) and future needs (Right) extracted from (Eggen et al. 2014)	15
Figure 2.5 Micropollutant adsorption onto sludge and onto dissolved and colloidal matter extracted from (Margot et al. 2015).....	16
Figure 2.6. Number of entries searching "ozonation" in Science Direct (only Journal Publications).....	25
Figure 2.7. Ozone resonance structures (Am Water Works Res et al. 1991)	26
Figure 2.8. Ozone Electric discharge Generator adapted from (Rakness 2011)	27
Figure 2.9. Concentration profiles of gas absorption extracted from (Sotelo et al. 1989). a. Physical absorption; b. Chemical absorption (fast kinetic regime); c. chemical absorption (slow kinetic regime). 28	
Figure 2.10. Ozone reactivity extracted from (Hoigne and Bader 1976)	30
Figure 2.11. 1,3-dipolar cycloaddition mechanism extracted from (Baig and Mouchet 2010).....	30
Figure 2.12. Electrophilic substitution in aromatic compound from (Baig and Mouchet 2010).....	31
Figure 2.13. Reaction diagram for ozone decomposition from (LANGLAIS (B.) 1991)	32
Figure 2.14. Reaction scheme for bromate formation during ozonation of bromide containing waters. .	33
Figure 3.1. Ozone Set Up.....	36
Figure 3.2. Picture of the lab ozone set up	37
Figure 3.3. Biological Set Up.....	38
Figure 3.4. BMP test equipment.	39
Figure 3.5. High range COD samples	40
Figure 3.6. Oxitop Device for BOD measurement	42
Figure 3.7. Typical LC-OCD Chromatogram of NOM in raw water extracted from (Huber 2016)	48
Figure 3.8. Sampling points at the WWTPs	49

Figure 4.1 Ozone inlet, outlet and dissolved concentrations and initial Ozone Demand (IOD) determination for P1 (A), P2 (B), P3 (C), P4 (D), T1(E) and T2(F).....	56
Figure 4.2 A) Initial Ozone Demand (IOD) determination for primary effluents. B) TOD and ozone transfer yield evolutions during primary effluents ozonation.	58
Figure 4.3 A) Initial Ozone Demand (IOD) determination for T1 and T2 effluents. B) TOD and ozone transfer yield evolutions during T1 and T2 ozonation.	59
Figure 4.4 A) Initial Ozone Demand (IOD) determination for drinking and tap water B) TOD and ozone transfer yield evolutions during primary effluents ozonation.....	59
Figure 4.5 A) Initial Ozone Demand (IOD) determination versus COD/COD ₀ evolution for primary effluent, P2; B) Initial Ozone Demand (IOD) determination versus COD/COD ₀ evolution for tertiary effluent, T1. 60	
Figure 4.6. A) Initial Ozone Demand (IOD) determination versus UV ₂₅₄ /UV _{254,0} evolution for primary effluent, P4 B) Initial Ozone Demand (IOD) determination versus UV ₂₅₄ /UV _{254,0} evolution for tertiary effluent, T2	60
Figure 4.7. COD (left axis) and UV 254 (right axis) vs IOD for P1, P2, P3, P4, T1, T2, D1 and V1.....	61
Figure 4.8 A) COD/COD ₀ versus transferred ozone dose. B) COD and LN(COD ₀ /COD) versus contact time, primary effluents.....	62
Figure 4.9. UV ₂₅₄ /UVA ₂₅₄₀ vs TOD for P1, P2, P3, P4,T1 and T2.....	63
Figure 4.10. Turbidity evolution versus TOD for Primary effluents.	64
Figure 4.11. Changes in the main water characteristics upon ozonation of raw and pre-filtered wastewaters,	65
Figure 4.12 A) Organic matter sub-fractions for raw effluents P3 and P4 before and after ozonation. B) Organic matter sub-fractions for effluent P3 and P4 before and after ozonation, both filtered (0.45 μm) before the ozone application.	66
Figure 4.13. AOX Residual Concentration vs TOD for each sampling campaign P3, P4, P5 and P7.	69
Figure 4.14. Removal of B-Blockers and Antibiotics versus the TODs (mg/L)	70
Figure 4.15. Removal of Anti-inflammatory and analgesic drugs versus the TODs (mg/L).....	70
Figure 4.16. Antifungal (Econazole), Anti-epileptic drug (Carbamazepine) and analgesic (Paracetamol) residual concentrations (%) versus TOD (mg/L)	71
Figure 4.17. LAS, Σnon-ionic surfactants, Σ4-nonylphenol and PBDEs concentration versus TOD (mg/L). 72	
Figure 4.18. PAHs (Acenaphthene and Phenanthrene) and Pesticides (Alachlor and Chlorpyrifos) residual concentrations depending on the TODs.....	73
Figure 4.19. Average removals of selected compounds for a TOD ≤ 5mg/L versus Log k ₀₃	75
Figure 5.1. COD solubilization rate versus TOD.....	85
Figure 5.2. UV ₂₅₄ / UV _{i254} versus TOD	86
Figure 5.3. Inorganic Carbon (IC) and soluble Total Nitrogen (TN) Evolution versus TOD gO ₃ / gSS.....	86

Figure 5.4. pH evolution versus the TOD	87
Figure 5.5. Normalized UV254 parameter versus TOD for S2, S3, S4, S5 and S6 sampling campaigns....	886
Figure 5.6. Changes in SVI versus TODs	89
Figure 5.7. Removal of B-Blockers and Antibiotics versus the TODs in CAS matrix	89
Figure 5.8. Removal of Anti-inflammatory, Anti-fungal and Anti-epileptic drugs versus the TODs in CAS matrix	89
Figure 5.9. (Left) Pharmaceutical average removals for a range of TOD= 10-20 mg/gSS versus Log KO ₃ , (right) KO ₃ of the presented compounds.....	90
Figure 5.10. CZP= Carbamazepine; PRO= Propranolol. Initial and residual Concentrations of CZP and PRO in sludge and supernatant phases for S3 and S4 sampling campaigns.	92
Figure 5.11. Persistence of Surfactants versus the TOD (gO ₃ / gSS).....	93
Figure 5.12. PAHs concentration (%) versus the TOD (gO ₃ /gSS)	97
Figure 5.13. Pesticides removal through 3 TODs : 0.001; 0.003 and 0.02 gO ₃ / gSS in S4. * n.a: non available	95
Figure 6.1. Evolution of sCOD/sCOD ₀ and UV ₂₅₄ /UV _{254,0} during the biological treatment for all the samples of P7 effluent.....	114
Figure 6.2. Evolution of normalized inorganic carbon and dissolved organic carbon during biological treatment.	119
Figure 6.3. Overall residual concentrations (normalized) of soluble COD (sCOD) and UV ₂₅₄ treatments for P6 (A) and P7(B).....	120
Figure 6.4 Determined OUR for all the samples of P7 versus time (min)	122
Figure 6.5. Removal of anionic surfactants (LAS), octylphenol, Nonylphenol, total amount of PBDEs and non-ionic surfactants for each performed treatment. A) Presents the results detected in sampling campaign P6 and B) presents the results for sampling campaign P7.....	123
Figure 6.6. Removal of the pesticides (Alachlor and Chlorpyrifos) for sampling campaign P6 (A) and P7 (B).	124
Figure 6.7. Removal of pharmaceuticals for sampling campaign P6 (A) and P7 (B).....	125
Figure 6.8. Removal of PAHs for sampling campaign P6 (A) and P7 (B,C).....	125
Figure 6.9. Residual concentrations of Pharmaceuticals (A) and Pesticides (B), initial and after two different transferred doses in secondary effluent, B1.	126
Figure 6.10. Residual concentrations of PAHs, initial and after two transferred doses for secondary effluent, B1.....	127
Figure 6.11. EC ₅₀ and BOD ₅ /COD ratio vs TOD for primary effluent, P7.	130
Figure 6.12. Phases of anaerobic digestion and biogas production. Source: Biobased Energy Education Materials Exchange System (BEEMS) - Modul B7.....	132

Figure 6.13. (Left) Residual Total COD elimination (%), residual SVI (%) and e_{COD} (%) versus TOD. (Right) Percentage of total COD removal for each TOD..... 133

Figure 6.14. Methane production along anaerobic treatment. A) Methane production represented considering the amount of volatile suspended solids (VSS) added and B) considering the amount of COD added..... 134

List of Tables

Table 2.1 List of organic priority substances in the field of water policy and certain other pollutants defined in the Directive 2013/39/EU extracted from (Ribeiro et al. 2015). ^a Other pollutants defined in the Directive, not included in the priority substances list. ^b Group of substances listed as a class.....	12
Table 2.2. Sources of micropollutants in the aquatic environment adapted from (Luo et al. 2014).	17
Table 2.3 Fate of 84 micropollutants in Conventional WWTPs adapted from (Margot et al. 2015).....	20
Table 2.4 Different AOPs based on the method for radical production (Esplugas et al. 2002, Giannakis et al. 2016, Hu and Long 2016, Pera-Titus et al. 2004).....	23
Table 2.5 Standard oxidation potentials (Parsons 2004)	26
Table 2.6 Ozone Properties.....	27
Table 3.1 LOQs in effluent matrix for the different analyzed compounds: AOX, Pharmaceuticals and Surfactants.	44
Table 3.2 LOQs in effluent matrix for the different analyzed compounds: PBDEs, PAHs and DEHP.	44
Table 3.3 LOQs in the effluent matrix for the different analyzed compounds: Pesticides.....	45
Table 3.4 LOQs in CAS matrix for the different analyzed compounds: AOX, Pharmaceuticals and Surfactants.	46
Table 3.5 LOQs in CAS matrix for the different analyzed compounds: PBDEs and PAHs.	46
Table 3.6 LOQs in CAS matrix for Pesticides.	47
Table 3.7 Fractions of NOM	48
Table 4.1 Initial water quality parameters	52
Table 4.2 Operating conditions	53
Table 4.3 k_d , K_{La} and IOD values different types of effluents.....	55
Table 4.4 COD pseudo-first order kinetic constants.	62
Table 4.5 UV_{254} absorbance, turbidity and COD variations for P3 and P4 before and after ozone application.	64
Table 4.6 Impact of ozone dose and filtration before ozonation on the molecular weight distribution. DOC > 20000 g/mol, DOC ~1000 g/mol, DOC ≤ 500 g/L belong to the hydrophilic group.	67
Table 4.7 Initial concentration of Micropollutants for different sampling campaigns: P3, P4, P5, P6 and P7	68
Table 4.8 Molecular Structure, Classification and reactivity of the monitored compounds	74
Table 4.9 Initial concentration and removal percentages of the monitored pharmaceuticals of P3	76
Table 4.10 Initial concentration and removal percentages of the monitored Surfactants and AOX of P3	76
Table 4.11 Initial concentration and removal percentages of the monitored pharmaceuticals of P4	77

Table 4.12 Initial concentration and removal percentages of the monitored Surfactants and AOX of P4	77
Table 4.13 Initial concentration and removal percentages of the monitored pharmaceuticals of P5 77
Table 4.14 Initial concentration and removal percentages of the monitored Surfactants and AOX of P5	77
Table 4.15 Initial concentration and removal percentages of the monitored pharmaceuticals of P6 78
Table 4.16 Initial concentration and removal percentages of the monitored Surfactants and PBDEs of P6 78
Table 4.17 Initial concentration and removal percentages of the monitored pesticides of P6 78
Table 4.18 Initial concentration and removal percentages of the monitored PAHs of P6 78
Table 4.19 Initial concentration and removal percentages of the monitored Pharmaceuticals of P7 78
Table 4.20 Initial concentration and removal percentages of the monitored Surfactants, AOX and PBDEs of P7 79
Table 4.21 Initial concentration and removal percentages of the monitored Pesticides of P7 79
Table 4.22 Initial concentration and removal percentages of the monitored Pesticides of P7 79
Table 5.1 Initial parameters of the CAS sampling Campaigns 82
Table 5.2 Operating conditions 83
Table 5.3 tCOD and sCOD at the specified TOD, after IOD completion. 82
Table 5.4 AOX, Surfactant and pharmaceuticals average concentrations in the outlet of primary clarifier, recirculation loop of CAS and in the outlet of the secondary Effluent. n.q = lower than LOQ 87
Table 5.5 AOX, Surfactant and pharmaceuticals initials concentrations for CAS. n.q = Lower than LOQ.	88
Table 5.6 Log K_{ow} for the studied pharmaceuticals. 92
Table 5.7 Mass balance for the studied pharmaceuticals of S1. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available data; n.q.= below the limit of quantification. 97
Table 5.8 Mass balance for the studied surfactants of S1. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification ..	97
Table 5.9 Mass balance for the studied pharmaceuticals of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal.n.a =non available; n.q.= below the limit of quantification. 98
Table 5.10 Mass balance for the studied pharmaceuticals of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal.n.a =non available; n.q.= below the limit of quantification. 99

Table 5.11 Mass balance for the studied surfactants of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification.100

Table 5.12 Mass balance for the studied surfactants of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification.103

Table 5.13 Mass balance for the studied pharmaceuticals of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal.n.a =non available; n.q.= below the limit of quantification. 103

Table 5.14 Mass balance for the studied pharmaceuticals of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal.n.a = non available; n.q.= below the limit of quantification. 104

Table 5.15 Mass balance for the studied surfactants of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification. 101

Table 5.16 Mass balance for the studied surfactants of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification.105

Table 5.17 Mass balance for the studied PAHs of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q . = below the limit of quantification. 105

Table 5.18 Mass balance for the studied PAHs of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q . = below the limit of quantification. 106

Table 5.19 Mass balance for the studied PBDEs of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q . = below the limit of quantification. 107

Table 5.20 Mass balance for the studied pharmaceuticals of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal.n.a = non available; n.q . = below the limit of quantification. 108

Table 5.21 Mass balance for the studied surfactants of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q . = below the limit of quantification. 109

Table 5.22 Mass balance for the studied PAHs of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q . = below the limit of quantification. 110

Table 5.23 Mass balance for the studied PBDEs of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q .= below the limit of quantification.	111
Table 5.24 Mass balance for the studied pesticides of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal.n.a = non available; n.q .= below the limit of quantification.	112
Table 6.1 Initial water quality parameters	115
Table 6.2 Initial quality of sludge samples from aerobic (S5,S6) and anaerobic (I1) biological treatment.	115
Table 6.3 Operating conditions for ozone experiments.....	112
Table 6.4 Toxicity levels regarding TU values.....	113
Table 6.5 Residual concentration (%) of DOC, sCOD, UV ₂₅₄ achieved after the biological treatment for P6 an P7.....	118
Table 6.6 Values of different parameters for initial, ozone treatment and ozone treatment coupled with biological aerobic treatment for P6 and P7, as well as, the parameters for B1 for ozone treated and untreated sample.	12017
Table 6.7 Pharmaceuticals and Surfactants analyzed in P7 and B1; n.q = non quantified and X= quantified	128
Table 6.8 PBDEs and PAHs analyzed in P7 and B1; n.q = non quantified and X= quantified.....	1296
Table 6.9 Pesticides analyzed in P7 and B1; n.q = non quantified and X= quantified	129
Table 6.10 Toxicity of primary effluent P7 expressed as Effective Concentration that reduces bioluminescence 50% (EC ₅₀), Toxicity Units (TU) and toxicity removal efficiency.	130
Table 6.11 Total VFA concentrations at the end of the batch experiment for each transferred dose. ...	134
Table 6.12 Biogas enhancement, methane content and methane production (accumulated at the end of the test)	134
Table 6.13 Initial concentration and removal percentages of the monitored pharmaceuticals of P6	137
Table 6.14 Initial concentrations and removals of anionic surfactants, alkylphenols and PBDEs for P6.....	1375
Table 6.15 Initial concentrations and removals of pesticides for P6.	137
Table 6.16 Initial concentrations and removals of PAHs for P6.	138
Table 6.17 Initial concentrations and removals of Paracetamol (pharmaceuticals) for P7.	138
Table 6.18 Initial concentrations and removals of anionic surfactants, alkylphenols and PBDEs for P7 .	138
Table 6.19 Initial concentrations and removals of pesticides for P7	139
Table 6.20 Initial concentrations and removals of PAHs for P7	139

Table 6.21 Initial concentrations and residual concentrations of screened Pharmaceuticals for B1	140
Table 6.22 Initial concentrations and residual concentrations of monitored pesticides for B1	140
Table 6.23 Initial concentrations and residual concentrations of monitored PAHs for B1.....	141

List of abbreviations, acronyms and symbols

[O₃]_{gas,in}	Ozone gas phase inlet concentration	EC₅₀	Effective Concentration that reduces the bioluminescence to 50%
[O₃]_{gas,out}	Ozone gas phase outlet concentration	EDC	Endocrine Disrupting Compound
AE	Alcohol Ethoxylates	EfOM	Effluent Organic Matter
AOPs	Advanced Oxidation Processes	EPA	Environmental Protection Agency
AOXs	Adsorbable Organohalogenes	EPS	Extracellular Polymeric Substance
BMP	Biomethane Potential test	EU	European Union
C*_{o3}	Ozone concentration in liquid phase in the equilibrium	FELST	Fish early life stage toxicity
CAS	Conventional Activated Sludge	FID	Flame Ionization Detector
CEC	Contaminants of Emerging Concern	GAC	Granular Activated Carbon
CH₄	Methane	GC	Gas Chromatograph
CO₂	Carbon Dioxide	H	Henry's constant
COD	Chemical Oxygen Demand	H₂	Hydrogen
COD_t	Total Chemical Oxygen Demand	Ha	Hatta Number
CPC	Compound Parabolic Collector	H₂S	Hydrogen Sulfide
CSIC	Consejo Superior de Investigaciones Científicas	IARC	International Agency for Research of Cancer
CWA	Clean Water Act	IC	Inorganic Carbon
DBO	Demanda Biológica d'Oxigen	ID	Internal Diameter
DBP	Disinfection Byproduct	IDAEA	Instituto de Diagnóstico Ambiental y Estudios Del Agua
DDT	Dichlorodiphenyl-trichloroethane	IEC	Ion Exchange Chromatography
dEfOM	Dissolved Effluent Organic Matter	IOD	Immediate or Initial Ozone Demand
DOC	Dissolved Organic Carbon	k_{bio}	Biological degradation rate constant
DON	Dissolved Organic Nitrogen	k_d	First order decay constant of dissolved ozone
DOP	Dissolved Organic Phosphorus	k_{La}	Volumetric mass transfer coefficient.
DQO	Demanda Química Oxigen		
EC	European Commission		

K_{ow}	Octanol – water partition coefficient	Q_{Gas}	Gas Flow rate
LAS	Linear alkylbenzene sulfonates	RO	Reverse Osmosis
MBR	Membrane Bioreactors	sCOD	Soluble Chemical Oxygen Demand
MF	Microfiltration	SIR	Substrate to Inoculum ratio
MW	Molecular Weight	SMP	Soluble Microbial Products
MWWTP	Municipal Wastewater Treatment Plant	SOC	Synthetic Organic Compound
NDIR	Infrared Gas Analyzer	SPE	Solid Phase Extraction
NDMA	N-nitrosodimethylamine	SS	Total Suspended Solids
NF	Nanofiltration	SUVA	Specific Ultraviolet Absorbance
NH₃	Ammonia	TCD	Thermal Conductivity Detector
NL	Normalized Liters	TDS	Total Dry Solids
NOM	Natural Organic Matter	TN	Total Nitrogen
NP	Nonylphenol	TOD	Transferred Ozone Dose
NPDES	Natural Pollutant Discharge Elimination System	tr	Reaction time
NSAID	Non-steroidal anti-inflammatory drug	TRO	Total Residual oxidants
NTP	Normal Temperature and Pressure Conditions (1 atm, 0°C)	TS	Total Solids
θ_{COD}	COD solubilization rate	UF	Ultrafiltration
ONTE	1-(1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-naphthalenyl)	UNGA	General Assembly of the United Nations
OUR	Oxygen Uptake Rate	USA	United States of America
PAH	Polycyclic Aromatic Hydrocarbon	UV₂₅₄	Ultraviolet absorbance at 254 nm
PBDE	Polybrominated diphenyl ether	VFA	Volatile Fatty Acids
PCB	Polychlorinated biphenyl	V_{Liq}	Effluent volume in the reactor
PES	Polyether Sulfone filter	VS	Total Volatile Solids
P_{O₃}	Ozone Partial Pressure	VSS	Volatile suspended solids
POC	Particulate Organic Carbon	WFD	Water Frame Directive
PPCPs	Pharmaceutical and Personal Care Products	WHO	World Health Organization
		WQS	Water Quality Standards
		WWAP	World Water Assessment Program
		WWTP	Wastewater Treatment Plant

1. BRIEF INTRODUCTION AND THESIS OBJECTIVES

1.1 Brief Introduction

Distinct environments, cultures and realities establish the complex organization of our current society. Despite its complexity, we could consider that our society is mainly arranged in residing and working cities. Among years, the wastewater treatment and the sewage system of these cities have been studied and planned to offer a better quality of life, to enhance their cleanliness and to increase their livability.

The economical, technological and social developments have promoted significant lifestyle benefits but in parallel have subdued under pressure the water resources. This fact generates a challenge for the current and next generations.

Last years, a deeply awareness of our environment is gaining importance, which is translated in a stronger understanding of the risks and consequences of the city ecological footprint. Regarding this fact, there is a growing ambition to reduce the ecological footprint and to turn them into more sustainable cities.

In this scenario, the importance and implication of the water sector should increase in the structural definition and organization of the cities modifying and improving the existing water management systems. In this direction, it is needed to improve the wastewater treatment plants, to facilitate its reuse and to minimize its consumption.

Upgrading the water systems implies important and big scale modifications. To do so, several studies at lab and pilot scale should be performed in advance. At the end, the variety of the results and clues obtained could participate in the enhancement of wastewater treatment plants. The presented work attempts to participate towards this progress.

Lot of work has been done applying ozone at the end of the treatment chain, especially in the tertiary treatment and in the water purification unit or plant. The usage of this highly reactive chemical compound in other points of the treatment chain has frequently generated some reticence and doubts. The presented work aims to plunge into the possible benefits of ozone application among the water treatment chain.

1.2 EU Water Framework Directive

Different surveys have been performed in the European Union countries regarding environmental issues. The Eurobarometer performed in 2012 showed that 68% of the population considered water-related problems as potential concerns (EU-Comission 2012). Moreover, the 47% surveyed contemplated the water pollution as the most worrying environmental issue (EU-Comission 2012, EU 2016). Moving back in time, during the mid-90s, the pressure for a reformulation of the community water policy increased which pushed the European Water Framework policy forward. The early fruit was obtained in the 2000, with the Directive 2000/60/EC that aimed at identifying hazardous substances for the aquatic environment (Directive 2000, Ribeiro et al. 2015). Eight years later, in 2008, the Directive 2008/105/EC was defined, establishing the environmental quality standards (EQS) for 33 priority substances and other 8 pollutants (Directive 2008, Ribeiro et al. 2015). In 2013, the last Directive was presented: Directive 2013/39/EU where the preventive action is promoted. It is based in the recognition of pollution causes, handling pollutant emissions at the source, and developing

alternative and cheaper water/wastewater treatment technologies (Directive 2013, Ribeiro et al. 2015). The updated Water framework Directive now includes 45 substances and other pollutants with the respective EQS for each one. The Directive 2013/39/EU focuses on the monitoring of emerging pollutants that were not considered before but that can promote ecotoxicity and toxic effects (Ribeiro et al. 2015). The importance of the Advanced Oxidation Technologies and related research as alternative treatment technologies is increasing in this scheme.

1.3 TRIUMPH Project.

The presented research has been carried out in collaboration with the Company Suez, branch Suez International formerly named Degremont, under the framework of TRIUMPH project supported by the European Eureka cluster ACQUEAU. A consortium of five research institutes and three companies have been involved. TRIUMPH is the acronym of **T**reating **U**rban **M**icropollutants and **P**harmaceuticals. The project pretends to achieve new oxidation processes for the removal of micropollutants and pharmaceuticals in urban wastewater achieving an integrated chemical/ biological oxidative treatment.

Precisely, the collaboration between Suez and University of Barcelona has taken place in the working package 2: Development of Ozone application. And therefore, it has been focus on ozone application, study on kinetics, dose impact and ozone impact in micropollutants and organic matter.

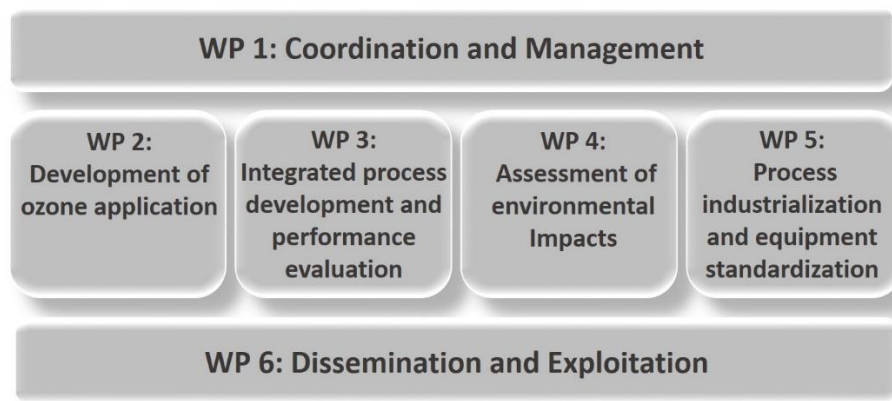


Figure 1.1 Work package (WP) breakdown of the TRIUMPH project.

1.4 Design factors for the combined system

The combination of different processes is needed to achieve suitable economic and technically options. The first possibility is to position the AOP in a sequence of physical, chemical and biological treatments. In general, this type of sequences involve one AOP step and one biological treatment step. The exact configuration depends on the cost, minimizing the AOP treatment step and maximizing the biological stage as a consequence of the differences between costs (Oller et al. 2011, Scott and Ollis 1995).

Nevertheless, pre-oxidation steps have been considered when the wastewater has low biodegradable character, since high biodegradable wastewater will promote unnecessary

consumption of chemicals (Esplugas et al. 2004, Scott and Ollis 1995). So, conventionally, post oxidation is recommended followed by a polishing step in this case.

On the other hand, the measurement of the process efficiency depends on the purpose of the treatment, but optimization of each step (biological and chemical) has to be analyzed. Accomplishment of dissolved organic carbon limits, reduction of toxicity and elimination of specific pollutants are different targets that could be achieved by means of combined systems.

Regarding these considerations, ozone application in this thesis has been focus in point 1. and 2. (Figure 1.2) to prove the suitability of the complete wastewater treatment system comparing two strategies.

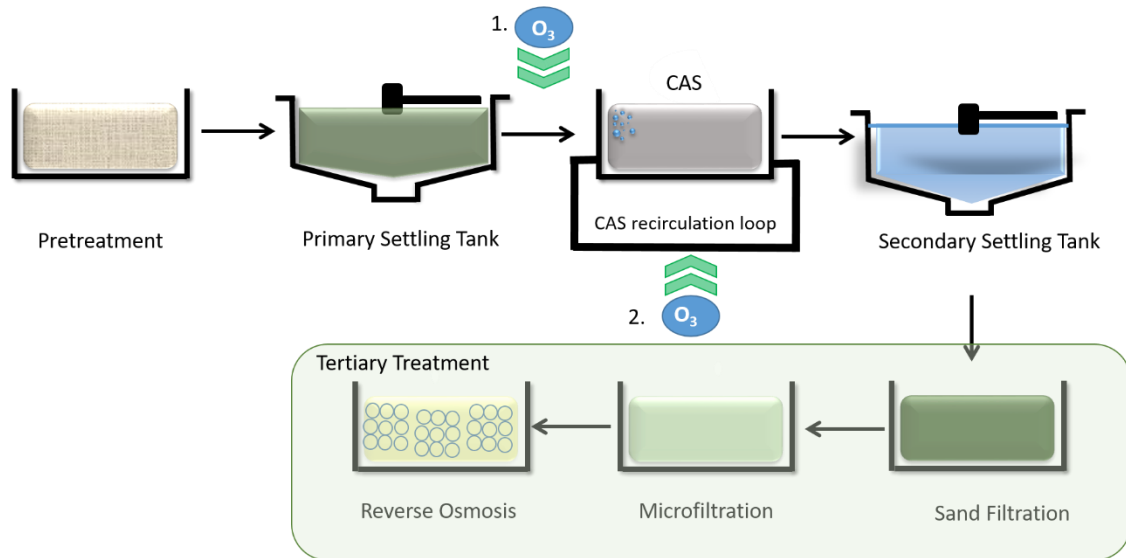


Figure 1.2. Ozone application strategy

1.5 Structure of the PhD Thesis

The main objective of this work is to analyze the possible benefits of the ozone application in non-conventional ozone application points along the wastewater treatment chain in order to mitigate the micropollutant issue. Thus, ozone was applied at the outlet of the primary effluent clarifier before the biological treatment (Conventional activated Sludge) and at the recycling loop of the Conventional Activated Sludge. In this thesis, ozonation process has been chosen for its already known capacity to oxidize and degrade organic matter. This PhD dissertation pretends to evaluate the ozonation impact on the quality of the effluents, mainly on the removal and degradation of micropollutants and organic matter at lab scale. The work aims at assessing the suitability of ozonation for the enhancement of the water quality. Moreover, other aspects related to the ozone technology have been deeply studied with the purpose of participate in a better implementation of the process.

The second chapter consists in an introduction to the water problematic: current state of art of the water-related issues, their causes and effects. Furthermore, it describes the advanced oxidation technologies giving information about the implementation of these processes and the benefits of their application. At the end of this chapter, ozonation appears as the main technology applied: its mechanisms and applications are discussed. Finally, micropollutants occurrence, organic matter classification and relevant legislations are exposed.

Materials and methods used in the research works are described in the third chapter. Here, aspects related with samples collection, wastewater characterization, sample preparation, analytical devices and experimental set up are discussed. Moreover, analytical methods for micropollutant analysis and further analysis are presented.

The fourth chapter presents the results obtained from the ozone application to primary effluents. The discussion involves the technical aspects related to ozone demand, organic matter and aggregate parameters. In addition, application of low ozone doses for degradation of micropollutants as a pre-treatment of the biological process has been analyzed.

Chapter fifth is reserved to ozonation applied to the Conventional Activated Sludge (CAS): its impact in the sludge quality and behavior with focus on micropollutants removal has been studied. Moreover, the aspects related with the ozone dosage and demand has been described.

The impact of ozonation on next biological processes has been tested and presented in chapter six. To do so, a primary effluent previously ozonated has been used as an inlet effluent for a biological treatment at lab scale. The idea of this work was to check if the combination of processes promotes a synergetic effect over water and sludge quality. Moreover the toxicity and its relationship with biodegradability was tested in this chapter. Afterward, a complimentary study was perform combining sludge ozonation and anaerobic treatment in order to investigate if ozonation of sludge could enhance anaerobic treatment and biogas production.

Finally, the seventh and last chapter is dedicated to the main conclusions based on the objectives of each individual chapter and their respective results. It is in this chapter where some recommendations and further steps are mentioned to complete and develop the determined conclusions.

2. STATE OF ART

2.1 Water Role: Importance, perspectives and sustainable development.

Water (H₂O), chemically the result of two bonds between oxygen and two atoms of hydrogen, is essential for life in all the levels: humans, animals and plants depend on it for their existence. In the human magnitude, sustainable water management, water infrastructures and water quality play key-roles in living standards, economic growth and social cohesion (WWAP 2016). From the point of view of economics, environmental or social, water is also extremely related with jobs. Almost 80% of the jobs that are considered the global workforce are dependent upon having access to an adequate supply of water-related services, including sanitation (WWAP 2016). Additionally, on top of the biological importance, water is also the core of our development.

The world's water distribution and availability, over time and space, greatly depends on the continuous cycle of evaporation, precipitation and runoff: the water cycle. However, human actions interfere with the natural water cycle and therefore they should be considered when the real water cycle is analyzed.

The unsustainable growth, the changes in the consumption pattern and the climate change have positioned water resources under pressure (WWAP 2015, 2016). Over the past century, the population growth and rising living standards (food, textile and energy) of the middle class have increased the water demand becoming in some cases unsustainable. However, the relationship between water demand and population growth is not linear. As it is described in the WWAP 2016 report, an increase of 33% in the world population and of 60% in the food demand is expected until 2050. Furthermore, social patterns like the increasing meat consumption, bigger homes, the use of motor vehicles and electrical devices will rise the global water demand since water consumption is needed for both, production and use (WWAP 2015). Moving to numbers, the estimated global water deficit will be of 40% in 2030. On the other hand, climate change has a significant impact in the water balance, quality and availability: variability in precipitation patterns, increase on the temperature, run offs that sweep along pollutants and intrusion of seawaters (WWAP 2015).

Besides the different causes of water scarcity, three levels of water scarcity can be considered:

1. **Physical water scarcity:** when the water resources development exceeds the sustainable limits.
2. **Economic water scarcity:** when the problematic involve financial limitations that drive to a lack of infrastructures.
3. **Institutional water scarcity:** when the public organisms are not able to ensure secure and equitable supply of water to users.

Figure 2.1 presents the global physical and economical water scarcity. There are some areas where the rainfall is concentrated during a concrete season. However, the same area can suffer a drought during the following seasons. Supposing that this area has conceived infrastructures to store and manage the water, the drought can be compensated and the population will not suffer the water scarcity crisis. Thus, in addition to the physical water scarcity, the funding for infrastructures as well as the political and institutional decisions have an important role in the water management.

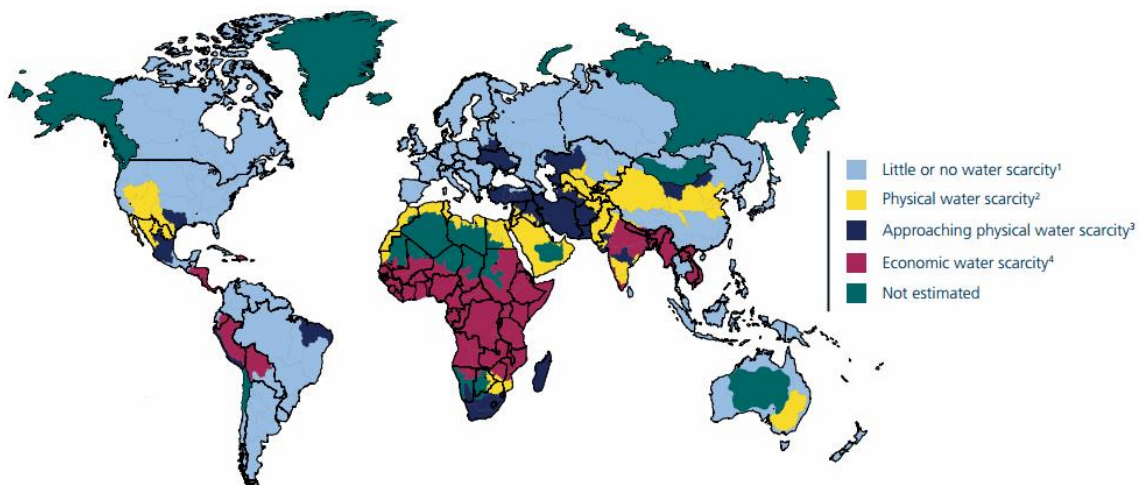


Figure 2.1 Global Physical and Economic Water Scarcity (WWAP 2016).

1. Abundant water resources and less than 25% of water from rivers withdrawn for human purposes; 2. Non-abundant water resources and more than 75% of rivers flow withdrawn for human purposes; 3. Non-abundant water resources and more than 60% of river flows are withdrawn; 4. Water resources are abundant compared to use but less than 25% of water from rivers is withdrawn for human purposes.

The right to safe drinking water and sanitation is a recognized human right. It is interrelated with other human rights like the right to life and dignity, to food and housing and to healthy occupational and environmental conditions (UNGA 2010). However, 663 million people do not have access to drinking water separately to the water that is used by animals and can contain faecal contamination. Furthermore, at least 1.8 billion people do not have access to water with enough quality to be safe for human health and finally, 2.4 billion people (more than a third of the global population) do not use improved sanitation facilities (Unicef/WHO 2015). All these information reflect the need for the governments to display their efforts towards measures for safe drinking water and sanitation.

In this scenario where the water quality and quantity are a worldwide concern, research and development have analyzed and generated various emerging technologies that can promote the use of alternative sources of water. Indeed, the use of municipal wastewater represents approximately 35% of the total water used in some countries (WWAP 2016). So, nowadays, there is a value in used water. Resource recovery and the analysis of the possible hazards related with the reuse of wastewater are gaining importance regarding the economic and environmental context. Currently, important actions are being considered to speed up innovation and development establishing a link between research, market needs, public perception, institutions and environment.

2.2 Wastewater Reuse

Wastewater reclamation might represent a real option to generate supplementary water sources and to cover a part of the water demand. Bixio et al. (Bixio et al. 2006) defined certain measures that should be targeted to reinforce the use of reclaimed water: 1. Modification of water legislation, 2. Intensification of the collaboration between partners, 3. Definition of protocols and guidelines for wastewater reuse, 4. Promotion of economic benefits from

wastewater reuse and 5. Raising social support. Various applications for reclaimed wastewater can be considered: Irrigation of agricultural and urban areas, for recreational uses, for cooling systems of industries and for enrichment of groundwater bodies (environmental uses) (Bixio et al. 2006, Rizzo et al. 2013).

Different uses have been observed for water reuse in Europe depending on the geographical area. In northern Europe 55% of the reclaimed water is involve in urban or environmental uses and 33% for industrial functions. In southern Europe, however, the reuse is mainly for agricultural irrigation (44%) and urban or environmental applications (37%). France is an exception since it has only published guidelines for agricultural irrigation (Bixio et al. 2006).

Despite the restricted uses in agriculture irrigation and industrial applications, one third of the reclaimed water depends on the secondary treatment. The implementation of Membrane Bioreactors (MBR) technologies have promoted the improvement of the secondary effluent quality satisfying the faecal coliforms criteria of WHO guideline and for instance, permitting its use for unrestricted agricultural irrigation (i.e. Schilde WWTP, Belgium) (Bixio et al. 2006). Tertiary treatment is needed when conventional secondary treatment is applied to fulfill the requirements for unrestricted agricultural irrigation. To obtain the desired standards, filtration followed by disinfection (Chlorination, UV, Ozone and Peracetic Acid application) are commonly used (Bixio et al. 2006). Higher level of treatment is required when the possible applications are aquifer recharge, industrial process water, mixed urban- agriculture irrigation and household uses. In this cases, two steps of filtration are demanded: Microfiltration (MF) or Ultrafiltration (UF) followed by Nanofiltration (NF) or Reverse Osmosis (RO) (Bixio et al. 2006).

The challenge is to obtain the desired quality and sufficient quantity by means of the most sustainable process. Moreover, it is important to define different levels of qualities for different types of reuse and to find adequate treatments and technologies to assure the quality limits. For instance, the reclaimed water used for agricultural and urban irrigation, must fulfill standards since the water pollutants can bioaccumulate in plants and non-target organisms (Fatta-Kassinos et al. 2016). Indeed, the uncomplete removal of organic contaminants of emerging concern (CECs) by the conventional WWTPs is a limitation for the reuse (Fatta-Kassinos et al. 2016) because is a gate for the pollutants to the terrestrial and aquatic environment.

The mobility, persistence and bioaccumulation of CECs greatly depends on their physico-chemical properties even though climatic conditions and a variety of other environmental factors are also determining. Different studies have been performed regarding the link between reclaimed water and the fate of pollutants in the environment. Xu et al. (Xu et al. 2008) , for instance, detected levels between 0.55-9.08 ng/g of Clofibric Acid, Ibuprofen, Naproxen, Triclosan, Bisphenol A and Estrone in a soil from a Golf Course in California irrigated with reused water. In Guanzhou, China, six Pharmaceuticals and Personal Care Products (PPCPs) were detected in samples of irrigated areas (Bisphenol-A, 4-Nonylphenol, Triclosan, Triclocarban, Salicylic Acid and Clorifibric Acid). As it has been described above, different compounds have been detected in soils previously irrigated with reclaimed water even though there are a lots of data not detected in soils in different countries (Li 2014).

The reclaimed water is not the only pathway to introduce CECs to the environment, the use of sludge from WWTPs to enhance land and fertilize agricultural soils is another major via (Fatta-Kassinos et al. 2016).

On the other hand, toxicity is an important aspect to considerate regarding wastewater reuse. Indeed, an array of bioassays to monitor any impact in the different levels of organisms is

needed. The adverse effects have been reported even at the level of ng/L in the case of chronic exposures and µg/L in the case of acute toxicity (Fatta-Kassinos et al. 2016).

Thus, it is crucial to continue the research either in lab scale or in industrial scale of the micropollutants and their relationship with the reused water.

2.3 Wastewater characteristics

There is a high variability of liquid and solid wastes between communities. Wastewater can be defined as the combination of the liquid waste or water carried wastes removed from residences, institutions, commercial and industrial places and might be mixed with groundwater, surface water and storm water (Tchobanoglous and Burton 1991).

Wastewater treatment aims to protect the quality of freshwater and make the reclaimed water more acceptable for reuse (Shon et al. 2006). It started at the end of the 1800s and beginning of the 1900s (Tchobanoglous and Burton 1991). Until 1940, wastewater had mainly a domestic origin. In the case of the EEUU, during the 40s, the industrial development increased the industrial wastewater discharged in the municipal WWTPs. This new scenario changed the composition of the wastewater introducing heavy metals and synthetic organic compounds (Tchobanoglous and Burton 1991). Similar situation happened in Europe and currently in the developing countries.

It is important to be aware of the wastewater composition since it can be crucial to understand the interactions between the organic and inorganic compounds (Shon et al. 2006). In addition to the organic matter, wastewater contains pathogenic microorganisms, nutrients and toxic compounds that may be mutagenic or carcinogenic between others (Tchobanoglous and Burton 1991). The organic composition of wastewater is about 50% proteins, 40% carbohydrates, 10% fats and oils, and trace amounts of priority compounds, surfactants and emerging pollutants (Shon et al. 2006).

2.4 Effluent Organic Matter

The organic matter found in WWTP effluents is named Effluent Organic Matter (EfOM). EfOM is composed of heterogeneous organic compounds based on wide-spread molecular weight (MW) distribution and polydispersity (Nam and Amy 2008). EfOM is characterized by three main components (Jarusutthirak et al. 2002, Krasner et al. 2009, Shon et al. 2006):

- a. Natural Organic Matter (NOM)**
- b. Synthetic organic compounds (SOC)**
- c. Soluble microbial products (SMP)**

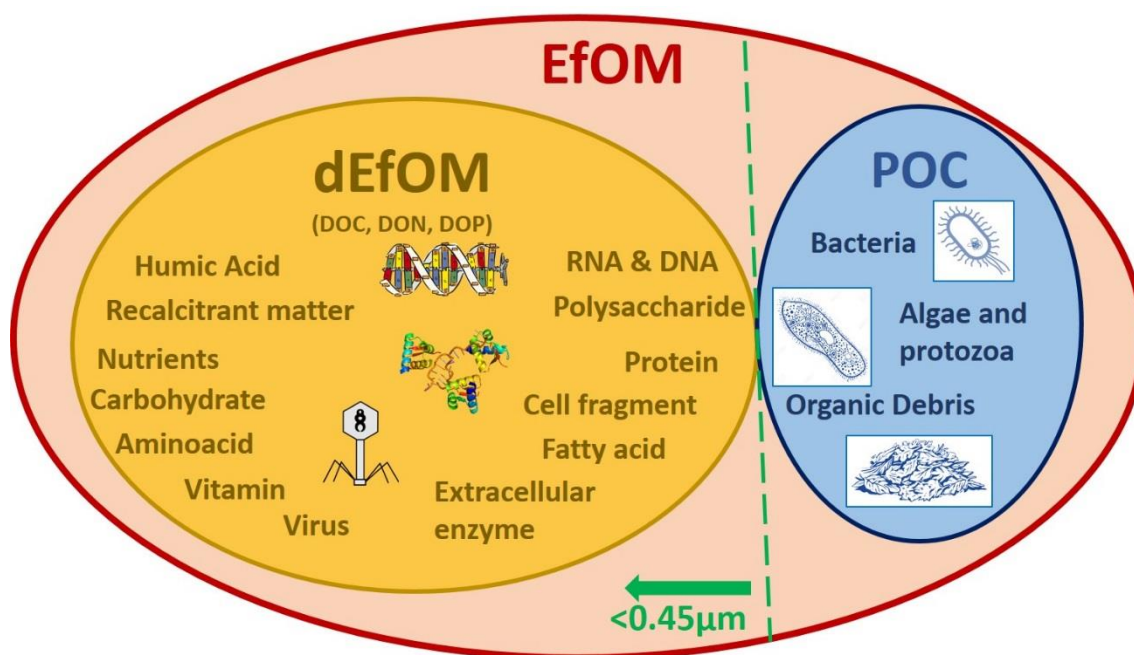


Figure 2.2 Organic constituents of EfOM divided by dEfOM and particulate EfOM (POC) Organic constituents of EfOM divided by dEfOM and particulate EfOM (POC)

Moreover, dissolved Effluent Organic Matter (dEfOM) is the major constituent of EfOM (86% of the COD (Shon et al. 2006). This fraction is smaller than $0.45\mu\text{m}$. Thus, the EfOM is classified in two main groups regarding the size criteria:

- Particulate organic carbon having a size higher than $0.45\mu\text{m}$
- Dissolved organic carbon having a size smaller than $0.45\mu\text{m}$, it can be also named dEfOM. Dissolved organic carbon (DOC) fraction, dissolved organic nitrogen (DON) fraction and Dissolved Organic Phosphorous (DOP) fraction can be differentiated.

In Figure 2.2, the EfOM compounds according to Levine et al. (Levine et al. 1985) are shown. Specific treatments should be used to remove each compound depending on their size. POC can be removed easily by solid liquid separation processes (Shon et al. 2006). Nonetheless, the smaller compounds (dEfOM) can pass through the different treatment steps and are more difficult to eliminate with the conventional treatment (Shon et al. 2006).

2.4.1 Natural Organic Matter

Natural Organic Matter (NOM) is a key parameter for water treatment design and operation (Eikebrokk et al. 2004). It is originated from the decomposition of plants and microbial materials and it is present ubiquitously in natural waters but also in soils and sediments (Nebbioso and Piccolo 2013). Indeed, in a wastewater, 75% approximately of the suspended solids and 40% of the filterable solids are organic in nature (Shon et al. 2006). NOM is composed mainly of carbon, hydrogen, oxygen and in a minor level from heteroatoms as nitrogen, sulfur and phosphorus (Hertkorn et al. 2008). Besides the atomic composition, NOM is formed by a wide range of compounds: from aliphatic to aromatic, from highly charged to uncharged and with different molecular sizes (Matilainen and Sillanpää 2010). Moreover, climate variations and the hydrological regimes are determinant to the amount of NOM in water. Likewise, the nature of NOM varies between sources and seasons (Matilainen and Sillanpää 2010). An increase in the quantity of NOM has been observed in surface waters during the last 9-42 years, depending on

the location (Eikebrokk et al. 2004, Worrall and Burt 2010). This fact can be due to air and water temperature increases, rainfall intensity and atmospheric CO₂ increase (Matilainen and Sillanpää 2010). NOM may have a negative impact in the water quality affecting its color, taste, odor and promoting biological growth and corrosion in the distribution systems (Eikebrokk et al. 2004). Furthermore, it can be complexed with heavy metals, it can adsorb organic micropollutants, and can promote the formation of disinfection byproducts (DBPs) and therefore is considered as a health hazard (Eikebrokk et al. 2004).

2.4.2 From Organic Pollutants to Emerging micropollutants

As it has been mentioned before, reuse of wastewater is a strategy that can lead to a better and more sustainable water management. Nonetheless, the pollution of freshwater with SOCs is rising nowadays (Eggen et al. 2014). SOCs as Pharmaceuticals, hormones, PPCPs, artificial sweeteners, perfluorinated compounds, brominated flame retardants and surfactants between others, can represent a limitation since their partial removal and byproducts can damage terrestrial and aquatic environment (Fatta-Kassinos et al. 2016).

During the last years, environmental research has extended its focus from the conventional environmental pollutants (PCBs, DDT, dioxins and pesticides) to the emerging contaminants (Pharmaceuticals and PPCPs)(Ternes and Joss 2006). The fast development and the increasing use of new analytical tools have enabled the identification of organic pollutants in a range of low concentrations (ng/L- µg/L) and in wide variety of water matrices (wastewater, surface water, groundwater, drinking water) and solid matrices (sewage sludge, manure, soil, sediment)(Fatta-Kassinos et al. 2016, Jelic et al. 2011, Ternes and Joss 2006).

The chemical pollution of the aquatic environment by our society is an experiment in real scale. Indeed, we have just analyzed the possible future impacts but right now, we are not able to anticipate the full list of effects for chronic exposure and pollution(Luo et al. 2014). However, the ecological effects of a group of compounds named Endocrine Disrupting Compounds (EDCs) have been already noticed (Luo et al. 2014). Due to their molecular structure, this group of compounds can mimic or interfere with the natural hormone pathways (Clara et al. 2005, Luo et al. 2014). Thus, these compounds have been associated with the feminization of male fish changing the sex ratios and therefore, modifying population densities (Liu et al. 2009, Luo et al. 2014, Tan et al. 2007).

2.4.3 Soluble microbial products and extracellular polymeric substances

Soluble microbial products (SMPs) and extracellular polymeric substances (EPSs) are the major fraction of dEfOM in wastewater (Jarusutthirak and Amy 2007). They are biologically generated from substrate metabolism during biomass growth and released from cell lysis, diffuse through cell membrane or excreted for other purposes (Shon et al. 2006). Their characteristics can vary between WWTPs as a result of the different treatment processes and water characteristics. In general, they exhibit high MW, hydrophilic and low SUVA character (Jarusutthirak and Amy 2007).

2.5 General Legal Framework

The environmental awareness of our society has increased during the last 50 years. In 1972, the United States of America (USA) by means of the Federal Water Pollution Control Act, better known as Clean Water Act (CWA), created the National Pollutant Discharge Elimination System (NPDES). CWA established the basic structure for regulating discharges of pollutants into the USA waters and for regulating quality standards for surface water. Indeed, NPDES provided two levels of control, the technology-based limits and water quality-based limits. After the major NPDES amendment in 1977, point source discharges to surface waters were regulated, including municipal wastewater effluents (Benedetti 2006). In USA, the minimum water quality standards (WQS) are settled by the Environmental Protection Agency (EPA), even though states with delegated authority can set more stringent requirements (Benedetti 2006). NPDES program has been updated and expanded several times, being the last amended version from the summer of 2016.

In Europe, the water legislation also began in the early 70s. The first European action was done in 1975 regarding drinking water quality and the water sources used for the water abstraction. This process concluded in 1980, establishing the quality targets for drinking water. Moreover, it also included other issues as legislation on fish, shellfish, bathing and ground waters. The main measure was focused in the Dangerous Substances Directive (67/548/EEC)(Directive 1967).

The Urban Waste Water Treatment Directive (91/271/EEC) was launched in 1991, promoting the secondary treatment and additional treatments whenever it is required. The Directive demanded that all the European agglomerations with a size higher than 2000 population equivalents had to be equipped with collecting and treatment systems for their wastewaters (Council 1991). It aimed to protect the environment from the negative effects of urban wastewater discharges and specific industrial discharges. Moreover, it identified and established polluted water areas, nitrate vulnerable zones, codes of good practices regarding agriculture, action programs and national monitoring (EU 2016). At the same time, the Nitrates Directive, concerning the nitrates from agriculture, was approved. Five years later, the Directive for Integrated pollution and Prevention Control was adopted (EU 2016). It was focused on pollution related with industrial installations. In 1998, a new Drinking Water Directive was approved.

In 2000, the Water Framework Directive 2000/60/EC was created to provide measures against the surface water pollution. It was divided in two main sections:

- a. **Selection and identification of hazardous substances (Priority Compounds) at European Union level**
- b. **Selection and identification of hazardous substances at national level (specific river basin pollutants).**

The first consequence of the Directive 2000/60/EC was the decision 2455/2001/EC that presented the first list of priority substances. Some years later, the Groundwater Directive (2006/118/EC) was adopted introducing actions to prevent or limit inputs of pollutants into groundwater. Moreover, in 2008 a new directive was approved establishing the environmental quality standards (Directive 2008/105/EC) and amending the Directive 2000/60/EC. It established the limit on concentrations of 33 priority pollutants and 8 other pollutants (Directive 2008). One year later, the Commission Directive 2009/90/EC was adopted providing quality rules for chemical analysis and monitoring of water, sediment and biota (EU 2016). In 2013, the last Directive 2013/39/EU was launched focusing in developing new technologies to deal with

water pollution. In addition, it expanded the list of priority compounds from 33 to 45 substances or/and groups of substances (Ribeiro et al. 2015).

Table 2.1 List of organic priority substances in the field of water policy and certain other pollutants defined in the Directive 2013/39/EU extracted from (Ribeiro et al. 2015). ^a Other pollutants defined in the Directive, not included in the priority substances list. ^b Group of substances listed as a class.

Class	Compounds	AA-EQS (µg/L)	MAC-EQS (µg/L)	EQS biota (µg/kg wet weight)	Priority hazardous substance
Organochlorine pesticides	Cyclodiene pesticides ^a including aldrin, dieldrin, endrin and isodrin	Σ:0.005-0.01	n.a.	-	No
	Endosulfan	0.0005-0.005	0.004-0.01	-	Yes
	Dicofol	3.2×10^{-5} - 1.3×10^{-3}	n.a.	33	Yes
	Heptachlor and heptachlor epoxide	1×10^{-8} - 2×10^{-7}	3×10^{-5} - 3×10^{-4}	6.7×10^{-3}	Yes
	Pentachlorophenol	0.4	1.0	-	No
	Hexachlorocyclohexane (HCH):e.g. γ-HCH or lindane	0.002-0.02	0.02-0.04	-	Yes
	Hexachlorobenzene	-	0.05	10	Yes
	Hexachlorobutandiene	-	0.6	55	Yes
	Dichlorodiphenyltrichloroethane (DDT) total ^a and p,p'-DDT ^a	0.025 (DDT total), 0.01 (p,p'-DDT)	n.a.	-	No
	Organophosphorus pesticides	Chlorfenvinphos	0.1	0.3	-
Chlorpyrifos (Chlorpyrifos-ethyl)		0.03	0.1	-	No
Dichlorvos		6×10^{-5} - 6×10^{-4}	7×10^{-5} - 7×10^{-4}	-	Yes
Triazine pesticides	Atrazine	0.6	2.0	-	No
	Cybutryne	0.0025	0.016	-	No
	Simazine	1.0	4.0	-	No
	Terbutryn	0.0065-0.065	0.034-0.34	-	No
Phenylurea pesticides	Diuron	0.2	1.8	-	No
	Isoproturon	0.3	1.0	-	No
Chloroacetanilide pesticide	Alachlor	0.3	0.7	-	No
Dinitroaniline pesticide	Trifluralin	0.03	n.a.	-	Yes
Pyrethroid Pesticide	Cypermethrin	8×10^{-6} - 8×10^{-5}	6×10^{-5} - 8×10^{-4}	-	No
Diphenyl ethers pesticides	Aclonifen	0.012-0.12	0.012-12	-	No
	Bifenox	0.0012-0.012	0.004-0.04	-	No
Quinoline pesticide	Quinoxifen	0.015-0.15	0.54-2.7	-	Yes
Organotin	Tributyltin compounds including tributyltin-cation	0.0002	0.0015	-	Yes
Brominated diphenylethers		-	0.014-0.14	0.0085	Yes
Hexabromocyclododecanes		0.0008 - 0.0016	0.05-0.5	167	Yes
Polyaromatic hydrocarbons (PAHs) ^b	Benzo(a)pyrene	1.7×10^{-4}	0.027-0.27	5	Yes
	Benzo(b)fluoranthene	Benzo(a)pyrene is considered as a marker for the other PAHs	0.017	Benzo(a) pyrene is considered as a marker for the other PAHs	Yes
	Benzo(k)fluoranthene		0.017		Yes
	Benzo(g,h,i)-perylene		8.2×10^{-4} - 8.2×10^{-3}		Yes
	Indeno(1,2,3-cd)-pyrene		n.a.		Yes
PAHs listed separately	Anthracene	0.1	0.1	-	Yes
	Fluoranthene	0.0063	0.12	30	No
	Naphtalene	2.0	130	-	No
Dioxins and dioxin-like compounds ^b	Polychlorinated dibenzo-p-dioxins (PCDDs)	-	n.a.	Toxic equivalents(PCDDs +PCDFs + PCB-DL): 0.0065	Yes
	Polychlorinated dibenzofurans (PCDFs)				

	Dioxin-like polychlorinated biphenyls (PCB-DL)				
Solvents	Benzene	8-10	50	-	No
	Trichlorobenzenes	0.4	n.a.	-	No
	Pentachlorobenzene	0.0007-0.007	n.a.	-	Yes
	Chloroalkanes, C10-13	0.4	1.4	-	Yes
	1,2-Dichloroethane	10	n.a.	-	No
	Dichloromethane	20	n.a.	-	No
	Trichloromethane	2.5	n.a.	-	No
	Carbon Tetrachloride ^a	12	n.a.	-	No
	Tetrachloro-ethylene ^a	10	n.a.	-	No
	Trichloro-ethylene ^a	10	n.a.	-	No
Industrial Compounds	Di(2-ethylhexyl)phthalate (DEHP)	1.3	n.a.	-	Yes
	Perfluorooctane sulfonic acids and its derivatives(PFOS)	1.3x10 ⁻⁴ -6.5x10 ⁻⁴	7.2 - 36	9.1	Yes
	Nonylphenol including isomer 4-nonylphenol	0.3	2.0	-	Yes
	Octylphenol including isomer 4-(1,1',3,3'-tetramethylbutyl)- phenol	0.01-0.1	n.a.	-	No

Finally, on March 2015, the Commission Decision (EU) 2015/495 established a watch list of 10 substances or/and group of substances. The selected substances may pose a significant risk to or via the aquatic environment but there is still not enough data to state a conclusion. The watch list included pharmaceuticals as Diclofenac, 17- β - estradiol (E2), 17- α - ethinylestradiol (EE2) and the macrolide antibiotics Erythromycin, Clarithromycin, Azithromycin.

2.6 Conventional Municipal Wastewater treatment

Nowadays, different combinations of processes and technologies can conform a Municipal Wastewater Treatment Plant (MWWTP). Nonetheless, the cost and other considerations limit the range of real options (SUEZ 2016). According to the last version of SUEZ's Degremont® Water Handbook, the most important and conventional restrictions when designing a MWWTP are:

- The characteristics of the effluent to be treated
- Water's quality objective and its reliability
- Final destination of the Sludge produced
- The plant situation
- Different construction layouts
- Parcel size
- The concerns related with sustainable development

Commonly, the Municipal WWTPs are organized in four stages that include physical, chemical and biological processes. In Figure 2.3, the conventional wastewater treatment with an additional tertiary step is presented. The first step of treatment train is usually a preliminary treatment (screens and grit chambers) to remove floating and inorganic solids, such as sand and grit particles. These solids can produce blockages and scrapes in pipelines and the treatment system. Secondly, the primary treatment consists in the removal of suspended solids by means of settling tanks and clarifiers. Afterwards, the secondary biological treatment takes place which aims to degrade the biodegradable binding organic matter and nutrients, mainly present under dissolved form. This step that it is the "core" of the wastewater treatment uses a wide range of microorganisms and bacteria. Finally, when reclamation is pursued or in case of discharge in sensitive areas, it is need an additional tertiary treatment which involves different filtration steps and disinfection by Chlorine, Ozone or UV.

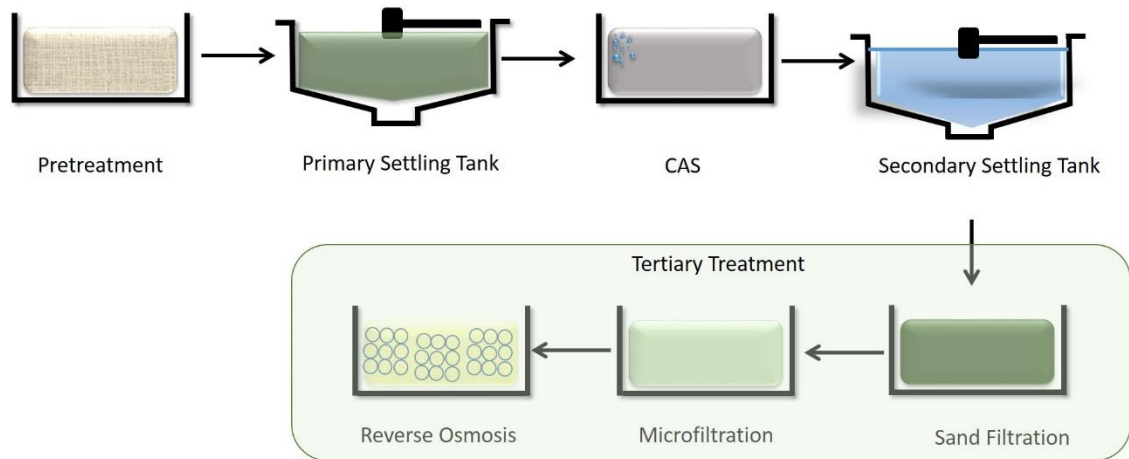


Figure 2.3 Conventional Wastewater Treatment with an additional tertiary treatment

Wastewater treatment plants (WWTPs) will have an important role in the future eco-cities since will provide energy by means of a system characterized by the smallest possible ecological footprint (Lazarova et al. 2012). In addition, it is important to optimize the consumption of energy needed for the wastewater treatment. So, the future objectives to achieve are defined by:

- Minimization of the energy needed for the wastewater treatment.
- Reduction of the carbon footprint
- Promotion of wastewater treatment self-sufficiency.

However, several ecological effects have been observed downstream of WWTP outfalls, probably due to the incomplete removal of pollutants by the conventional WWTPs (Margot et al. 2015). The analysis and understanding of the pollutants fate in Conventional WWTPs is fully necessary to create measures to reduce their release in the environment. Thus, another set of future objectives regarding micropollutants and quality standards must be considered (Eggen et al. 2014):

- Removal of nutrient excess to avoid eutrophication of aquatic ecosystems
- Removal of pathogens and fecal bacteria to enhance hygienic conditions of the receiving waters
- Improvement of water quality (degradable organics and micropollutants) to protect the ecosystem and to facilitate the intake downstream for drinking water purposes.

These objectives are presented schematically in the figure below (Figure 2.4)

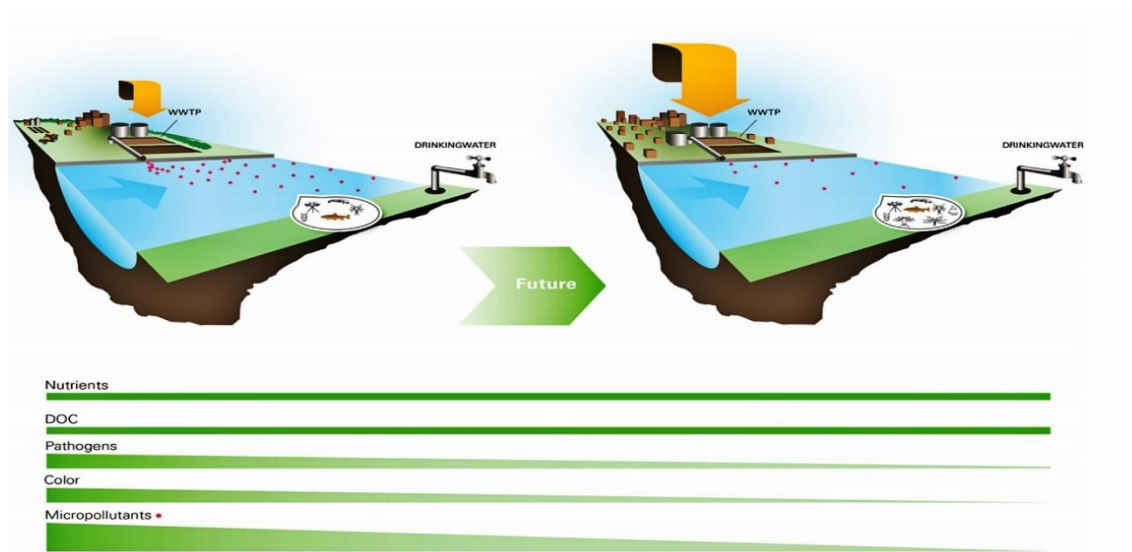


Figure 2.4 Schematic diagrams of current (left) and future needs (Right) extracted from (Eggen et al. 2014)

2.6.1 Micropollutant occurrence and fate in WWTPs

Even though, conventional WWTPs are designed to treat solid wastes, suspended solids and biodegradable dEfOM, many micropollutants are also affected by the treatment train (Margot et al. 2015). Hence, half of the micropollutant load is eliminated either by sorption to the sludge, biological degradation, volatilization and abiotic degradation (Eggen et al. 2014, Margot et al. 2015). Despite this fact, some hydrophilic compounds are neither adsorbed into the sludge nor eliminated in the discharge effluents (Eggen et al. 2014). Consequently, some of these micropollutants can end up in the aquatic environment generating negative effects, including long-term and short-term toxicity (Luo et al. 2014). The different mechanisms that can affect micropollutants during the conventional treatment train are described below:

- a. **Sorption:** Hydrophobic micropollutants and positively charged micropollutants can sorb onto sludge and/or particulate matter but also colloidal matter (1 nm to 1 μ m). In the case of Sludge, there are two types of interactions: Hydrophobic between the micropollutants and EPS, cell membrane and suspended solids; and Electrostatic interactions between positive charged micropollutants and negative charged surface of microorganisms and EfOM (Margot et al. 2015). When micropollutants are adsorbed into colloidal matter their solubility increases limiting their removal by sorption. In the case of sorption, the fate of micropollutants will fall onto the final fate of the sludge.

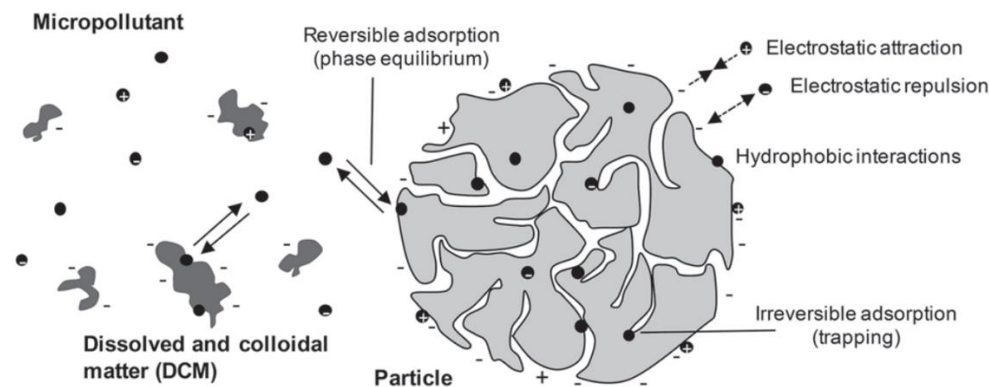


Figure 2.5 Micropollutant adsorption onto sludge and onto dissolved and colloidal matter extracted from (Margot et al. 2015)

- b. Biological Transformation:** as the concentration of micropollutants is low (ng/L - μ L), biological transformation needs the presence of extra carbon and energy sources (Tran et al. 2013). Biological transformation is the main removal treatment for hydrophilic compounds. Biological transformation can occur in two main pathways (Margot et al. 2015):
1. Metabolic reactions on mixed substrate: where the micropollutants are used as a growth substrate together with other organic compounds.
 2. Co-metabolic reactions: micropollutants are transformed by side reactions catalyzed by means of enzymes or cofactors produced during the microbial conversion of the growth substrate.

Moreover, the degree of biological transformation depends on different working conditions as: the type and amount of microorganisms, biodegradability of this pollutants, the hydraulic retention time of the reactor, temperature, pH, redox conditions and the availability of co-substrates (Cirja et al. 2008, Petrovic et al. 2013, Ternes and Joss 2006).

- c. Volatilization:** even though surface volatilization can occur, it mainly takes place through stripping during aeration. This process depends on the volatility of the compounds (Henry Law Constant, K_H) (Margot et al. 2015) and it is considered a minor that it occurs in a minor degree (Luo et al. 2014).
- d. Abiotic degradation:** During wastewater treatment, organic micropollutants can be degraded by abiotic reactions such as photolysis and hydrolysis. Photolysis leads the bond cleavage by de absorption of photons and therefore, the surface-to- volume ratio and turbidity are crucial parameters. This is a minor process WWTPs. On the other hand, hydrolysis which is the result of the cleavage of chemical groups by substitution for H_2O or OH . This process is almost negligible but it affects some antibiotics (β -lactam, macrolide and tetracycline types)(Margot et al. 2015).

As not all the micropollutants are removed through the wastewater treatment, the fate of some groups of micropollutants typically found in WWTPs are described below. The fate of micropollutants is influenced by internal and external factors understanding as internal the chemical structures and properties and by external the specific conditions of each WWTPS (Luo et al. 2014).

Table 2.2. Sources of micropollutants in the aquatic environment adapted from (Luo et al. 2014).

Category	Subclasses	Major sources	
		Distinct	Non exclusive
Surfactants	Non-ionic and anionic	Domestic Wastewater (bathing, laundry, dishwashing, etc.) Industrial Wastewater (industrial cleaning discharges)	Sources that are not exclusive from one category include: Industrial wastewater (from product manufacturing discharges) Landfill leachate (from improper disposal of used, defective or expired items)
Pharmaceuticals	Analgesics, anti-inflammatory, antibiotics, iodinated contrast media, antidiabetics, antihypertensive drugs, β -blockers, lipid regulators, psychiatric drugs and antihistamines	Domestic Wastewater (Urea and feces) Hospital effluent Run off from animal agriculture and aquaculture	
Steroid hormones	Estrogens	Domestic Wastewater (Urea and feces) Run off from animal agriculture and aquaculture	
PPCPs	Fragrances, Sunscreen Filters, Preservatives, antimicrobials and insect Repellents	Domestic Wastewater (bathing, shaving, spraying, swimming)	
Pesticides	Insecticides, herbicides, algaecides and fungicides	Agricultural run off Domestic wastewater (from improper cleaning, run-off from gardens, lawns and roadways etc.)	
PAHs		From incomplete combustion of oil, , petroleum, coal and wood	
Industrial Chemicals	Flame Retardants, plasticizers, anticorrosives	Domestic wastewater (by leaching out the material)	

In general, pharmaceuticals and steroid hormones are highly removed by biodegradation but it doesn't occur for pesticides and antibiotics. On the other hand, industrial compounds and PPCPs are removed by sorption (Luo et al. 2014).

Surfactants are found in industrial applications (cleaners, PPCPs, textiles, paint additives, lacquers and plastics) as well as household products (detergents and cleaners). In 2005, the most used surfactants were soaps (23.5%), alcohol ethoxylates (AE, 17.9%) and linear alkylbenzene

sulfonates (LAS, 16.6%)(Berna et al. 2007). As their consumption is high ($> 7.5\text{g day}^{-1}\text{ capita}^{-1}$) and they are discharged directly into the sewage system, their concentration in raw water is high ($>40\text{mg/L}$) and it may represent the 20-30% of the DOC present in the wastewater(Matthijs et al. 1999). Despite they are mainly removed by biodegradation (70-95%) and up to 30% by sorption, surfactants are detected in a range of concentrations from 1-150 $\mu\text{g/L}$ in WWTP effluents. As they are persistently release, they could promote negative effects on sensitive aquatic organisms (Margot et al. 2015). In fact, Nonylphenol (NP) and NP ethoxylates have been recognized as priority compounds by the European Water Frame Directive (WFD)(Directive 2013) and as toxic substances by the Canadian Government (Luo et al. 2014).

Pharmaceuticals are highly consumed nowadays. Even though 3000 pharmaceutical products are available in Europe (Ternes and Joss 2006), the 99% of the consumed pharmaceuticals correspond to 60 drugs(de García et al. 2013). In Western Europe, the average of active ingredients consumed per day is 300 mg per inhabitant. Pharmaceuticals and their metabolites are mainly discharged by means of urine and faces into the sewage system. The concentrations of pharmaceuticals can vary from less than 1ng/L to over $100\ \mu\text{g/L}$. The most abundant ($0.1 - 10 < \mu\text{g/L}$) pharmaceutical groups found in wastewater are: analgesics, anti-inflammatory drugs, antibiotics, iodinated contrast media, antidiabetics, antihypertensive drugs, β -blockers, lipid regulators, psychiatric drugs and antihistamines (Margot et al. 2015).

The fate of the pharmaceuticals in the WWTPs depend greatly on the biodegradability and hydrophobic capacity but the major part of the studied drugs have lower removal rates than 50%. However, some hydrophobic and positively charged pharmaceuticals show removals between 10-80% by sorption (i.e. mefenamic acid, fenofibrate, ofloxacin, norfloxacin and ciprofloxacin). In these cases, the problem is the final fate of the sludge because some compounds can persist even after anaerobic digestion. Pharmaceuticals with higher solubility and low hydrophobicity, are often negative charge at neutral pH and present lower removal by sorption ($<5\%$)(Verlicchi et al. 2012). Thus, the pharmaceuticals concentrations measured in the WWTP effluents are in the range of $\text{ng/L} - \mu\text{g/L}$, but they can differ depending on the country(Luo et al. 2014, Margot et al. 2015). The environmental risk (to the aquatic and terrestrial organisms) is not only because the effect of each compound separately but because of the effect of the complex mixture of compounds. Regarding specific antibiotics highly used nowadays, Sulfamethoxazole show a moderated removal (65%) and Erythromycin shows even a low removal (3%) after the wastewater treatment (Luo et al. 2014). Also, in the group of Non-steroidal anti-inflammatory drugs (NSAIDS) disparities have been observed between different pharmaceuticals, for instance, the Ibuprofen removal is higher than 70% but Diclofenac shows an average removal of 36%. The variations between removals are also found in the case of β -blockers, being in a range of (38-73%) (Luo et al. 2014).

Human pharmaceutical metabolites are found in the same ranges of the parent compounds, however they are more polar and hydrophilic than the active pharmaceuticals (Ikehata et al. 2006). They are not significantly removed by sorption, but depending on the compound can be biodegraded. Illicit drugs (cocaine, MDMA, amphetamines, etc.) can be found in the range 100-2000 ng/L in the raw wastewater, and it highly increase during the weekends in large cities. In general, the removals for these drugs are found between 79 – 98%, except for MDMA (0-26%)(Bijlsma et al. 2012, Kasprzyk-Hordern et al. 2009).

Steroid hormones are mainly introduced to the aquatic environment by household wastewater and from animal agriculture and aquaculture (Luo et al. 2014). In general, steroid hormones present concentrations lower than $1\mu\text{g/L}$ in raw effluents (Luo et al. 2014). This value fall until

<100 ng/L in the wastewater effluent but it is still a concern due to the high estrogenic effect (Luo et al. 2014).

Personal Care Products are found in shampoos, washing lotions, skin care products, dental care products, sunscreen creams and perfumes between others. Due to their application, they are introduced to the wastewater effluent by the wash off during showering or bathing. Inside this group of products, we find different subclasses:

- **Fragrances:** the main synthetic musk found in the environment are Galaxolide and Tonalide (polycyclic), and the bicyclic hydrocarbon fragrance OTNE. Their concentration range between 0.5-13µg/L in raw wastewater in spite of that, they show a high hydrophobicity character which facilitates their removal (60-99%) by sorption. Nevertheless, their concentrations in wastewater effluent are between 250-1300 ng/L. The problematic regarding these substances fall on their lipophilicity which produces the bioaccumulation mostly in fish tissues (Margot et al. 2015).
- **Preservatives, insect repellents and antimicrobials:** parabens are used as antimicrobials preservatives. They have a small estrogenic effect and bioaccumulate in human tissues. However, they are well removed in WWTPs (>95%), obtaining really low concentrations in the effluent (<100 ng/L). Antimicrobial agents as Triclocarban and Triclosan, are used in PCPPs. The concentration range in raw wastewater is 0.1-10 µg/L, but due to their hydrophobicity, the removal by sorption is significant (80%). One of the main active ingredients is the N, N-diethyl-m-toluamide (DEET). The DEET removals are highly variable ranging from 10-99% depending on the plant and the season (Margot et al. 2015).
- **Sunscreen Filters:** Organic UV filters enter to the aquatic environment directly from the recreational activities or indirectly through municipal wastewater. Usually around 90% of these compounds are removed in WWTPs. Some UV filters are lipophilic, thus, 50-95% tend to sorb onto particles, but in general are removed by biodegradation (Margot et al. 2015).

Biocides and pesticides are designed to control the growth of plants (herbicides), algae (algicides), insects (insecticides) or fungi (fungicides). In Europe, 500 of these compounds are approved for use. Even though the agricultural source is considered the main source of these compounds in surface water, some studies have shown that urban origin is also a significant contributor to have them in the water effluents. In general, the average concentration of these compounds in the raw wastewater is lower than 1 µg/L and the efficiencies achieved in the WWTPs are also low (<50%). Thus, the concentrations of these compounds are found between 5-300ng/L(Margot et al. 2015). Among the possible chronic effects of these compounds are carcinogenesis, neurotoxicity, effects on reproduction and cell development (Oller et al. 2011).

Polycyclic Aromatic Hydrocarbons (PAHs) are originated from the incomplete combustion of organic material such as oil, petroleum, coal and wood. They consist in a different combinations of benzene rings being the structure with two benzene ring the simplest form. Between them, only naphthalene is used for commercial purposes as a lubricant, in bathroom products or in plasticizers. Some of them, are highly carcinogenic, mutagenic, teratogenic and relatively persistent. 8 PAHs have been listed as a Priority Compounds in Europe. PAHs removal, mainly by sorption, shows variations but it is found between 60-90%. Moreover, 80% of the most toxic PAHs (compounds with higher molecular weight) are removed in WWTP(Margot et al. 2015).

Industrial Chemicals as Flame retardants are used for inhibit fires and are integrated in a variety of household equipment as electrical devices, building materials, furniture and plastics. Some brominated flame retardants have been classified as a persistent organic pollutants due to their persistence, bioaccumulation and toxicity. Polybrominated diphenyl ethers (PBDEs) are a family of flame retardants commonly found in wastewater and formed by 209 congeners. The most frequently detected in wastewater are the BDE-47,-99,-100,-153 and -209. As a consequence of their hydrophobicity and low biodegradability, they are mainly removed by sorption onto the sludge during the wastewater treatment achieving 90% of elimination(Margot et al. 2015).

Regarding the different families of micropollutants and their removals presented before, it is evident that the sludge sorption plays an important role in the wastewater treatment. Furthermore, it is important to improve the sludge management in order to avoid pollution from the sludge to the terrestrial and aquatic environment. Moreover, the improvement of the existing treatment technologies and addition of new treatments should be considered in order to reduce the micropollutant discharges.

Table 2.3. Fate of 84 micropollutants in Conventional WWTPs adapted from (Margot et al. 2015)

Substance	Family	Typical WWTP removal	Typical Effluent Concentration	EQS	PNEC	Priorization ⁽⁶⁾		
		% ⁽¹⁾	ng/L ⁽²⁾	ng/L ⁽⁴⁾	ng/L ⁽⁵⁾	Load	Toxicity	Persistence
Surfactants								
Soap (palmític acid/lauric acid)	Anionic Surfactant	99	150000	-	22000/44000	x	x	
Linear alkylbenzene sulfonates (LAS)	Anionic Surfactant	97	50000	-	21000 (C10-C13)	x	x	
Alcohol Ethoxylates (AE)	Non-ionic Surfactant	99	5000	-	1560 (C12-18)/71100(C9-11)	x	x	
Nonylphenol ethoxylates (NPES)	Non-ionic Surfactant	90	6000	13 (NP)	500 (NPES)/30 (NP)	x	x	
Pharmaceuticals								
Ibuprofen	Anti-inflammatory	80	81-460	300	1		x	
Paracetamol	Analgesic	100	<8-178	-	500			
Salicylic acid	Analgesic	99	78	-	3200			
Atenolol	β-blocker	41	843-940	150000	6400000			x
Azithromycin	Antibiotic	39	220-408	90	-		x	x
Bezafibrate	Anti-cholesterol	41	25-320	460	0.03		x	x
Ciprofloxacin	Antibiotic	69	67-179	89	1.2		x	
Clarithromycin	Antibiotic	33	130-276	60	20		x	x
Eprosartan	Anti-hypertensive	37	227-880	-	-		?	x
Erythromycin	Antibiotic	45	42-830	40	200		x	x
Iohexol	Contrast medium	31	15191	-	320000000	x		x
Iomeprol	Contrast medium	34	376-10534	-	-	x	?	x
Iopromide	Contrast medium	41	2460-2700	-	-	x	?	x
Ketoprofen	Anti-inflammatory	40	86-190	-	-		?	x
Metmorfin	Anti-diabetic	57	10347-27800	1000000	2200000	x		
Naproxen	Anti-inflammatory	40	193-462	1700	320		x	x

Norfloxacin	Antibiotic	69	39-70	-	160			
Ofloxacin	Antibiotic	58	10-251	-	2100			
Pravastatin	Anti-cholesterol	37	420	-	-		?	x
Sulfamethoxazole	Antibiotic	44	238-1190	600	13		x	x
Venlafaxine	Anti-depressant	40	119-150	-	5.7		?	x
Carbamazepine	Anticonvulsant	16	140-832	500	89		x	x
Clindamycin	Antibiotic	10	50-115	-	0.22		?	x
Diclofenac	Anti-inflammatory	20	260-647	50	500		x	x
Fluconazole	Antifungal	15	108-110	-	6		?	x
Gabapentin	Anticonvulsant	15	1910	-	10000	x		x
Irbersartan	Anti-hypertensive	10	480-1700	704000	-	x		x
Metropolol	β -blocker	25	240-410	64000	146000			x
Propranolol	β -blocker	28	33-140	160	100		x	x
Oxazepam	Anxiolytic	13	162-350	-	100000000			x
Hormones								
Estrone (E1)	Natural hormone	76	12-217	3.6	3.6		x	
17 β -estradiol (E2)	Natural hormone	90	1.3-4	0.4	0.042		x	
Estriol	Natural hormone	99	1	-	67			
17 α - ethinyl estradiol (EE2)	Contraceptive	60	0.5-2	0.037	0.004		x	
Illicit drugs								
Amphetamine	Nervous system stimulant	98	2	-	4.901			
Cocaine	Nervous system stimulant	79	30	-	-		?	
MDMA (Ecstasy)	Psychedelic Drug	15	100	-	-		?	x
THC-COOH (Cannabis metabolite)	Psychedelic Drug	98	13	-	-		?	
Personal care products								
Galaxolide	Fragances	85	850	-	6800			
Tonalide	Fragances	85	250	-	3920			
Iso E Super(OTNE)	Fragances	65	1400	-	560	x		x
Methyl-paraben	Preservatives	95	19	-	4000			
Triclosan	Biocides	90	200	20	1.5			x
Chloroxylenol	Biocides	95	300	-	26			x
N,N- diethyl-m-toluamide (DEET)	Biocides	62	700	41000	800			
4-methylbenzylidene camphor (4-MBC)	UV filters	72	800	-	-			
Benzophenone-3 (BP-3)	UV filters	90	270	-	1600			
Octocrylene (OC)	UV filters	96	52	-	10000000			
Household chemicals								
Acesulfame	Sweeteners	5	30000	-	20000000	x		x
Saccharin	Sweeteners	99	500	-	9983000			
Sucralose	Sweeteners	5	10000	-	-	x	?	x
Bisphenol A (BPA)	Plastic additives	80	200	1500	175		x	
Di-n-butyl phthalate (DnBP)	Plastic additives	69	570	8000	340		x	

Benzotriazole	Corrosion inhibitor	26	6600	30000	40000	x	x
Methylbenzotriazole	Corrosion inhibitor	30	2900	75000	40000	x	x
Decabromodiphenyl ether (BDE-209)	Brominated flame retardants	90	2	-	40		
2,2',4,4'-tetrabromodiphenyl ether (BDE-99)	Brominated flame retardants	91	0.7-8	0.5	500	x	
Biocides and Pesticides							
Atrazine	Herbicide	23	10	600	0.011	x	x
Diuron	Herbicide, algicide	33	70	1500000	11000	x	x
Isoproturon	Herbicide, algicide	42	25	320	174		x
Mecoprop	Herbicide	25	500	3600	514700		x
Terbutryn	Herbicide, algicide	60	20	60	200		
Aldrin	Insecticide	86	1	Σ=10	36		
Dieldrin	Insecticide	77	8.9		1		
Endrin	Insecticide	81	2.8		3.4		
Endosulfan	Insecticide	84	2.7	5	1	x	
Heptachlor	Insecticide	91	6.4	0.0002	46	x	
Polycyclic aromatic hydrocarbons (PAHs)							
Acenaphthene		85	23	-			
Anthracene		90	2	100			
Fluoranthene		80	10	6.3		x	
Fluorene		90	13	-			
Naphthalene		60	49	2000			
Phenanthrene		80	12	-		x	
Pyrene		70	15	-			
Benzo[b]fluoranthene		80	3	Σ=17			
Benzo[k]fluoranthene		90	2				
Benzo[a]pyrene		70	1.1	0.17		x	
Indeno[1,2,3-cd]pyrene		80	1.4	Σ=2		x	
Benzo[ghi]perylene		80	1.1			x	

- (1) Average removal in conventional WWTPs (mainly activated sludge), observed if available in national studies on a wide range of WWTPs in Europe or United States.
- (2) Average effluent concentrations observed if available, in national studies in WWTPs in Europe or United States
- (3) Chronic environmental quality standards (EQS) for inland surface waters (annual average value).
- (4) Predicted no-effect concentration (PNEC): concentration below which exposure to a substance is not expected to cause adverse effects.
- (5) Prioritization of the micropollutants based on their load (for substances with effluent concentration <1000ng/L); toxicity (for substances with effluent concentration >PNEC); and their persistence in WWTPs (for substances removed less than 50% in the conventional treatments).

2.7 Advanced Oxidation Processes - State of art

In the problematic water pollution scenario mentioned before, advanced oxidation processes (AOPs) emerge as a possible alternative to treat the biologically persistent wastewater

improving water quality and therefore restoring the aquatic environment. These processes degrade organic pollutants by mainly forming hydroxyl radicals ($\text{OH}\cdot$) which are highly reactive and non-selective (Glaze et al. 1987). However, other organic radicals might also be formed. Nowadays, AOPs include also the processes that involve other radicals as sulfate radicals ($\text{SO}_4^{2-\cdot}$) (Anipsitakis and Dionysiou 2003, De Luca et al. 2016). AOPs can oxidize and mineralize several organic molecules to yield CO_2 and inorganic ions as final products (Gozzi et al. 2012, Ikehata et al. 2006, Ribeiro et al. 2015). Nonetheless, AOPs are usually considered expensive for complete mineralization so nowadays, the trend is to use them as a pretreatment to convert the persistent pollutants into more biodegradable intermediates. In this case, the chemical oxidation step would be followed by a biological oxidation step reducing in this way the cost (Beltran-Heredia et al. 2000, Pulgarin et al. 1999). Hence, the rate of mineralization should be minimal during the pre-treatment stage to avoid unnecessary expenditure of chemicals and energy. However, if the pre-treatment is too short the intermediates generated could be extremely similar to the parent compound and so, still recalcitrant (Oller et al. 2011).

For every AOP pretreatment, lab scale trials should be consider to identify all the possible effects within the effluent: formation of less biodegradable intermediates, lack of selectivity on the more recalcitrant fractions or the excess of oxidant dose.

Different AOPs classified depending on method for radical production are shown in Table 2.4:

Table 2.4. Different AOPs based on the method for radical production (Esplugas et al. 2002, Giannakis et al. 2016, Hu and Long 2016, Pera-Titus et al. 2004)

Photolysis	Ozone	Hydroxyl Radical	Sulfate Radical	High energy
<ul style="list-style-type: none"> • UV Photolysis • V-UV Photolysis 	<ul style="list-style-type: none"> • Ozonation (alkaline conditions) • Ozonation + UV and or H_2O_2 • Ozonation + catalyst 	<ul style="list-style-type: none"> • Fenton • Fenton-like • Photo-fenton • UV/ H_2O_2 • Electro-Fenton • Photocatalysis 	<ul style="list-style-type: none"> • UV/PS and UV/PMS • Catalyst/PS and Catalyst/PMS • Heat/PS and Heat/ PMS 	<ul style="list-style-type: none"> • Ultrasound technologies • Electrochemical oxidation • Electron beam oxidation • Microwaves enhanced processes • Hydrocavitation • Non Thermal plasma

Moreover, the chemical changes greatly depend on the interaction between the reagent and the target compounds when homogeneous processes are applied. However, in the case of heterogeneous processes, the chemical changes also depend on the adsorption of reactants and desorption of products that occur at the active sites of the catalytic surface (Ribeiro et al. 2015).

2.7.1 Removal of Micropollutants by AOP's in wastewater

Many AOPs have been studied for the removal of different micropollutants. For instance, photochemical processes such as UV/O_3 and $\text{UV}/\text{H}_2\text{O}_2$, photocatalytic technologies like TiO_2/UV , Fenton and photo-fenton, and chemical oxidation processes as O_3 , $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ have been investigated for the removal of pesticides. Heterogeneous photocatalysis using TiO_2 supported in glass rings and using solar light has been able to completely eliminate Isoproturon (Parra et al. 2002). Some studies have reported on Ozonation and UV/O_3 for the removal of

pesticides as Destamethrin, achieving 95% of elimination (Lafi and Al-Qodah 2006). Activated sludge has also been used in an immobilized biomass reactor combined with solar photo-fenton compound parabolic collectors (CPCs) for the degradation of a mixture of 5 pesticides: methomyl, dimethoate, oxamyl, cymoxanil and pyrimethanil (Oller et al. 2007). Nevertheless, wide screening studies should be performed in order to see the effect of each oxidation technology on each pesticide and in the total mixture.

A lack of data exists regarding degradation of flame retardants by means of AOPs and few reports have been found regarding AOPs applications for alkylphenols (Ribeiro et al. 2015). However, concerning the alkylphenols compounds, some comparative studies have been performed between Fenton-based, photocatalysis and ozonation.

Degradation of pharmaceuticals by using AOPs has been studied, especially the anti-inflammatory drug diclofenac and the hormones 17- β - estradiol and 17- α -ethinylestradiol. Good results were achieved with the conventional AOPs but also with the new hybrid technologies such as photocatalytic ozonation and sonophotocatalysis (Ribeiro et al. 2015).

Although application of AOPs have shown good effectiveness degrading PAHs, synergetic effects have been observed applying simultaneously different AOPS (Rubio-Clemente et al. 2014). However, optimization of the cost- effectivity and further combination with biological treatment should be performed.

Three tertiary treatments were applied to a real MWWTP effluent in a pilot scale study: mild solar photocatalysis with TiO_2 , mild solar photo-Fenton (54 mg/L of H_2O_2) and ozonation (ozone consumption = 9.5 mg/L) were able to eliminate micropollutants found in a concentration of 40-80 $\mu\text{g/L}$. However, Photocatalysis with TiO_2 showed less efficiency in terms of time and energy than photo-Fenton and ozonation. 98% of the total micropollutant sum (pharmaceuticals, pesticides and related metabolites) was removed by means of an ozone consumed dose of 9.5 mg/L and with 54 mg/L of H_2O_2 in the case of solar photo Fenton (Prieto-Rodríguez et al. 2013).

Margot et al. studied the removal of 70 potential micropollutants (pharmaceuticals, pesticides, endocrine disruptors, drugs metabolites and other common chemicals), from a conventional MWWTP of Switzerland, by ozonation followed sand filtration (Margot et al. 2013). In the mentioned study, the micropollutant removals reached the 80% compared with raw water for an ozone dose of 5.7 mg/L. Different removals were observed depending on the compound reactivity towards ozone. Thus, 12 substances, mainly pharmaceuticals, were eliminated over 90% with the lower ozone dose (2.3 mg/L). Moreover, they observed a reduction in the toxicity when the treatment was applied.

Pursuing the evaluation of the efficacy of advanced wastewater treatment processes for micropollutants and pathogens elimination, Ternes et al. applied ozonation (specific ozone consumption of $0.98 \pm 0.24 \text{ g}_{\text{O}_3}/\text{g}_{\text{DOC}}$) to a biotreated effluent in a pilot scale. Different removals were achieved depending on the compound but in general good performances were obtained (removals: Diclofenac 99%, mecoprop 92%, carbamazepine 99%, clarithromycin 75%, roxithromycin 83%, trimethoprim 86%, sucralose 62%) except for the Benzotriazole (removal 5%)(Ternes et al. 2017).

Ozonation and AOPs have achieved significant micropollutant degradation (Ikehata et al. 2006, Pérez-Estrada et al. 2011). Even though, the application of AOPs to wastewater containing micropollutants has been deeply studied, there are not many cost effective chemical and biological treatment combinations (Marco et al. 1997, Rosal et al. 2010).

2.8 Ozonation

Although, ozone was related with electrical storms during all mankind history, ozone was discovered by Christian Friedrich Schönbein in 1839 (Rubin 2001). Schönbein gave the name of ozone because of its strong smell since the term ozone come from the Greek work “ózein” which means to smell (Sonntag and Von Gunten 2012). Some years later, in 1906, the first major application of ozone for drinking water was inaugurated in Nice, France (Loeb et al. 2012). The situation is quite different nowadays as only in the area of Paris there are until 12 water plants using ozone. In the United States, ozone was firstly used in 1908 and had a minimal growth until 1985. However, in the past two decades, more than 300 ozone plants have been constructed (Rakness 2011). Indeed, ozone is gaining importance in real applications and research as it is shown in Figure 2.6 where it is presented the increasing trend of articles published in academic journals containing the word “ozonation” since 2000.

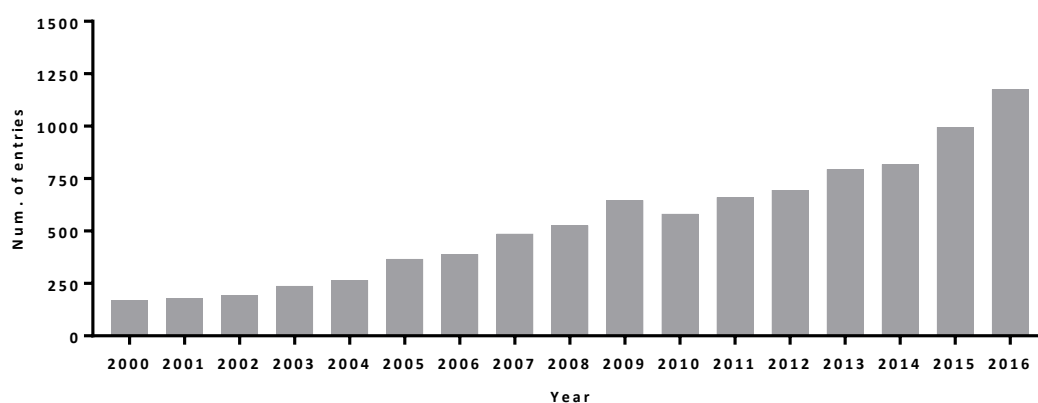


Figure 2.6. Number of entries searching "ozonation" in Science Direct (only Journal Publications)

Ozone application is used in wastewater, disinfection and air treatment to minimize the pollution. This process has two main strengths: on one hand, the strong oxidant potential and secondly, the lack of residues after its application. In

Table 2.5, different standard oxidation potentials are presented. On the top of the list, fluorine is the most oxidant but it is followed by the hydroxyl radical and in the fourth place for ozone. Since ozone decomposition can produce hydroxyl radicals, it points out the importance of ozone in oxidation.

Table 2.5. Standard oxidation potentials (Parsons 2004)

Oxidant	E° (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Potassium permanganate	1.67
Hyprobromous acid	1.59
Chlorine dioxide	1.50
Hypochlorous acid	1.49
Chlorine	1.36
Oxygen	1.20
Bromine	1.09

2.8.1 Ozone physico-chemical properties

Ozone is composed for three atoms of oxygen. Its smell is sensitive for human nose from an indicative level of $15\mu\text{g}/\text{m}^3$ to a clear identification when ozone concentration is $30\text{-}40\ \mu\text{g}/\text{m}^3$ (Cain et al. 2007). At room temperature, ozone is an unstable gas and it is blue when it is viewed under sufficient thickness (Baig and Mouchet 2010). Ozone is a polar molecule so it has a dipole moment of 0.537 D but it does not present paramagnetic character (Baig and Mouchet 2010, Sonntag and Von Gunten 2012). The following ozone resonance structures can be found (Figure 2.7):

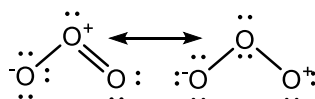


Figure 2.7. Ozone resonance structures (Am Water Works Res 1991)

Moreover, a summary of ozone physico-chemical and thermodynamic properties extracted from (Baig and Mouchet 2010), (Beltran 2003) and (Sonntag and Von Gunten 2012) is presented in Table 2.6.

Table 2.6. Ozone Properties

Property	Value
Molecular weight	48 Da
Dipole moment	0.537 D
Bond length	1.28 Å
Bond Angle	116°45'
Melting point	-192.7°C
Boiling point	-110.5°C
Henry constant at 0°C	35 atm/M
Henry constant at 20°C	100 atm/M
Explosion threshold	10% Ozon
Solubility in water (0°C, 1 atm)	1370 mg/L
Density (air reference)	1.657
Free molar formation entalpy	+142.2 KJ/mol

2.8.2 Ozone Generation

As ozone is an unstable gas, it should be produced in situ (Baig and Mouchet 2010). The ozone generator that is used nowadays for industrial applications is an evolution of the one invented by Werner von Siemens in 1857, only its invention made ozone industrial applications possible (Sonntag and Von Gunten 2012). From all the techniques to generate ozone: electrolysis of water, high tension electric discharge inside an oxygen flow, photolysis of oxygen by UV radiation ($\lambda < 220$ nm) and oxygen radiolysis by constant radiation; only the electric discharge (Corona) allows the industrial production (> 2 kg/h) since with the other systems, ozone quickly reverts to oxygen (Baig and Mouchet 2010).

The corona electric discharge consists in an electrical energy flow passing through a narrow gap filled with oxygen or air. When it happens, the oxygen molecules split into oxygen atoms (O^{\cdot}) and these atoms combine with other oxygen molecules (O_2) giving ozone (O_3).

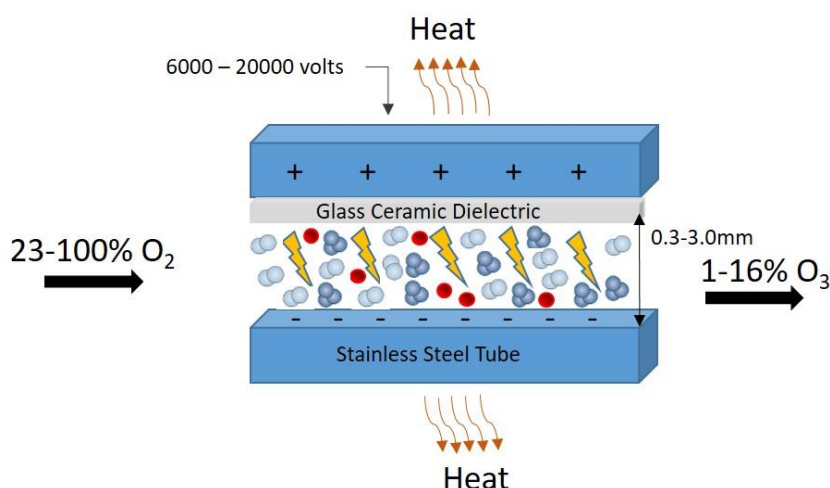


Figure 2.8. Ozone Electric discharge Generator adapted from (Rakness 2011)

The produced ozone concentration varies depending on the feed gas, for instance, for oxygen-fed ozone systems, the range is 6-16 %wt (typically 8-12%), and for air-fed ozone systems the range of 1-4 %wt (Rakness 2011).

2.8.3 Ozone Solubility in Water and Mass Transfer

Since ozone is generated in gas phase but applied in water phase, it is important to describe ozone solubility in water. Evaluation of ozone mass transfer is crucial because it will condition the ozone reactivity. On the other hand, ozone solubility in water is almost ten times higher than the oxygen solubility (Sonntag and Von Gunten 2012).

Two phenomena are important to determine the solubility characteristics of ozone in a typical laboratory ozonation system: the mass transfer of the gaseous ozone into the aqueous phase and the rate of decomposition (Roth and Sullivan 1981). Moreover, the absorption of ozone in water is influenced by the operating variables: temperature, pH and ionic strength (Sotelo et al. 1989).

The importance of the mass transfer has been deeply studied as the ozone mass transfer to the aqueous phase requires energy. It is crucial to study this field and find efficient and improved ways to transfer ozone to the aqueous phase (Roustan et al. 1980).

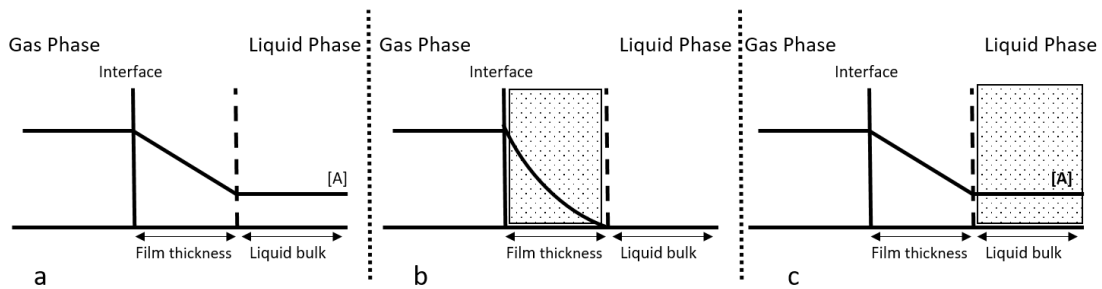


Figure 2.9. Concentration profiles of gas absorption extracted from (Sotelo et al. 1989). a. Physical absorption; b. Chemical absorption (fast kinetic regime); c. chemical absorption (slow kinetic regime).

In Figure 2.9 are represented three situations during the absorption of a gas into a liquid, considering that there is no resistance to mass transfer in gas phase. When the absorption is accompanied by an irreversible chemical reaction in the liquid, two situations can occur: the reaction can take place in the film (fast kinetic regime, Figure 2.9b) or the reaction can take place in the liquid bulk (slow kinetic regime, Figure 2.9c).

When we are in a gas absorption situation, the amount of transferred ozone per unit of time is defined by: the mass transfer coefficient, the interfacial area and the exchange potential (Roustan et al. 1980). Thus, the equation in liquid phase becomes:

$$N_{O_3} = k_L a (C_{O_3}^* - C_{O_3}) \quad [1]$$

Where N_{O_3} is the quantity of ozone transferred per unit time, $k_L a$ the volumetric mass transfer coefficient, $C_{O_3}^*$ the ozone concentration in the aqueous phase at the equilibrium with the gas phase, C_{O_3} the concentration of ozone in the liquid phase, per volume (V).

The concentration of ozone in water at the equilibrium is determined generally using the Henry's law equation (Kuosa et al. 2004, Sotelo et al. 1989):

$$P_{O_3} = H C_{O_3}^* \quad [2]$$

Where P_{O_3} is the partial pressure of ozone in the gas phase, H the Henry's law constant and $C^*_{O_3}$ the concentration of ozone in liquid phase in the equilibrium. The Henry's law constant is an increasing function of temperature (Danckwerts and Lannus 1970):

$$\frac{d \ln H}{d (1/T)} = \frac{-H_A}{R} \quad [3]$$

Being R the gas constant and H_A the heat of absorption (taken as positive) of the gas at the temperature considered. Regarding the salt effect, it can be expressed as (Danckwerts and Lannus 1970):

$$\text{Log} (H/H^\circ) = hI \quad [4]$$

Where H° is the value in water, I the ionic strength of the solution and h the sum of contributions referring to the species of positive and of negative ions present and to the species of gas.

Roth and Sullivan work (Roth and Sullivan 1981) about the apparent Henry's coefficient has led to the following equation:

$$H = 3.84 \times 10^7 [OH^-]^{0.035} \exp\left(\frac{2428}{T}\right) \quad [5]$$

The units of H are atm / (mol fraction) and the equation covers the temperature range of 3.5°C to 60°C and pH range of 0.65 to 10.2.

In the case of absorption with chemical reaction, it is important to determine whether the reaction increases the amount of ozone transferred. This determination can be done by the Enhancement factor E which is the ratio of the rate of transfer with chemical reaction to the rate of transfer without chemical reaction (Roustan et al. 1980) .

2.8.4 Ozone reactivity

Ozone can react under two forms: directly, via the molecular pathway and indirectly, via the hydroxyl radical which has a stronger oxidant character ($E^\circ = 2.80V$). Its duality has often generated a debate since some authors consider the ozone process as an AOP (when the hydroxyl radical is the main via) and other authors do not consider ozone as a treatment inside the AOPs group. As it is presented in Figure 2.10 , when ozone reacts directly by its molecular form, it has high selectivity and specific character.

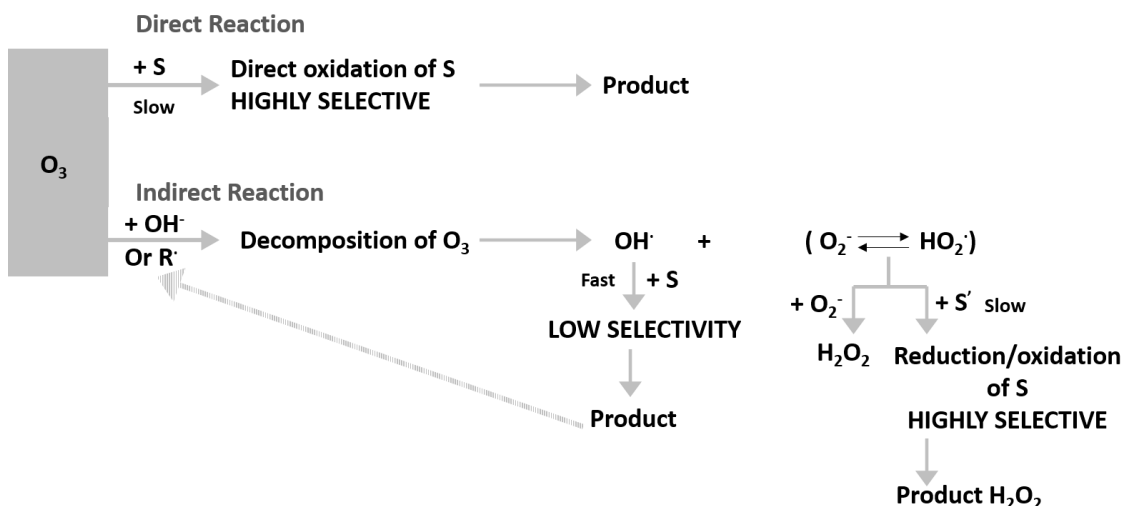


Figure 2.10. Ozone reactivity extracted from (Hoigne and Bader 1976)

However, ozone can decompose in water before reaction and it may give more reactive species which are responsible for the subsequent oxidation reactions (Hoigne and Bader 1976). The initiator of this chain reaction is the hydroxyl radical. In general the radical pathway is more reactive but less selective.

2.8.4.1 Direct reaction of Ozone with organic compounds.

Ozone molecule can act as a dipole, as an electrophilic agent and as a nucleophilic agent. All these behaviors will be explained in the following paragraphs.

a. Cyclo addition (Criegee mechanism).

As a result of its dipolar structure, the ozone molecule may lead to 1-3 dipolar cycloaddition on unsaturated bonds, with the formation of primary ozonide, also named as molozonide. This primary ozonide is unstable in a protonic solvent such as water, decomposing into a carbonyl compound (ketone or aldehyde) and a zwitterion that quickly leads to hydrogen peroxide and a carbonyl compound (Baig and Mouchet 2010, LANGLAIS (B.) 1991).

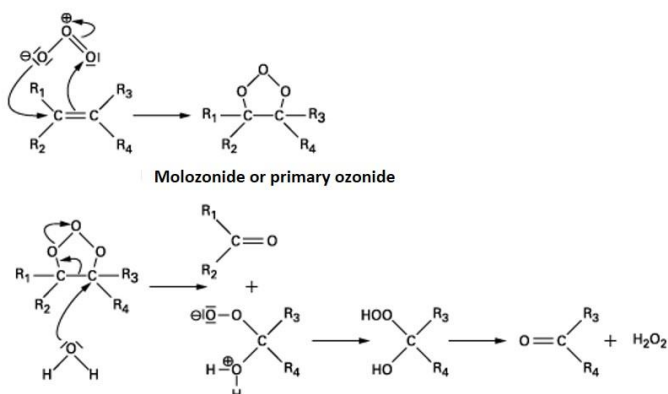


Figure 2.11. 1,3-dipolar cycloaddition mechanism extracted from (Baig and Mouchet 2010)

The 1-3 dipolar cycloaddition can occur in activated (C-H) bonds, in α position of an electro donor group as alcohol, ether or aldehyde. When it occurs in α of primary alcohol, the result is an aldehyde or carboxylate acid forming O_2 and H_2O_2 , respectively.

If the alcohol is a secondary alcohol, ketones are the major product. In the case of aldehydes, the obtained compound is a carboxylic acid (Baig and Mouchet 2010).

b. Electrophilic reaction

This reaction occurs in presence of molecular sites with a strong electronic density as aromatic compounds. Aromatics compounds substituted with electron donor groups (OH, NH₂, -OCH₃), amines and thiols, show high electronic densities on carbons located in the ortho and para positions and so are highly reactive with ozone at these positions. On the contrary, the aromatic compounds substituted with electron-withdrawing groups (-COOH, -NO₂) are weakly ozone reactive because the deactivating group orientates the electrophilic substitution into a meta position (Decoret et al. 1984). The attack of ozone leads to the formation of ortho- and para- hydroxylated by-products that are further reactive to ozone. So these compounds lead to the formation of quinoid and, due the opening of the aromatic cycle, to the formation of aliphatic products with carbonyl and carboxyl functions (Baig and Mouchet 2010, LANGLAIS (B.) 1991).

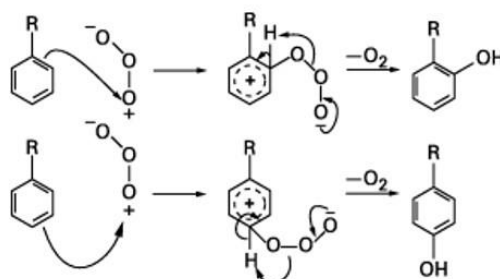


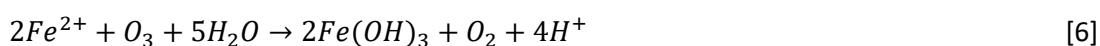
Figure 2.12. Electrophilic substitution in aromatic compound from (Baig and Mouchet 2010)

c. Nucleophilic reaction

It is found locally on molecular sites showing an electronic deficit and, more frequently, on carbons carrying electron-withdrawing groups. According to the resonance structures of ozone molecule, ozone presents a negative charge on one of oxygen atoms. This negative charge confers to ozone a nucleophilic character, at least theoretically. However, there is little information of this mechanism in water solvent (Beltran 2003).

2.8.4.2 Direct reaction of Ozone with inorganic compounds.

Ozone is capable to oxidase different inorganic compounds as iron and manganese converting them into iron hydroxide and oxide of manganese. However, the ozone reaction with iron is faster than with manganese. Ozone is able to oxidase sulfurs to sulfates and it strongly oxidase nitrites to nitrates. Moreover, theoretically ozone is capable to oxidase halogens even though different rates have been observed. The most reactive is iodide followed by bromate, and the less reactive is the chloride. Find below the equations related with these processes (Baig and Mouchet 2010).





2.8.4.3 Indirect reaction of Ozone.

Ozone rapidly decompose in a chain process divided in different steps: Initiation step (11, 11'), propagation steps (12-16) and break in chain reactions (17-18).

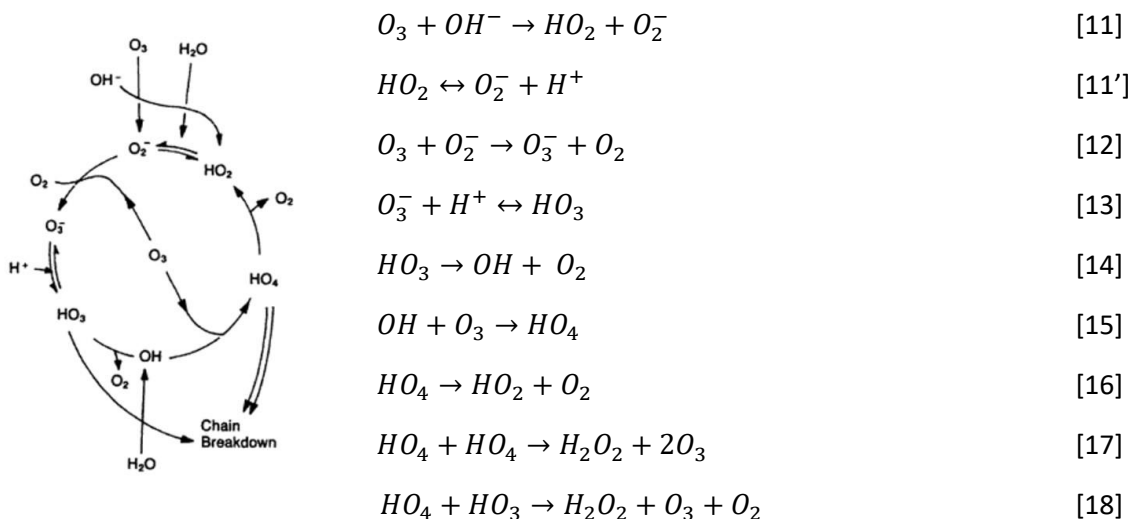


Figure 2.13. Reaction diagram for ozone decomposition from (LANGLAIS (B.) 1991).

Thus, ozone may decompose to form secondary oxidants, which then themselves immediately react with solutes. These different pathways of reactions lead to different oxidation products, and they are controlled by different kinetics (Staehelin and Hoigne 1985). Different factors as high pH or the addition of H_2O_2 promote the ozone decomposition (Von Gunten 2003a). The OH^\cdot radical is highly reactive and unselective, reacting with a wide range of organic compounds with kinetic constants between 10^6 and 10^{10} (Andreozzi et al. 1999). Regarding the decomposition chain, the initiation step consist in the reaction OH^- and ozone which leads to the formation of one superoxide anion (O_2^-) and one hydroperoxyl radical (HO_2^\cdot). In the propagation step, O_3^- decomposes into OH^\cdot radicals upon protonation. The termination step is characterized by the reaction of organic and inorganic substrates and OH^\cdot radicals. These scavengers generally terminate the chain reaction (Staehelin and Hoigne 1985). Natural waters already contain constituents that can initiate, promote and inhibit the chain reaction. However, NOM can affect ozone stability in two ways: can react directly with ozone or indirectly affect its stability through scavenging of OH^\cdot radicals. Moreover, it is more difficult to estimate the fraction of promotion and inhibition of NOM (Von Gunten 2003a).

2.8.5 Formation of byproducts as a result of Ozonation

In the past, the formation of ozone byproducts such as aldehydes, bromates and N-nitrosodimethylamines (NDMA) was not strongly considered. Nonetheless, nowadays, the use of advanced treated wastewater as a drinking water source is gaining importance, so this issue has become critical (Von Gunten and Hoigne 1994). In the early 1990s, bromate (BrO_3^-) was classified as potentially carcinogenic by the IARC (International Agency for research of cancer) (Pinkernell and Von Gunten 2001).

Bromate formation can occur during ozonation of bromide-containing waters by means of a complex mechanism involving molecular ozone and hydroxyl radical (Hollender et al. 2009,

Pinkernell and Von Gunten 2001). The proposed mechanism is presented in Figure 2.14. Hollender et al. found that the low levels of bromides in the secondary effluents lead to low concentrations of bromates after ozonation ($7.5 \mu\text{g BrO}_3^-/\text{L}$), specifically below the drinking water standard of $10 \mu\text{g/L}$ (limit in the United States and European Union) even for a high ozone doses (Hollender et al. 2009). As the proposed ecotoxicologically limit is 3 mg/L (Hutchinson et al. 1997) to protect aquatic organisms from long-term adverse effects, the levels mentioned above are not problematic. Bromate concentration, contrarily to NDMA, are not reduced during the sand filtration. Thus, it is recommended to use low ozone doses (Margot et al. 2013).

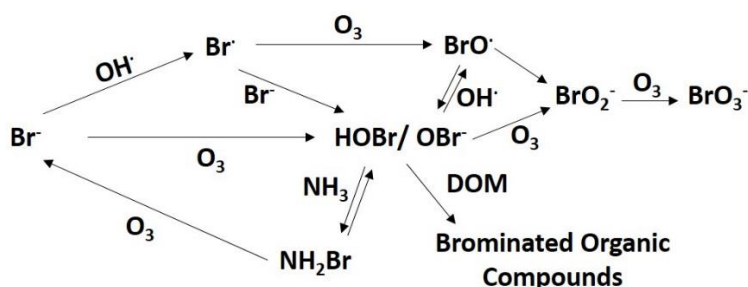


Figure 2.14. Reaction scheme for bromate formation during ozonation of bromide containing waters.

NDMAs are also a common byproduct of ozonation. Due to their demonstrated carcinogenicity, California has established a public health goal of 3 ng/L , a notification limit of 10 ng/L and a response limit of 300 ng/L (Gerrity and Snyder 2011). Low levels of NDMA have been detected in different works in accordance to 20 WWTPs in Switzerland (Hollender et al. 2009). Nevertheless, it has been observed that ozone-specific NDMA precursors vary considerably between wastewaters (Von Gunten and Hoigne 1994). Moreover, the formation of NDMA did not correlate with the ozone dose (Hollender et al. 2009). Thus, the variability of NDMA concentration in the secondary clarifier was more significant than the ozone dose (Gerrity and Snyder 2011). A possible solution can be a post treatment filtration with a biological sand filter which is able to remove 50% of NDMA. This process becomes an useful technology for elimination of biodegradable compounds formed during ozonation such as NDMA (Hollender et al. 2009).

Other by-products apart from NDMA and bromates may be formed by biological and chemical oxidation when the organic matter from wastewater is degraded: halo-acids, halo-ketones and non-halogenated carboxylic acids. The formation of the mentioned hazardous compounds may lead to different negative effects in the aquatic biota including cytotoxicity, genotoxicity and reproductive injuries (Erbe et al. 2011, Wigh et al. 2015). Even though ozonation has been shown as a useful tool for disinfection and degradation of micropollutants (Huber et al. 2005, Tyrrell et al. 1995), the concentration of the parent and oxidized compounds (byproducts) should be tested. Therefore, ecotoxicological assessments are needed in order to evaluate correctly a possibly effluent residual toxicity. In these cases, different species should be chosen representing different trophic levels. Wigh et al. studied the mortality, development abnormalities and genotoxicity driven by conventional biological and ozonation processes determining a residual toxicity in both processes (Wigh et al. 2015). Furthermore, Stalter et al. performed the fish early life stage toxicity (FELST) test which concluded that ozonation, in some situations, may generate more toxic metabolites than the parent compounds (Stalter et al. 2010b). The same study recommended a subsequent polishing treatment after ozonation application since these compounds are more easily biodegradable (Hollender et al. 2009). These undesirable toxic oxidation by-products which increased the toxicity compared to non-ozonated

wastewater were also described in (Petala et al. 2006, Petala et al. 2008, Stalter et al. 2010a). Moreover, lately, Ternes et al. proposed the consideration of both, the removal of micropollutants and the removal of the transformation products, in the chemical assessment of their work (Ternes et al. 2017) to better evaluate the chemical impact.

2.8.6 Ozone applications in water

Different applications of ozone have been described along the last years. They can be splatted into 5 categories: a. Water for consumption; b. urban wastewaters; c. Swimming pool waters; d. Industrial wastewaters.

a. Water for consumption

The stability of Algal cells make difficult to remove algae from the traditional drinking water treatment. Algal organic matter in drinking water decrease its quality by releasing algal toxins, causing taste and odor problems and forming chlorinated disinfection byproducts. Preozonation might be a possible solution to enhance the algae elimination (Miao and Tao 2009, Montiel and Welté 1998, Xie et al. 2013).

On the other hand, ozone is a powerful disinfection agent and it has been applied for this purpose for almost one century (Von Gunten 2003b) in the drinking water field. Ozone is effective even for microorganisms such as protozoa which are difficult to inactivate with other technologies. Moreover ozone provides successful inactivation with low doses and contact times (Von Gunten 2003b).

Finally, it is also convenient to eliminate endocrine disrupting compounds in drinking water with doses of 10 mgO₃/L and retention time of 15 minutes (Baig et al. 2008).

b. Urban wastewater

After the physicochemical or biological treatment, to remove detergents, color, to decrease COD and to disinfect (Domenjoud et al. 2011b, Paraskeva and Graham 2002, Xu et al. 2002).

Moreover, ozonation has been proved as suitable for the removal of micropollutants such as hormones, pharmaceuticals and personal care products (Domenjoud et al. 2011a). Consequently, it can minimize the discharge of micropollutants from WWTPS to the receiving waters and thus it prevents the ecological negative effects (Hollender et al. 2009, Lee and von Gunten 2010). Moreover, Ashauer et al. showed that post-ozonation of the secondary effluent combined with sand filtration favourable impacts on the composition of the macroinvertebrate community and can improve water quality on the receiving stream (Ashauer 2016).

c. Swimming pool waters

When ozone is applied to swimming pool water, it can oxidize dissolved pollutants as DOC, decreasing at the same time the formation of disinfection byproducts (DPBs) (Hansen et al. 2016). Moreover, ozone doses from 0.5-1 mg/L are applied to eliminate anthropogenic compounds, mainly substances containing amines (Baig and Mouchet 2010).

d. Industrial Wastewater

Ozone has different applications in the industrial field: from the treatment of the industrial wastewater to increase the water quality for the electronic and food industry (Baig and Mouchet 2010).

For instance, ozone increases the biodegradability of the textile wastewater enabling the reuse in textile factories (Perkowski et al. 1996, Rice 1996). Ozone is also used for recycling marine aquaria wastewaters, for cyanide-containing electroplating wastewaters from aircraft manufacturing plants, electronic chip manufacture wastewaters and in petroleum refinery wastewaters to eliminate the phenols (Rice 1996). Ozone applied to olive mill effluents is able to oxidize phenols and unsaturated lipids (Andreozi et al. 1998).

3. MATERIALS AND METHODS

In this chapter, all the information regarding the experimental devices used to perform the experiments as well as the methodology used for the analysis of the organic matter, micropollutants and water quality parameters is presented. Moreover, at the end of the chapter, the sampling points used in the experimentation are described. Moreover, all the operating conditions and initial wastewater characteristics are found, later on, in each chapter to facilitate the data following.

3.1 Experimental Set Ups

3.1.1 Ozone set up

Ozone Experiments have been carried out at lab scale in a 2.5L jacketed semi batch reactor with 2L working volume. Experiments were performed without pH adjustment. Temperature was kept constant at 20 °C by means of water recirculated from a thermostatic bath. Ozone was produced from pure oxygen (Linde, Germany) by a Sander Labor Ozonizer 301.7 (Sander, Germany). This generator assures a maximum ozone concentration of 100 g/m³ and an ozone production of 12 g/h. Ozone gas was injected at the bottom of the reactor with a glass porous plate and the mechanical mixing ensured the good contact between the liquid and gas phases. Mixing rates were different between effluents: 750 rpm were used for the conventional activated sludge (CAS) experiments and 1000 rpm for the effluent experiments.

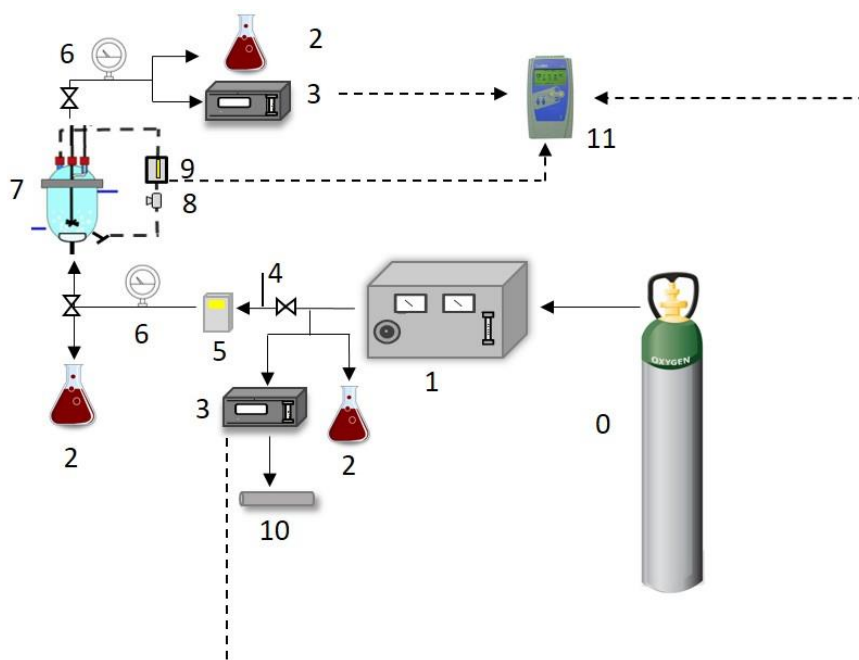


Figure 3.1. Ozone Set Up.

0. Cylinder of pure oxygen; 1. Ozone Generator; 2. KI solution; 3. Ozone analyzer gas phase; 4. Thermometer; 5. flowmeter and volume totalizer; 6. manometer; 7. Reactor; 8. Peristaltic pump; 9. Dissolved ozone probe; 10. Ozone Destruction; 11. Datalogger

To determine the transferred ozone dose (TOD), an ozone balance should be assessed. For this purpose, ozone concentrations were measured in the gas and water phase through 3 different analyzers. Thus, the input gas concentration was measured by BMT 963 BT (BMT Messtechnik GMBH, Germany) ozone analyzer and the output gas concentration was determined by BMT 964 BT (BMT Messtechnik GMBH, Germany) ozone analyzer, both in the gas phase. These analyzers are based in the maximum absorption of gaseous ozone at 253.7 nm, and therefore they have

ultraviolet (UV) unit which allows the detection in 253.7 nm and digital display (Rakness et al. 1996). In the liquid phase, ozone is measured thanks to the probe Q45H/64 (Analytical Technology, US) located in a recirculation loop. A peristaltic pump MasterFlex[®] model 77200 (Cole Parmer, USA) feeds the recirculation loop. The probe is based in a redox mechanism. Hence, the probe is equipped with an ozone selective membrane, a cathode and an anode and it measures the ozone reduction. The probe contains also a thermocouple which monitors the temperature along the reaction. The ozone concentrations given by the analyzers are already corrected to the normal conditions of temperature and pressure. To measure the instantaneous flow and the total volume at the end of reaction, a mass gas flow meter were used (GMF, Aalborg). Moreover, all the data along the experiments was saved in a datalogger DaqPRO[™] (Fourtec Fourier Technologies, USA). The ozone system is shown in both Figure 3.1 and Figure 3.2.



Figure 3.2. Picture of the lab ozone set up

Residual ozone is eliminated from the ozone system by catalytic destruction and chemical reduction. The chemical reduction consist into a solution of potassium iodide (20 g/L KI, Na₂HPO₄·2H₂O, 3.5 g/L KH₂PO₄). When the exciting ozone was bubbled to the potassium iodide solution, the unreacted ozone is reduced to oxygen. The reaction is described below:



The exciting ozone flow at the outlet of the analyzer was destroyed by means of catalytic destruction. A Catalyzing Cartridge CAT-Rs (BMT Messtechnik GMBH, Germany) fillet with 100 ml of Carulite 200g (Carus Corp, USA), an manganese dioxide/coper oxide catalyst, was used.

3.1.1.1 TOD determination

When applying ozone to wastewater samples, it is important to determine the transferred ozone dose (TOD). The global mass balance can by the equation:

$$[O_3, introduced] - [O_3, residual] = [O_3, accumulated] + [O_3, consumed] \quad [20]$$

The accumulation term refers to the dissolved ozone found in the aqueous phase and the ozone present in the dead volume of the system. Thus, the equation is:

$$[O_3, introduced] - [O_3, residual] = [O_3, dissolved] + [O_3, dead volume] + [O_3, consumed] \quad [21]$$

Defining TOD as the sum between the consumed ozone and the dissolved ozone in the aqueous phase, the equation become:

$$[O_3, introduced] - [O_3, residual] = [O_3, transferred] + [O_3, dead volume] \quad [22]$$

Thus, integrating equation [21], we obtain:

$$[O_3, transferred] = \int_0^t [O_3]_{g,i} \times Q_g \times dt - \int_0^t [O_3]_{g,0} \times Q_g \times dt - [O_3]_{g,0}(t) \times V_{dead} \quad [23]$$

Where:

Symbol	Definition	Units
t	Reaction time	min
Q_g	Volumetric Flow rate	L/ min NTP
V_{dead}	System Dead Volume	L NTP
$[O_3]_{g,i}$	Inlet gas ozone concentration	g/m ³ NTP
$[O_3]_{g,0}$	Outlet gas concentration	g/m ³ NTP
$[O_3]_{g,0}(t)$	Outlet gas concentration at the time t	g/m ³ NTP

3.1.2 Biological Set Up- Aerobic Experiments

Biological experiments were performed at lab scale in a 5 L batch reactor filled with a total working volume of 4.5 L.

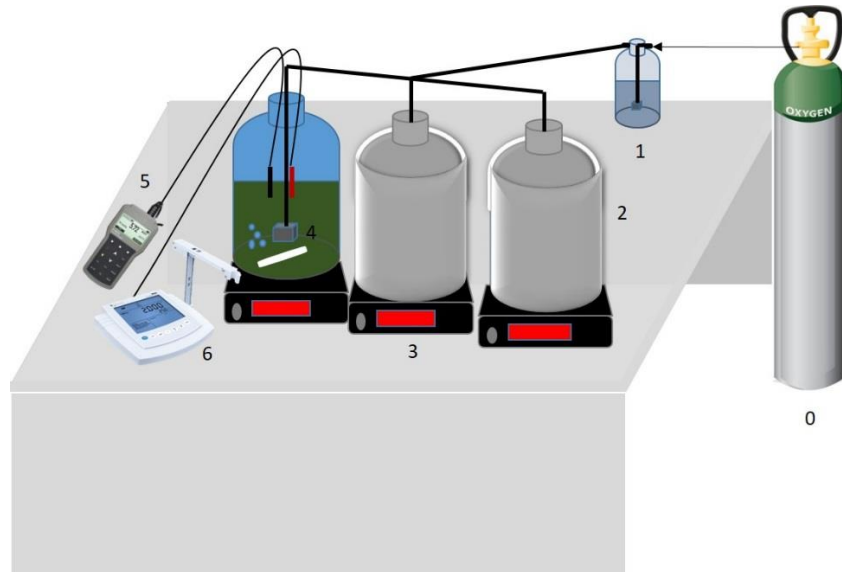


Figure 3.3. Biological Set Up.

0. Oxygen Cylinder; 1. Bottle with water; 2. Biological Reactor; 3. Magnetic Stirrer; 4. Ceramic diffuser; 5. Dissolved Oxygen Meter; 6. pHmeter

Three biological reactors worked in parallel at room temperature during one cycle of 4 hours: one with primary effluent without ozone pre-treatment, and the other two with ozone pre-treated primary effluent samples. The operation system consists in four steps: fill, react, settle and draw the reactor. The reactors were saturated with O₂ during each reaction by means of bubbling wet oxygen through ceramic diffusers. The bottles were filled in with 3.250 L of substrate (primary effluent ozonized and non- ozonized), the amount of sewage sludge (as inoculum) that met a COD_{substrate}- to- COD_{inoculum} ratio of 0.24. The final effective volume for all tests was 4L. Three magnetic stirrers were used to mix the each biological reactors (300 rpm).

The inoculum was collected in a Municipal WWTP. The pH was not adjusted at beginning of each reaction but it was monitored through the samples. The dissolved oxygen was monitored with the Portable Dissolved Oxygen Meter HI98193 (Hanna instruments, USA). The reactors were cover with aluminum soil to avoid the proliferation of algae inside the reactor as a consequence of solar light incidence (Micó 2013). The samples were quickly filtered for the water quality parameters. This system provides information about the organic matter and biodegradability, effluent toxicity and the evolution of the micropollutants.

3.1.3 Biological Set Up- Biomethane potential test

The Biomethane Potential Test (BMP) was performed in a 115mL serum glass bottles closed with PTFE- butyl Septum caps, which were fixed by an aluminum crimp cap. The bottles were filled in with 15 mL of inoculum, the amount of sewage sludge that met a $COD_{\text{substrate}} - \text{to} - COD_{\text{inoculum}}$ ratio of 0.5, and deionized water, used to adjust the same effective volume for all tests (80mL). The experiments were carried out following the directions of (Angelidaki et al. 2009). The blank assay, only filled with inoculum and deionized water, was used to determine the background effect of the inoculum and a control with ethanol was used to ensure the good performance of the test. The inoculum was collected in a Municipal WWTP. Before closing the bottles, all the digestion medium was flushed with nitrogen (1 min, 3L/min). The overpressure of the first hour was discarded. Temperature was kept constant at mesophilic conditions (37°C) by means of an incubator. The reactors were stirred in an orbital stirrer. The test was perform during 28 days.



Figure 3.4. BMP test equipment.

From left to right: (left) Schematic set up; (center) real picture inside of the incubator, (right) Vacuometer and serum bottle for BMP test.

The biogas production was measured by using a vacuometer (Ebro- VAM 320). The methane content of the biogas accumulated in the bottle headspace was measured for each sample by a GC analyzer. The methane production was obtained by multiplying the biogas production, once subtracted the vapor pressure and converted at standard temperature and pressure conditions (0°C and 1atm). All the test were carried out in triplicate.

3.2 Main analytical techniques and instruments

3.2.1 Determination of Dissolved Organic Carbon (DOC), Inorganic Carbon (IC) and Total Nitrogen (TN).

DOC determination was performed with a Shimadzu TOC 5055 analyzer (Shimadzu, Japan). The method used is based in the direct measure of the DOC in the sample. Firstly, the inorganic carbon is removed: sample acidification (Carbonates conversion to CO_2) is needed for the

subsequent CO₂ stripping with air. Then, a catalytic combustion at 680 °C takes place according to Standard Method 5310B procedures (APHA 2012) the CO₂ generated is cooled and dehumidified, and then detected by the Infrared Gas Analyzer (NDIR). The device was equipped with an ASI-V Autosampler (Shimadzu, Japan). Samples of 12 mL were filtered through 0.45 µm Polyethersulfone filter (PES) previous to being injected in the device. TN was also measured by means of the specific module TNM-1 (Shimadzu, Japan) coupled to the core device. IC was also measured by the TOC 5055 analyzer, firstly, acidifying the sample and isolating the CO₂, and detecting it by the NDIR.

3.2.2 Determination of Chemical Oxygen Demand (COD)

COD is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. It determines the amount of oxygen required to oxidize organic matter of a solution by means of strong oxidant agents. These analysis were carried out following the Standards Method 5220D Procedure Closed Reflux, Colorimetric method (APHA 2012). In our case, the oxidant was the dichromate ion (Cr₂O₇⁻²). When the sample is digested at high temperature (2h, 150°C), the dichromate ion oxidizes COD material in the sample. The analysis was carried out in hermetically sealed glass tubes. This results in the change of chromium from the hexavalent (VI) state to the trivalent (III). The chromic ion (Cr³⁺) strongly absorbs at 600 nm while the dichromate ion (Cr₂O₇⁻²) absorbs at 420nm.



Figure 3.5. High range COD samples

Two COD ranges were measured and therefore, two calibration curves were performed: 1. High range (0-1000 mgO₂/L) and 2. Low range (0-100 mgO₂/L). In the case of the low range, Standards Method 5220D was adapted to lower concentrations (4×10^{-3} mol/L K₂Cr₂O₇, 25g/L HgSO₄). When we used high range, 0-1000 mgO₂/L, we measured the absorption at 600nm and for instance, we measured the increase of the Cr³⁺ ion. On the other hand, when we worked in the low range, we measured the decrease of the Cr₂O₇⁻² ion at 420 nm. The absorptions were measured by means of the spectrophotometer Hach Odyssey DR/2500 (Hach, USA).

Duplicate measures were performed as is recommended in the Standard Method 5220D.

3.2.3 Determination of Biochemical Oxygen Demand (BOD)

BOD is used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test measures the molecular oxygen utilized during a specified incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. Before the analysis, a sample pH adjustment is needed between 6.5 and 7.5. Standards Method 5210D Procedure respirometric method (APHA 2012) was followed. It consist in the direct measurement of the oxygen consumed by microorganisms from an air or oxygen-enriched environment in a closed vessel under conditions of constant temperature and agitation. The incubation period was 5 days, for these reason we will refer it in the next chapters as BOD₅. OxiTop® equipment (WTW, Germany) was used during 5 days under constant stirring and controlled temperature (20± 1°C).

The OxiTop® system uses the cap of the bottle as a manometer. Thus, it relates the changes in the bottle pressure with the oxygen consumption.



Figure 3.6. Oxitop Device for BOD measurement

The incubation must take place in dark conditions. The microorganism seed, Lyophilized capsules 5466-00 (Cole-Parmer, USA) were aerated during two hours before the incubation. Nitrification during BOD determination was avoided by adding an inhibitor of nitrification (Allylthiourea). Moreover, the presence of toxic material in the sample may negatively influence the microbial activity, and therefore, lead to an underestimation of the oxygen uptake. If the toxicity is induced by containing oxidant material, it must be neutralized with sodium thiosulfate or sodium bisulfite, with a post aeration to eliminate the residual sodium thiosulfate or sodium bisulfite. Duplicate measures were performed.

3.2.4 Measurement Residual oxidants (Bromine)

The Total Residual oxidant (TRO) content (regarding Bromine) was measured by means of the Pocket Colorimeter™ (Hach, USA) and the Bromine Reagent (Hach, USA) in a range of 0.2 – 10.0 mg/L Br₂.

3.2.5 Measurement of aromaticity

Ultraviolet absorbance at 254nm (UV₂₅₄) parameter is directly linked with the content in unsaturated compounds and notably aromatic substances dissolved in the effluent. Aromatic and unsaturated compounds can be detected using UV₂₅₄ thanks to the significant absorption of the double bonds at 254nm wavelength. To measure UV₂₅₄, the sample must be previously filtered by 0.45 µm PES filters. Then, the sample is placed in a quartz cell which must be located in a spectrophotometer and reported in cm⁻¹. The spectrophotometer used in this work was Perkin Elmer UV/VIS Lambda 20 (Perkin Elmer, USA).

3.2.6 Ion- Exchange Chromatography (IEC)

The salt content can be quantified by IEC since it can detect inorganic anions and cations. This technique allows the separation of ions and polar molecules based on their charge and on their coulombic interaction with the stationary phase. Sample must be previously filtered by 0.45 µm PES filters. The liquid sample is injected in the device and passes through a column where the stationary phase retains the electrolytes according with their charge and affinity. The instrument used for these measures was an 861 Advance Compact IC (Metrohm, Switzerland).

3.2.7 Alkalinity

Alkalinity is the capacity of an aqueous (water or wastewater) solution to neutralize acids, and therefore, it measures the buffering capacity of an aqueous solution. In general, this measure relates the buffering capacity with the hydrogen Carbonate (HCO₃⁻) and bicarbonate (CO₃²⁻) content. Nevertheless, other species such as hydroxides, borates, silicates, phosphates, ammonium, sulphides and organic ligands can provide alkalinity to the samples. The alkalinity

determination was performed with an automatic titration device: CRISON pH Burette 24 (CRISON, Spain) coupled with the pH meter CRISON basic 20 (CRISON, Spain).

3.2.8 Acute toxicity - Microtox®

The acute toxicity was assessed by the Microtox® Toxicity Test (Modern Water, UK), using luminescent *Vibrio Fischeri* Bacteria. This test is based on the inhibition of *Vibrio Fischeri* microorganism (Modern Water, UK) (Cho et al. 2004, Farré and Barceló 2003). Analysis were conducted according to the standard Microtox® procedures recommended by the manufacturer (Modern Water, UK). Toxicity is expressed as effective concentration that reduces the bioluminescence to 50% (EC₅₀) value, the concentration of sample that causes a 50% reduction in light emission after 15 min of contact. The device used was the Microtox® Model 500 Analyzer (Modern Water, UK).

3.2.9 Determination of Solid content: Suspended Solids (SS), Volatile Suspended Solids (VSS), Volatile Solids (VS) and Total Solids (TS)

Regarding the solids content, Standard Methods 2540 procedures were followed. Different measures regarding the solid content were performed. In the case of TS and VS, Standard Methods 2540 B (APHA 2012) were followed. TS measurement consist in evaporate a well-mixed sample in the oven at the constant temperature of 105°C. The increase in the weight over that of the empty dish represented the TS. The dish material was porcelain to afterwards introduce it in the muffle furnace at 550°C and determinate the VS content. In the case of SS and VSS, Standard Methods 2540 D (APHA 2012) were followed. Principally, the sample was filtered through a weighted standard glass fiber filter (Merck- Millipore USA), with a 0.7 µm pore size and then, the filter was dried at 105°C. The VSS were measured introducing the filter used for SS determination in the muffle furnace at 550°C.

3.2.10 Analysis of micropollutants

Analysis of micropollutants were performed in collaboration with the Mass Spectroscopy Laboratory of the Instituto de Diagnóstico Ambiental y Estudios Del Agua (IDAEA) in the Consejo Superior de Investigaciones Científicas (CSIC). In the case of the analysis of pharmaceuticals, the procedure was based on the USEPA-Method 1694, consisting in a solid phase extraction (SPE) with HLB cartridge (Waters, USA). The extraction of the other analyzed compounds was carried out by liquid-liquid extraction. Pharmaceuticals and surfactants have been carried out by LC-HRMS (Orbitrap-Exactive, Thermo Scientific). Pesticides, PAHs, Alkylphenols and PBDEs were analysed by GC-MS/MS (EVOQ GC-TQ, Bruker). Identification and quantification were carried out by isotope dilution method. The assurance of results was performed by analyzing blanks of laboratory and spiked samples. The limit of quantification (LOQ) for each compound in the effluent matrix is presented in the tables below (Table 3.1, Table 3.2 and

Table 3.3).

Table 3.1 LOQs in effluent matrix for the different analyzed compounds: AOX, Pharmaceuticals and Surfactants.

Categories	Compound	LOQ	Units
AOX		0.03	mg Cl/L
Pharmaceuticals	Atenolol	0.01	µg/L
	Paracetamol	0.20	µg/L
	Ciprofloxacin	0.02	µg/L
	Sulfamethoxazole	0.01	µg/L
	Propranolol	0.01	µg/L
	Econazole	0.01	µg/L
	Carbamezapine	0.01	µg/L
	Ketoprofen	0.30	µg/L
	Diclofenac	0.01	µg/L
	Acetylsalicylic acid	0.20	µg/L
	Ibuprofen	0.05	µg/L
	Ethinylestradiol	0.50	µg/L
	Non Ionic Surfactants: alkylphenols and alkylphenol ethoxylates	nonylphenol polyethoxylated	0.50
polyethoxylated alcohol C10		0.50	µg/L
polyethoxylated alcohol C11		0.50	µg/L
polyethoxylated alcohol C12		0.50	µg/L
polyethoxylated alcohol C13		0.50	µg/L
polyethoxylated alcohol C14		0.50	µg/L
polyethoxylated alcohol C15		0.50	µg/L
polyethoxylated alcohol C16		0.50	µg/L
polyethoxylated alcohol C17		0.50	µg/L
polyethoxylated alcohol C18		0.50	µg/L
Σ4-nonylphenol		0.03	µg/L
Octylphenol		0.04	µg/L
Anionic surfactants	Linear alkylbenzene sulphonates	0.001	mg/L

Table 3.2 LOQs in effluent matrix for the different analyzed compounds: PBDEs, PAHs and DEHP.

Categories	Compound	LOQ	Units
Polybrominated diphenyl ethers (PBDEs)	BDE-28	0.01	ng/L
	BDE-47	0.02	ng/L
	BDE-99	0.01	ng/L
	BDE-100	0.01	ng/L
	BDE-153	0.01	ng/L
	BDE-154	0.01	ng/L
	BDE-183	0.01	ng/L
	BDE-197	0.01	ng/L
	BDE-209	0.03	ng/L
Polycyclic aromatic hydrocarbons (PAHs)	Napthalene	8.54	ng/L
	Acenaphthene	0.33	ng/L
	Fluorene	0.75	ng/L
	Acenaphthylene	0.09	ng/L
	Phenanthrene	1.64	ng/L
	Anthracene	0.12	ng/L
	Fluoranthene	0.36	ng/L
	Pyrene	0.47	ng/L
	Benz[a]anthracene	0.05	ng/L
	Chrysene	0.07	ng/L
	Benzo(b)fluoranthene	0.04	ng/L

	Benzo(k)fluoranthene	0.03	ng/L
	Benzo(a)pyrene	0.03	ng/L
	Indeno(1,2,3-cd)pyrene	0.05	ng/L
	Benzo[g,h,i]perylene	0.05	ng/L
	Dibenzo[a,h]anthracene	0.03	ng/L
Plasticizer	DEHP	0.045	µg/L

Table 3.3 LOQs in the effluent matrix for the different analyzed compounds: Pesticides

Categories	Compound	LOQ	Units
	Isoproturon	0.08	ng/L
	Dichlorvos	0.62	ng/L
	Diuron	1.54	ng/L
	DEA	0.19	ng/L
	Trifluralin	0.09	ng/L
	Dimethoate	2.66	ng/L
	Simazine	0.14	ng/L
	Atrazine	0.14	ng/L
	Tebuthylazine	0.04	ng/L
	Diazinon	0.17	ng/L
	Alachlor	0.14	ng/L
	Heptachlor	0.03	ng/L
	Terbutryn	1.33	ng/L
	Metolachlor	0.02	ng/L
	Chlorpyrifos	0.09	ng/L
	4,4-dichlorobenzophenone	0.04	ng/L
	Heptachlor epoxide B	0.03	ng/L
	Chlorphenvinfos	0.08	ng/L
	Cybutrine	0.42	ng/L
	α-Endosulfan	0.05	ng/L
	β-Endosulfan	0.19	ng/L
	Aclonifen	0.11	ng/L
Pesticides	Endosulfan sulphate	0.10	ng/L
	Quinoxifen	0.21	ng/L
	Dicofol p,p'	1.01	ng/L
	Cypermethrin	2.90	ng/L
	1,2,3 Trichlorobenzene	0.14	ng/L
	1,2,4 Trichlorobenzene	0.13	ng/L
	1,3,5 Trichlorobenzene	0.22	ng/L
	Hexachlorobutadiene	0.35	ng/L
	Pentachlorobenzene	0.05	ng/L
	Hexachlorobenzene	0.05	ng/L
	α-HCH	0.05	ng/L
	β-HCH	0.02	ng/L
	γ-HCH	0.05	ng/L
	δ-HCH	0.02	ng/L
	o,p'-DDE	0.07	ng/L
	p,p'-DDE	0.05	ng/L
	o,p'-DDD	0.03	ng/L
	p,p'-DDD + o,p'-DDT	0.05	ng/L
	p,p'-DDT	0.05	ng/L
	Aldrin	0.01	ng/L
	Isodrin	0.01	ng/L
	Dieldrin	0.05	ng/L
	Endrin	0.04	ng/L

Moreover, the LOQ in the case of CAS matrix are presented in Table 3.4, Table 3.5 and Table 3.6.

Table 3.4 LOQs in CAS matrix for the different analyzed compounds: AOX, Pharmaceuticals and Surfactants.

Categories	Compound	LOQ	Units
AOX		0.03	mg Cl/kg
Pharmaceuticals	Atenolol	0.01	µg/kg
	Paracetamol	0.20	µg/kg
	Ciprofloxacin	0.20	µg/kg
	Sulfamethoxazole	0.01	µg/kg
	Propranolol	0.01	µg/kg
	Econazole	0.10	µg/kg
	Carbamezapine	0.01	µg/kg
	Ketoprofen	0.01	µg/kg
	Diclofenac	0.01	µg/kg
	Acetylsalicylic acid	0.20	µg/kg
	Ibuprofen	0.02	µg/kg
	Ethinylestradiol	20.00	µg/kg
	Non Ionic Surfactants: alkylphenols and alkylphenol ethoxylates	nonylphenol polyethoxylated	0.001
polyethoxylated alcohol C10		0.001	µg/kg
polyethoxylated alcohol C11		0.001	µg/kg
polyethoxylated alcohol C12		0.001	µg/kg
polyethoxylated alcohol C13		0.001	µg/kg
polyethoxylated alcohol C14		0.001	µg/kg
polyethoxylated alcohol C15		0.001	µg/kg
polyethoxylated alcohol C16		0.001	µg/kg
polyethoxylated alcohol C17		0.001	µg/kg
polyethoxylated alcohol C18		0.001	µg/kg
Σ4-nonylphenol		0.001	µg/kg
Octylphenol		0.001	µg/kg
Anionic surfactants	Linear alkylbenzene sulphonates	0.001	mg/kg

Table 3.5. LOQs in CAS matrix for the different analyzed compounds: PBDEs and PAHs.

Categories	Compound	LOQ	Units
Polybrominated diphenyl ethers (PBDEs)	BDE-28	0.05	µg/kg
	BDE-47	0.05	µg/kg
	BDE-99	0.05	µg/kg
	BDE-100	0.05	µg/kg
	BDE-153	0.05	µg/kg
	BDE-154	0.05	µg/kg
	BDE-183	0.05	µg/kg
	BDE-197	0.05	µg/kg
	BDE-209	0.50	µg/kg
	Polycyclic aromatic hydrocarbons (PAHs)	Napthalene	3.00
Acenaphthene		0.30	µg/kg
Fluorene		0.25	µg/kg
Acenaphthylene		0.20	µg/kg
Phenanthrene		0.15	µg/kg
Anthracene		0.25	µg/kg
Fluoranthene		3.51	µg/kg
Pyrene		4.93	µg/kg
Benz[a]anthracene		0.20	µg/kg
Chrysene		0.50	µg/kg
Benzo(b)fluoranthene		0.60	µg/kg

	Benzo(k)fluoranthene	0.60	µg/kg
	Benzo(a)pyrene	2.16	µg/kg
	Indeno(1,2,3-cd)pyrene	1.44	µg/kg
	Benzo[g,h,i]perylene	1.20	µg/kg
	Dibenzo[a,h]anthracene	0.20	µg/kg

Table 3.6 LOQs in CAS matrix for Pesticides.

Categories	Compound	LOQ	Units
Pesticides	Isoproturon	0.10	µg/kg
	Dichlorvos	0.28	µg/kg
	Diuron	0.38	µg/kg
	DEA	0.09	µg/kg
	Trifluralin	0.09	µg/kg
	Dimethoate	0.67	µg/kg
	Simazine	0.20	µg/kg
	Atrazine	0.13	µg/kg
	Tebuthylazine	0.01	µg/kg
	Diazinon	0.04	µg/kg
	Alachlor	0.17	µg/kg
	Heptachlor	0.01	µg/kg
	Terbutryn	0.15	µg/kg
	Metolachlor	0.15	µg/kg
	Chlorpyrifos	0.24	µg/kg
	4,4-dichlorobenzophenone	0.05	µg/kg
	Heptachlor epoxide B	0.01	µg/kg
	Chlorphenvinfos	0.07	µg/kg
	Cybutrine	0.05	µg/kg
	α-Endosulfan	0.03	µg/kg
β-Endosulfan	0.10	µg/kg	
Aclonifen	0.21	µg/kg	
Endosulfan sulphate	0.03	µg/kg	
Quinoxifen	0.04	µg/kg	
Dicofol p,p'	0.25	µg/kg	
Cypermethrin	0.22	µg/kg	

3.2.11 Liquid Chromatography with size exclusion (LC-OCD-OND)

Further analysis of the organic matter were performed in collaboration with DOC-Labor- Dr. Huber. The analysis method employed is based on size exclusion chromatography followed by organic carbon, organic nitrogen and UV₂₅₄ detectors (SEC-OCD-OND-UVD). Briefly, this technique separate in different fractions the organic matter depending on the molecule size. Indeed, the substances with lower molecular size can access easily to the internal pore spaces than those with higher molecular weight. The different fractions are presented in the table below (Batsch et al. 2005, Huber et al. 2011a).

Table 3.7 Fractions of NOM

Fraction	Molecular weight (Da)	Description
Biopolymers	>20,000	Polysaccharides, proteins, aminosugars; hydrophilic fraction with high molecular weight.
Humic substances (HS)	~ 1000	Consists of humins (non-soluble), humic acids (insoluble in acids and basis) and fulvic acids (soluble in acids and basis)
Building Blocks	300-500	Mono-oligosaccharides, alcohols, aldehydes, ketones and aminosugars. Intermediates of the degradation process of fulvic acids.
Low molecular- weight acids	<350	Low molecular mass organic acids, often resulting from degradation of organics.
Low molecular-weight neutrals	<350	Low molecular weight weakly charged hydrophilic or slightly hydrophobic (amphiphilic), such as alcohols, aldehydes, ketones and amino acids.

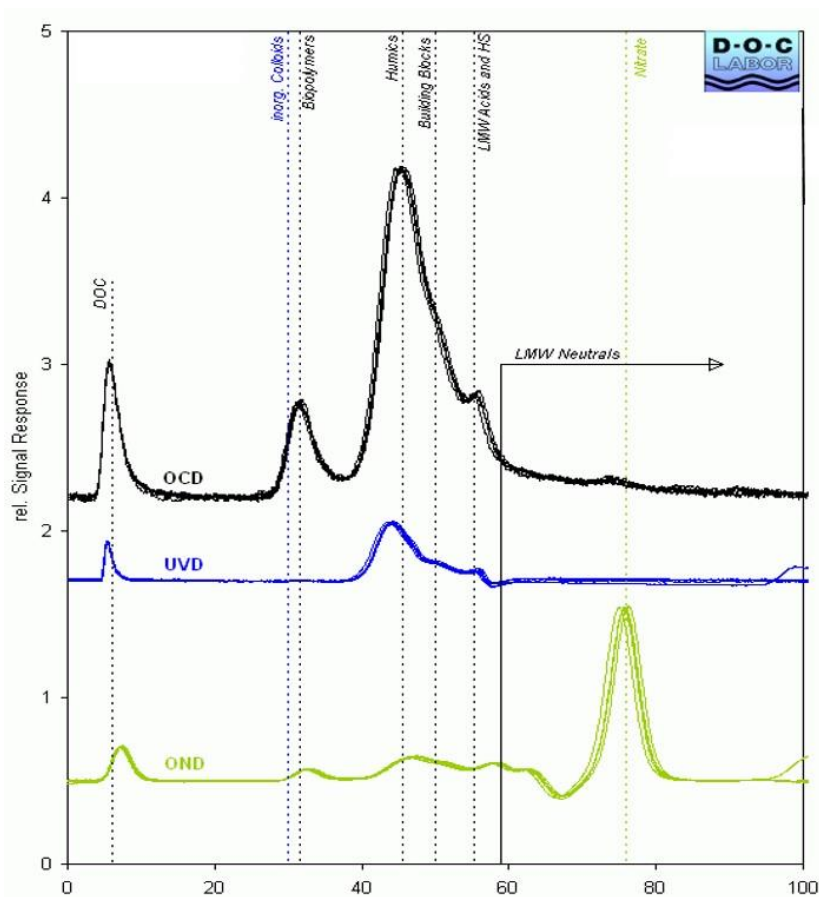


Figure 3.7. Typical LC-OCD Chromatogram of NOM in raw water extracted from (Huber 2016)

Moreover, information about the fraction hydrophobicity is given. Further details of the analysis can be found elsewhere (Huber et al. 2011a).

3.3 Origin and type of wastewater samples

The sampling campaigns were collected in two different WWTPs. The first one, WWTP- A, is located in province of Tarragona in the coastal area of Catalonia (Spain). It corresponds to a conventional treatment plant, using CAS as biological treatment and containing tertiary treatment. The tertiary treatment is managed by a golf resort since was planned to provide reclaimed water for irrigation. Moreover, the tertiary treatment consist in sand filtration followed by microfiltration and reverse osmosis. The second one, WWTP- B, was located close to Lyon (France). It is formed by two lines: one with a CAS biological treatment and the other one with a Moving Bed Biofilm Reactor (MBBR) as a biological treatment. However, all the samples collected for the presented studies correspond to the CAS Biological treatment line.

As it is presented in Figure 3.8, three sampling points have been used for the presented work. However, sample of the outlet of the secondary settling tank was collected to support the study on the ozone impact in the primary effluent. So, the most significant sampling campaigns correspond to the outlet of the Primary Settling Tank and the CAS Recirculation Loop.

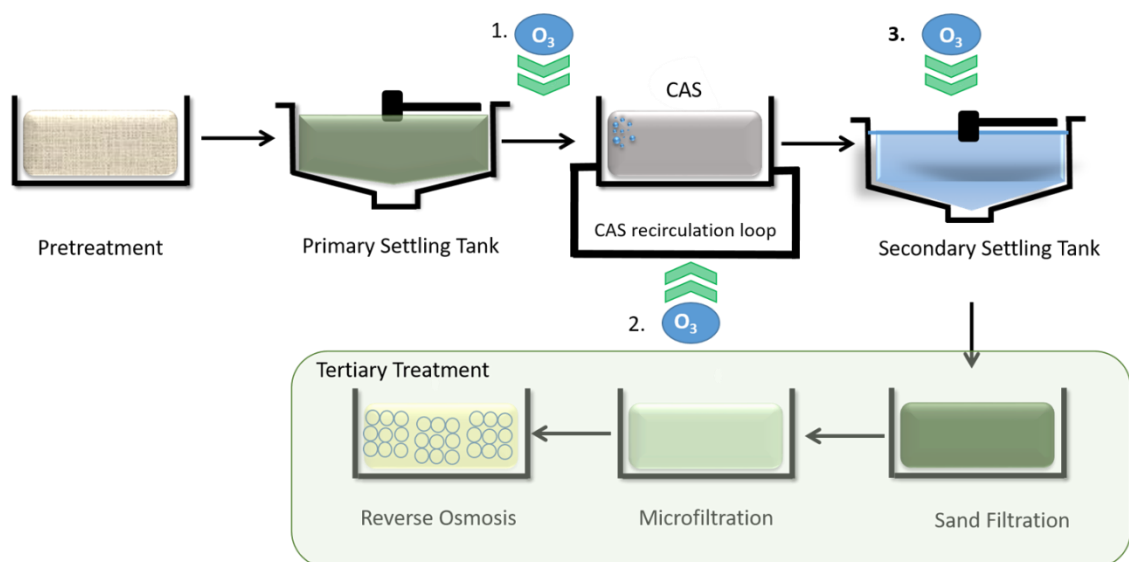


Figure 3.8. Sampling points at the WWTPs

Even though, the water quality parameters are specified in the next chapters, an overview of the parameters are described below. The COD range for CAS effluent was 3-6.9 g/L and for primary effluent was 0.27-0.89 g/L. The DOC range was found between 9 and 260 mg C/L for the CAS effluent and between 69 and 110 mg C/L for the primary effluent. The aromaticity described by UV₂₅₄ was 27-96 m⁻¹ for primary effluent and 10-253 m⁻¹ for CAS effluent.

4. APPLICATION OF OZONE ON PRIMARY EFFLUENT: MODELING, CHANGES ON ORGANIC MATTER DISTRIBUTION AND MICROPOLLUTANT REMOVAL.

4.1 Introduction

Wastewater reclamation has been recognized as one of the most powerful alternatives to improve accessibility to fresh water, reducing at the same time the demand of freshwater. The reclamation concept involves the restoration of water bodies and the decrease in the quantity of chemicals discharged into water courses (González et al. 2013, Reungoat et al. 2012, Shon et al. 2006).

Even though, the biological treatment is the “core” of the conventional treatment, classical parameters to control the degree of pollution (as COD or BOD) can be decreased combining the biological treatment with chemical oxidation processes as ozonation (Beltrán et al. 1997).

On the other hand, the complex water matrix of wastewater effluents generates competitive reactions with ozone that contributes to the ozone demand. The ozone demand is characterized by two parameters: the immediate ozone demand (IOD) and the k_d , the decay kinetic constant (Domenjoud et al. 2013, Janex et al. 2000). The immediate ozone demand (IOD) is defined as the minimum amount of ozone to be transferred to the effluent to detect dissolved ozone in water. The study of the parameters related with ozone demand and mass transfer for wastewater effluents appeared as important since Wert et al. demonstrated that EfOM reactivity impacts O_3 decomposition (Wert et al. 2009), Xu et al. determined that molecular dissolved ozone is an important factor for disinfection (Xu et al. 2002) and IOD was observed to have an important role in both micropollutant removal (Domenjoud et al. 2013, Wert et al. 2009) and in process design. Moreover, other studies have shown the importance on the ozone demand of the inorganic substances (carbonate, ammonia, etc.) present in the effluent matrix (Domenjoud et al. 2011b).

Beltrán et al. observed that ozonation of urban primary effluent reduces levels of COD and enhance biodegradability using a relative high optimum dose of $100 \text{ mgO}_3/\text{L}$ (Beltrán et al. 1997). Moreover, working on the tertiary effluent, Wert et al. showed different molecular weight distribution of EfOM before and after IOD fulfillment (Wert et al. 2009). In addition, other studies have shown that the application of ozone to secondary effluents (from CAS and MBR) modified the distribution of dEfOM (Audenaert et al. 2013, Domenjoud et al. 2011a, González et al. 2013). Thus, the selectivity of molecular ozone generated a large reduction of the biopolymers and aromatic humic substances leading to an accumulation of the low molecular acids and neutrals in the early stages of the ozonation process, when $0.72 \text{ mM } O_3$ were consumed (González et al. 2013).

Regarding micropollutant removal, several studies have considered ozonation as one of the easiest and quick technology for micropollutant removal and prevention of a subsequent release of these compounds in the environment (Joss et al. 2008). Moreover, a wide range of micropollutants were degraded in a biologically treated wastewater by applying $10 \text{ mgO}_3/\text{L}$ (Ternes et al. 2003). Moreover, Margot et al. achieved a removal higher of 70% with an average ozone dose of $5.65 \text{ mgO}_3/\text{L}$ of the remaining compounds in a biologically treated effluent (Margot et al. 2013).

The following chapter presents the work related with the application of ozone to primary effluent. Different aspects were investigated and discussed: firstly, the ozone mass transfer and ozone demand; secondly, the organic matter removal (main quality parameters) and transformation (distribution of organic matter – LC-OCD); and finally, the micropollutant removal. Moreover, it has been studied the relationship between the three mentioned sections. Some of the results of this chapter have been published in the *Chemical Engineering Journal* (Section 4.6 Appendix).

4.2 Materials and methods

4.2.1 Wastewater Characterization

For this study, samples of wastewater effluents were collected from a coastal WWTP (WWTP-A) located in the province of Tarragona (Spain) and from a WWTP located close to Lyon (France), (WWTP-B). Sampling campaigns were performed at the outlet of the primary treatment and at the outlet of the tertiary treatment consisting in sand and micro-filtration downstream conventional activated sludge system in the same urban tertiary treatment plant. Primary effluent samples were frozen at -20°C and tertiary effluents were refrigerated at 4°C prior to be use. Samples from the primary effluents collected during different campaigns from the coastal WWTP (Spain) are referenced as P1, P2, P5, P6 and P7; while P3 and P4 are samples from primary effluents collected at the WWTP located near Lyon. T1 and T2 are the ones obtained from the tertiary effluents. Finally, drinking water and tap water, referenced as D1 and V1 respectively, were used for comparison with the other effluents. Table 4.1 presents the initial parameters of the samples.

Table 4.1 Initial water quality parameters

Samples	UV ₂₅₄ m ⁻¹	SUVA L/(mg·m)	pH	tCOD mg/L	DOC mg/L	IC mg/L	TN mg/L	SS mg/L	Turbidity NTU	BOD ₅ /COD mg/L	Alkalinity mgCaCO ₃ /L
P1	26.9	0.39	7.6	265	70	86	n.q	67	131	0.47	352
P2	36.8	0.62	7.6	367	59	60	39	97	120	0.29	n.q
P3	96.3	0.88	7.4	778	110	107	20	250	170	0.37	468
P4	74.2	0.78	8.5	885	95	54	44	512	285	0.26	n.q
P5	38.9	0.69	7.9	255	55	82	38	46	124	0.42	378
P6	36.2	0.70	7.6	253	52	80	37	110	70	0.30	369
P7	40.7	0.53	7.3	398	62	75	24	161	144	0.35	415
T1	11.4	0.57	6.6	19	7	16	n.q	n.q	0.3	0.00	n.q
T2	26.2	0.49	8.5	50	13	52	n.q	n.q	0.1	0.12	n.q
D1	0.6	1.11	7.3	5	0.54	28	n.q	n.q	0.3	n.q	120
V1	2.2	1.11	7.3	26	2	31	n.q	n.q	0.3	n.q	168

The DOC range was 52-110 mgC/L for the primary effluent samples, 7-13 mgC/L for the tertiary effluent, 0.54 mgC/L for drinking water and 2 mgC/L for tap water. Samples had a COD value ranging from 253-885 mg O₂/L for primary effluents and 19-50 mg O₂/L for the tertiary ones. SUVA values range is 0.39-0.88 L/(mg·m), high SUVA values were found in tertiary effluents samples which could be correlated with high hydrophobic content, such as humics acids (Leenheer and Croué 2003). As it is expected, for D1 and V1 all the parameters are much lower compared with the wastewater effluents. Regarding turbidity and BOD₅, strong decrease is

observed in tertiary effluent compared to the primary as expected for biological treatment downstream effluents.

Moreover, the ion content was checked by ion chromatography (Section 3.2.6) for some sampling campaigns. Thus, neither bromide (Br^-) nor nitrite (NO_2^-) ions were detected in the case of three primary effluents P4, P5, P6; from both origins (France and Spain). Chloride (Cl^-) concentration for these sampling campaigns was found in the range 463.5-516.3 mg/L. However, concentrations of 2.6 and 8.1 mg Br^-/L were found in drinking water (D1) and tap water (V1), respectively. Moreover, in the case of D1 and V1, nitrite concentrations were 1.6 and 59.6 mg/L, respectively. Sulfate (SO_4^{2-}) concentrations of the primary effluent vary between 57.0-240.0 mg/L depending on the effluent P4, P5, P6. Cations analysis were performed for P1, P2, P3, P4, P6, D1 and V1. The highest cation concentration for all sampling campaigns corresponded to sodium ion (Na^+): Primary effluent range was 286.3-394.5 mg/L, drinking water value was 12.6 mg/L and tap water 60.3 mg/L. Lithium ion was not detected in all the samples. Ammonium cation concentration was found between 20-45 mg/L for primary effluents. In drinking water, it was detected but not quantified since it was lower than 0.05 mg/L. Tap water contained 1.6 mg/L of NH_4^+ .

4.2.2 Operating Conditions

In order to determine the Initial Ozone Demand (IOD), ozone mass transfer coefficient ($k_{\text{L}a}$) and the ozone decay rate (k_d), a set of experiments was performed. For these experiments, the gas flow rate and ozone inlet concentration were kept constant at 60 L/h NTP (0 °C and 1 atm) and 40 mg/L NTP during all the treatment, respectively. The second type of experiments consisted to apply a range of specific transferred ozone doses to determine the impact in the micropollutants and in the wastewater parameters. For this set of experiments, the gas flow rate and ozone inlet concentration were kept constant at 40 L/h NTP (0 °C and 1 atm) and 15 mg/L NTP during all the treatment, respectively.

Table 4.2 Operating conditions

Samples	Reaction Time min	Ozone Concentration in inlet gas, $[\text{O}_3]_{\text{g,in}}$	Gas flow rate
		mg/L NTP	L/h NTP
P1	180	39.70 ± 0.03	58.7 ± 0.1
P1	1.33;2.5; 4.5; 9.83	14.67 ± 0.20	38.4 ± 2.2
P2	180	40.04 ± 0.06	58.2 ± 0.1
P3	180	39.57 ± 0.06	58.2 ± 0.1
P3	1	9.80 ± 0.10	40.3 ± 1.7
P3	1.25; 2; 3	14.63 ± 0.15	40.3 ± 1.7
P3	4.5	40.14 ± 0.06	57.0 ± 0.1
P4	180	40.34 ± 0.06	58.0 ± 0.1
P4	1; 3.16;3.67;5.33	14.59 ± 0.12	36.3 ± 2.5
P5	120	39.97 ± 0.17	61.8 ± 0.4
P6	0.5;0.83;25	15.03 ± 0.05	38.6 ± 0.9
P7	0.83;3	15.00 ± 0.10	32.3 ± 2.3
T1	90	39.70 ± 0.60	62.3 ± 0.1
T2	180	40.20 ± 0.60	61.5 ± 0.1
D1	120	39.85 ± 0.04	57.3 ± 0.2
V1	120	39.4 ± 0.58	56.3 ± 0.1

4.2.3 Definitions

Ozone balance was assessed by continuous measurements of ozone concentrations in the gas phase, at the inlet and outlet of the reactor, and in the liquid phase. From the ozone mass balance, the TOD, which refers to the accumulated ozone transferred to the water sample per unit of sample volume, was calculated. It corresponds to the sum of ozone consumed during the treatment with the dissolved ozone. This parameter is defined by the following equation and calculated using the trapezoidal method of numerical integration:

$$TOD = \int_0^t \frac{Q_{Gas}}{V_{Liq}} \times ([O_3]_{gas\ in} - [O_3]_{gas\ out}) \times dt_r \quad [24]$$

Where Q_{Gas} , V_{Liq} and t_r are the gas flow rate, the effluent volume and the reaction time, respectively. $[O_3]_{gas,in}$ and $[O_3]_{gas,out}$ are the ozone gas phase concentrations at the inlet and outlet of the reactor, respectively.

The Immediate Ozone Demand (IOD) represents the minimum amount of ozone to be transferred through determining dissolved ozone in water. The evolution of dissolved ozone can be mathematically represented by the following equations:

$$\frac{d[O_3]}{dt} = k_{La} \times ([O_3]^* - [O_3]) - k_d \times [O_3] \text{ when } TOD > IOD \quad [25]$$

and

$$\frac{d[O_3]}{dt} = 0 \text{ and } [O_3] = 0 \text{ when } TOD < IOD \quad [26]$$

Where $[O_3]$ represents the concentration of dissolved ozone, K_{La} the volumetric mass transfer coefficient, k_d the first order decay constant of dissolved ozone, $[O_3]^*$ the ozone concentration in the aqueous phase at equilibrium with the gas phase. The value $[O_3]^*$ may be easily estimated from the ozone concentration in gas phase through the Henry's law (Sotelo et al. 1989).

$$P_{O_3} = Hx_{O_3^*} \quad [27]$$

Where P_{O_3} is the partial pressure of ozone in the gas phase and $x_{O_3^*}$ the molar fraction of ozone in the aqueous phase at equilibrium and H the Henry's constant. As ozone may easily undergo self-decomposition, the ozone equilibrium is better described by a pseudo Henry's constant with value depending mainly on the water pH and temperature. It can be evaluated by using the correlation found by Roth and Sullivan (Roth and Sullivan 1981):

$$H = 3.810^7 [HO^-]^{0.035} \exp(-2428/T) \quad 276.5\ K < T < 333\ K ; 0.65 < pH < 10.2 \quad [28]$$

Therefore, IOD and k_d can be both determined from the plot of the dissolved ozone concentration versus the transferred ozone dose (TOD): when the TOD exceeds IOD, dissolved ozone appears in the effluent.

Additionally, when $\frac{d[O_3]}{dt} = 0$ it can be demonstrated that:

$$[O_3]^* / [O_3]_{max} = (k_{La} + k_d) / k_{La} \quad [29]$$

These will lead to know good estimated values for k_{La} and k_d .

According to equation [25] the plot of $\ln \left(\frac{[O_3]_{max} - [O_3]}{[O_3]_{max}} \right)$ versus time will approach to a straight line with slope equal to $k_{La} + k_d$, being $[O_3]_{max}$ the maximum value of the ozone concentration in the water phase:

$$\ln \frac{[O_3]_{max} - [O_3]}{[O_3]_{max}} = - (k_{La} + k_d)t \quad [30]$$

For a better reliability, instead of using the ozone concentration in the aqueous phase and at equilibrium $[O_3]^*$, k_d value may be estimated through the ozone mass balance in the gas phase when the ozone concentration in the aqueous phase reaches a maximum. That is:

$$\frac{d[O_3]}{dt} = 0 \text{ and } [O_3]=[O_3]_{\max}$$

$$Q_{\text{Gas}}([O_3]_{\text{gas in}} - [O_3]_{\text{gas out}}) = k_{La}([O_3]^* - [O_3]_{\max})V_{\text{Liq}} = k_d[O_3]_{\max}V_{\text{Liq}} \quad [31]$$

4.3 Results and Discussion

4.3.1 Ozone mass transfer

In wastewater effluents, many compounds, either organic or inorganic, dissolved or suspended, may react with ozone with kinetic constants which span over a large range of values. Two parameters represent the ozone demand: IOD, the immediate ozone demand; and k_d , the decay kinetic constant due to overall ozone consumption by moderate or slow reactions considered as pseudo first order reactions. The compounds with fast kinetics contribute to the Immediate Ozone Demand.

Resolution of equation [25] allows the calculation of first order decay constant of dissolved ozone (k_d) as well as the mass transfer coefficient k_{La} along the ozone treatment. The ozone reactivity is influenced by the form and kinetics of ozone decomposition. Direct ozone reaction towards chemicals and microorganisms occurs when the ozone decay is slow. In these reactions, the ozone attack is highly selective and slow. On the other hand, in a scenario with an elevated organic content, the oxidations mostly occur through the hydroxyl radical pathway. This via is extremely reactive and non-selective (Gehr et al. 2003).

Both k_d and k_{La} have been calculated and presented in Table 4.3 for four primary samples, two tertiary effluents, one drinking sample and one tap water sample. In the case of primary effluent samples, the decay kinetic constant k_d is higher than all the others sampling campaigns. This fact points out the significant impact of the organic matter (COD and TOC) on the ozone consumption (Janex et al. 2000). The k_{La} variation highlights the influence of the water quality on the physical absorption of ozone probably through impact on the bubble size.

Table 4.3 k_d , k_{La} and IOD values different types of effluents.

Samples	k_{La} (min^{-1})	k_d (min^{-1})	IOD mg/L
P1	0.83	0.80	64
P2	0.76	0.19	83
P3	0.50	0.66	348
P4	0.79	0.30	249
T1	1.89	0.08	5
T2	0.67	0.10	10
D1	1.97	0.08	3
V1	3.94	0.09	3

Experimental plots of the ozone concentrations in gas and liquid phases obtained for the six wastewater effluents are shown in Figure 4.1. The important differences observed between effluents may be imputed to the nature and the load of pollution in the effluents. Indeed, primary effluents contain higher concentration of OM than the tertiary effluents. Drinking water

(D1) and Tap water (V1) have low organic matter content as it is showed by the parameters in Table 4.1. This fact, it is correlated with the different values of the decay constant.

Initial Ozone Demand (IOD) is an important parameter for disinfection (Xu et al. 2002), removal of micropollutants (Wert et al. 2009) and process design. The values of IOD are presented for all the water and wastewater samples in Table 4.3. Figure 4.2A shows the evolution of the dissolved ozone concentration present in the effluent during ozonation of all the primary effluent samples. These graphs (Figure 4.2) indicate an estimation of the ozone needed to satisfy the initial ozone demand of the effluents.

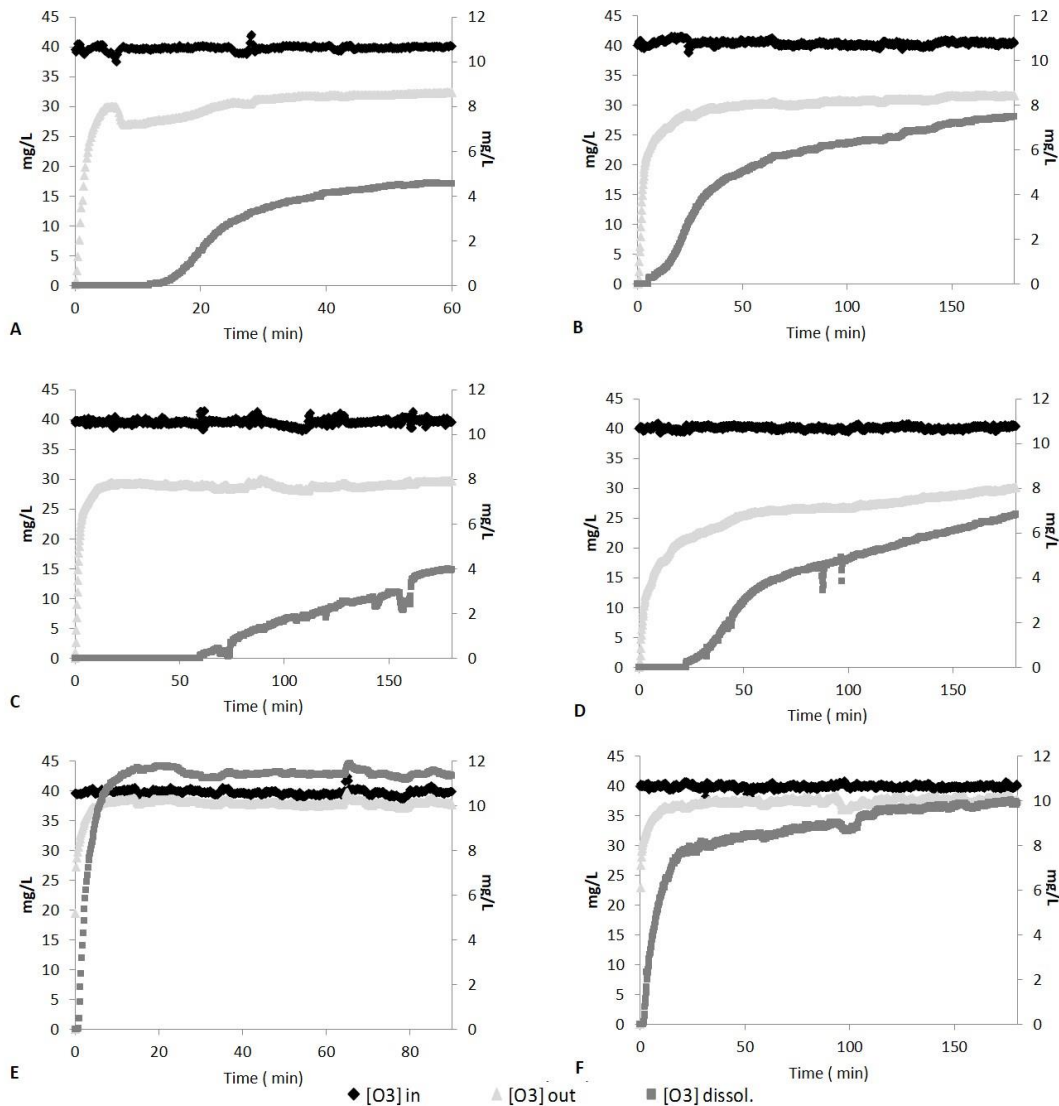


Figure 4.1 Ozone inlet, outlet and dissolved concentrations and initial Ozone Demand (IOD) determination for P1 (A), P2 (B), P3 (C), P4 (D), T1 (E) and T2 (F).

Figure 4.2 B) represents the evolution of the transferred ozone dose and the transfer ozone yield as a function of the applied ozone dose during the ozone treatment of P1, P2, P3 and P4 effluents. From the ozone transfer yield curve, two distinct regimes can be observed. During the first 100 mg/L of ozone transferred a high yield is observed and characterized by a strong depletion from 100 % to approximately 40 % for both P1 and P3, to 50% for P2 and 60% for P4. From 100 mg/L of ozone transferred up to the end of the reaction time, the transfer yield slowly decreases to finally reach a value of 15%, 25%, 30% and 35% for P1, P2, P3 and P4 respectively.

The lowest value of a TOD reached at the end of the reaction is 524mg/L in the case of P1 and the highest 1225 mg/L in the case of P4.

The obtained IOD values (Figure 4.2 A) are correlated with the transition observed in Figure 4.2 B) where the ozone transfer decrease from the initial 100% to a range of 40-60% ozone transfer yield depending on the primary sample.

This observation is in complete agreement with the double film theory equation used to describe the mass transfer of a poorly soluble compound from a gas to a liquid phase in presence of chemical reactions (Gottschalk et al. 2009):

$$\Phi = k_L a (C^* - C_L) E \quad [32]$$

Where Φ is Global adsorption flow per unit of liquid volume; C^* represents the ozone dissolved concentration at the interface; C_L defines the ozone dissolved concentration in the liquid phase; k_L stands for mass transfer coefficient in the liquid phase; a is the gas-liquid interfacial area per unit of liquid volume and E represents the enhancement factor.

Indeed, in absence of dissolved ozone, the driving force of ozone adsorption $C^* - C_L$ is maximum and then, once the IOD is satisfied, the increase of the ozone dissolved concentration reduces the adsorption flow.

During the stage of IOD completion, all the ozone transferred to the liquid phase is consumed at the interface or in the thin film around the gas bubbles. The reactions kinetic regime is then assumed to be instantaneous or fast and strongly favours the ozone transfer. Once IOD is completed, ozone kinetics are considered to be moderate or slow and so they are assumed to not influence the mass transfer. In this case, the enhancement factor E is equal to 1.

The same evolutions for each parameter are observed for tertiary effluents. The TOD, ozone mass transfer yield and dissolved ozone concentration curves are presented in Figure 4.3. It is possible to observe an initial high ozone transfer yield taking place during the first moment of the reaction and matching with the completion of the IOD. Afterwards, a stabilization stage was noticed, corresponding to a low transfer yield and a dissolved ozone concentration increase in the effluent. IOD is satisfied for a TOD equal to 5 and 10 mg/L. Similar results were found in other studies of ozonation of tertiary effluents (Domejoud 2013).

Figure 4.4 illustrates the TOD, ozone mass transfer yield and dissolved ozone concentrations for drinking water and tap water. It is observed similar behavior compared to the different wastewater effluents. Two regimes are observed from the ozone transfer yield curve: a high initial ozone transfer and a depletion after the IOD completion stage. The decrease achieve a transfer yield lower than 10% at the end of reaction. As it has been shown before, the depletion correlates with the detection of dissolved ozone in water. IOD is satisfied for a TOD equal to 3 mg/L in both cases.

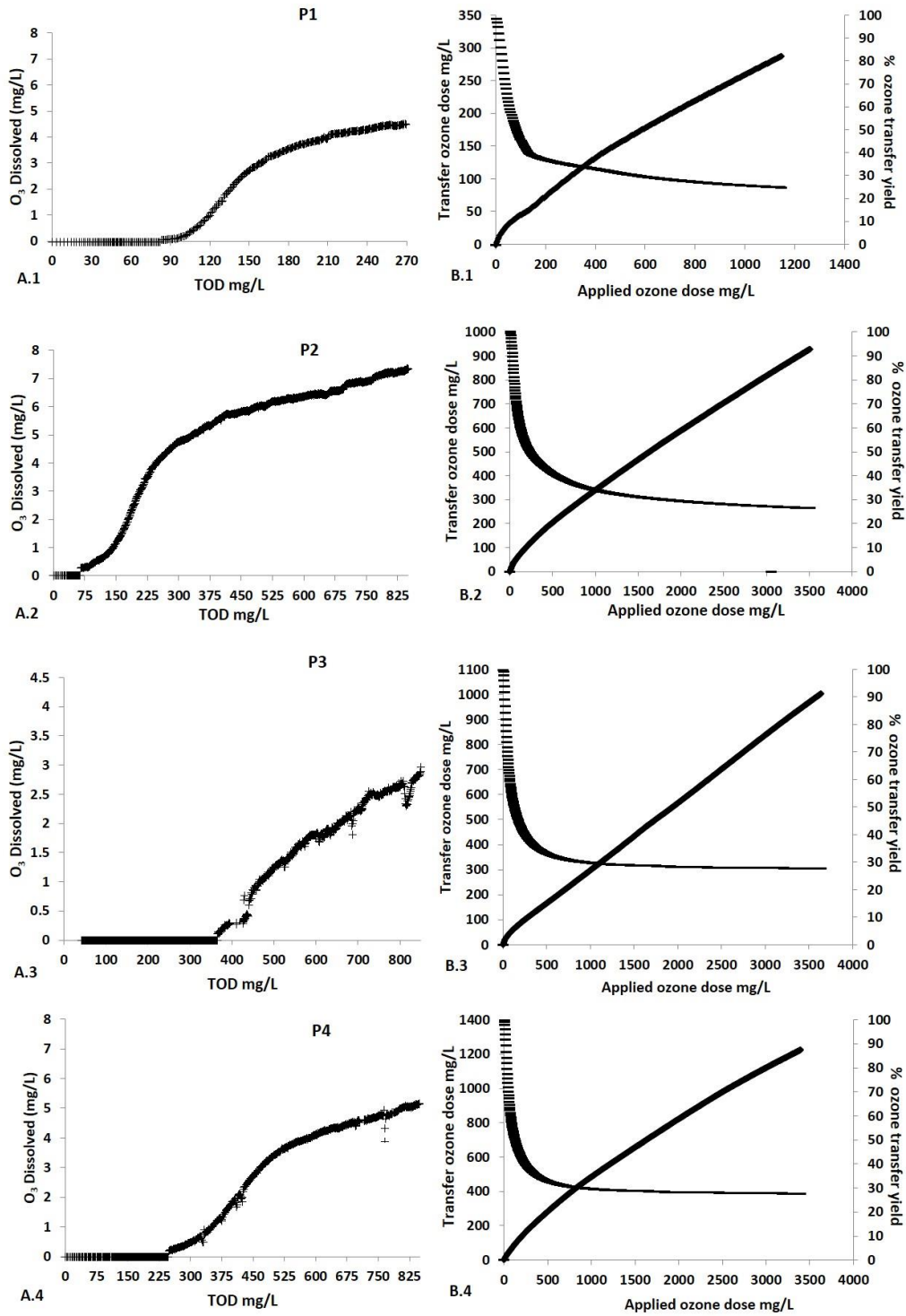


Figure 4.2 A) Initial Ozone Demand (IOD) determination for primary effluents. B) TOD and ozone transfer yield evolutions during primary effluents ozonation.

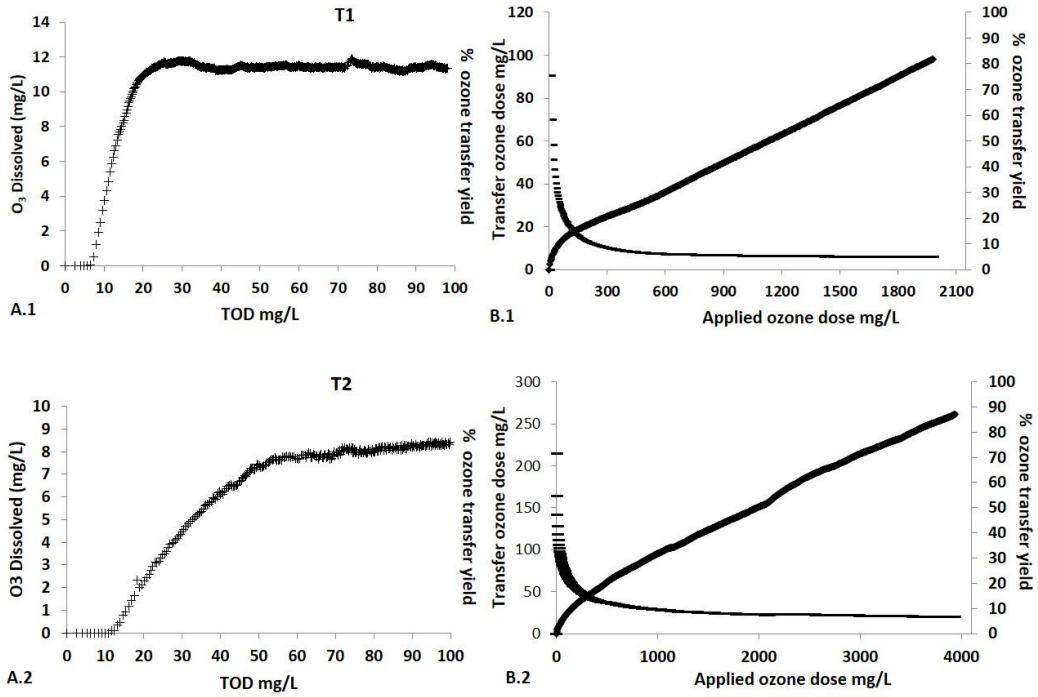


Figure 4.3 A) Initial Ozone Demand (IOD) determination for T1 and T2 effluents. B) TOD and ozone transfer yield evolutions during T1 and T2 ozonation.

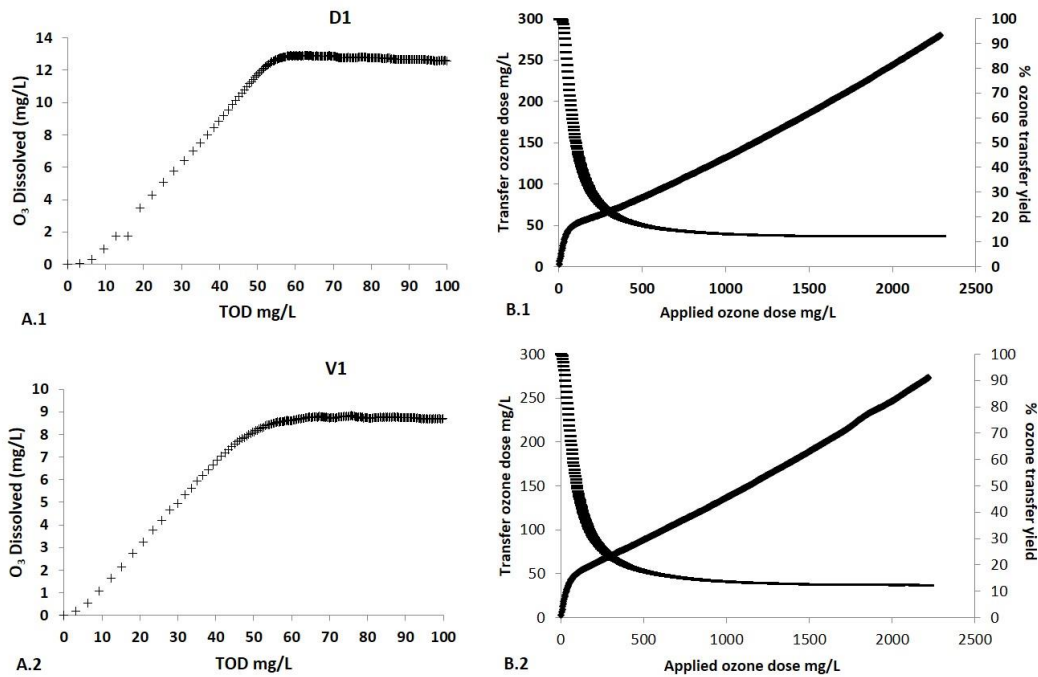


Figure 4.4 A) Initial Ozone Demand (IOD) determination for drinking and tap water B) TOD and ozone transfer yield evolutions during primary effluents ozonation.

4.3.2 Organic matter removal: ozone needs, kinetics and organic matter transformation

4.3.2.1 Ozone demand

In this section, the evolution of wastewater parameters in relation with the TOD and IOD will be analyzed. As the organic content of the drinking water and tap water was significantly low, only the primary and tertiary effluent samples were analyzed.

The evolution of COD versus TOD for P2 and T1 is presented in Figure 4.5. After an initial strong COD decrease, COD removal slowly decreases when the IOD is achieved. As it can be noticed, significant COD removal could be reached before ozone demand was achieved, when residual ozone was not measured in the water phase. Same behaviours are observed for primary and tertiary effluents.

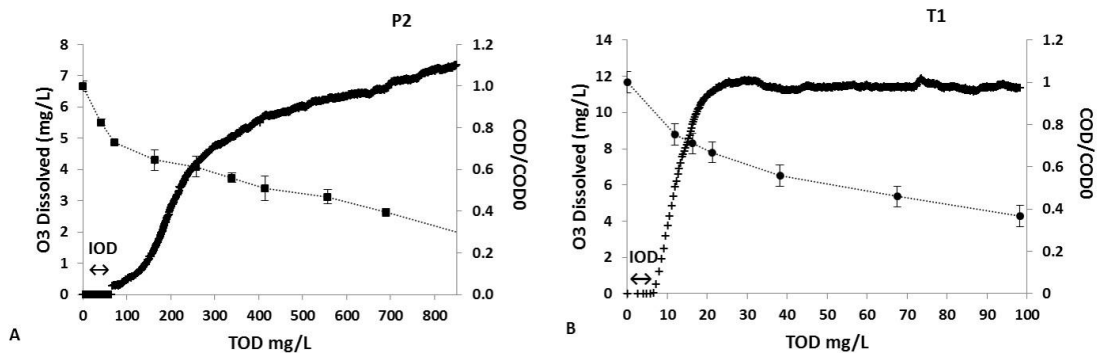


Figure 4.5 A) Initial Ozone Demand (IOD) determination versus COD/COD₀ evolution for primary effluent, P2; B) Initial Ozone Demand (IOD) determination versus COD/COD₀ evolution for tertiary effluent, T1.

In the case of UV₂₅₄, fast decrease it is also observed before the IOD is reached (Figure 4.6). This matches with the fact that most compounds that absorb in the wavelength of 254 nm, are organic compounds with double bonds and aromatic systems which are involved in fast reactions with ozone (Hoigné and Bader 1983b).

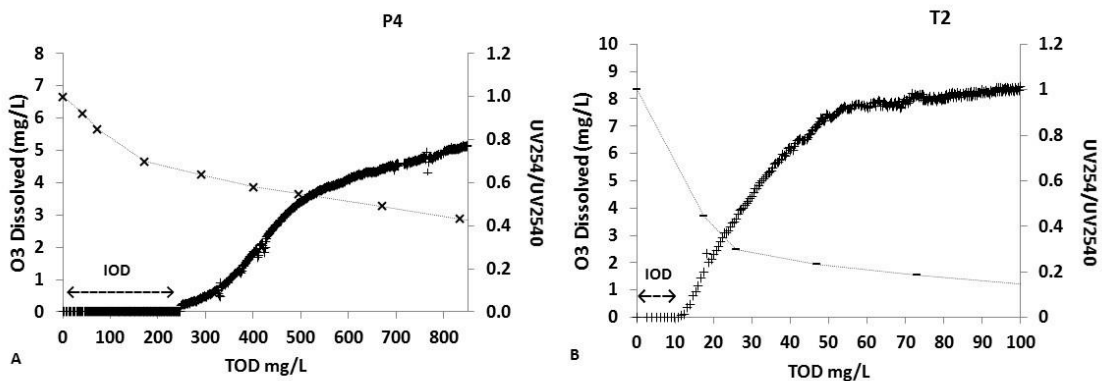


Figure 4.6. A) Initial Ozone Demand (IOD) determination versus UV₂₅₄/UV_{254,0} evolution for primary effluent, P4 B) Initial Ozone Demand (IOD) determination versus UV₂₅₄/UV_{254,0} evolution for tertiary effluent, T2

It has been observed a positive trend between the amount of organic matter, represented as COD and UV₂₅₄, and the IOD fulfillment. Thus, 3 zones have been observed and presented in Figure 4.7. In zone 1: Drinking water, tap water and tertiary effluent samples are found. The organic content of these samples is low (COD and UV₂₅₄) and the IOD is lower or equal to 10 mg/L. Regarding zone 2, we found two sampling campaigns of primary effluent (P3 and P4) from

the costal WWTP, the samples contained intermediate organic matter content and the IODs were higher than for zone 1 samples but lower than primary effluents with higher organic content (zone 3). Finally in zone 3, we found the primary effluents with highest UV₂₅₄ and COD values and consequently highest IODs.

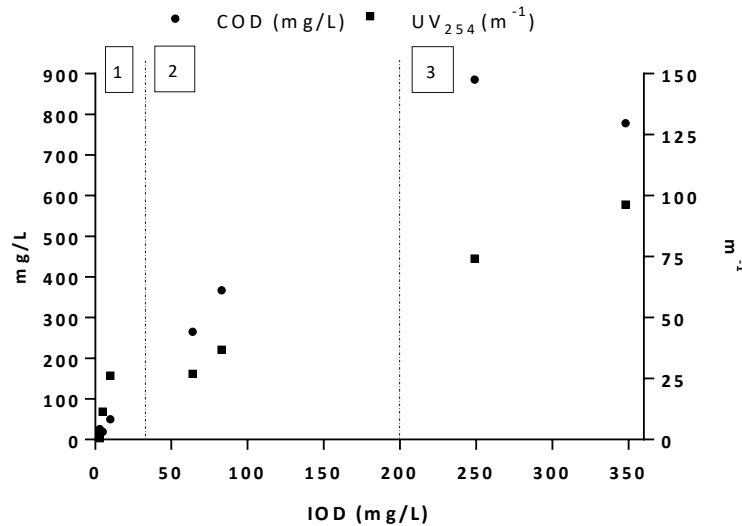


Figure 4.7. COD (left axis) and UV 254 (right axis) vs IOD for P1, P2, P3, P4, T1, T2, D1 and V1.

For primary effluents, the kinetic transition between fast and slow regime takes place when the TOD is smaller than IOD. The fast reaction is instantaneous and takes place almost within the film. In this situation, it is important to minimize the liquid hold up and increase the interfacial area, because mass transfer controls the process.

Regarding the tertiary effluents, the kinetic transition occurs at TOD higher than IOD completions. In this case, the ozone reaction is slow and takes place essentially within the bulk of the liquid phase. In this scenario, there is not any advantage in developing the interfacial area. However, the liquid hold up should be increased as much as possible pointing out the convenience of the bubble column reactors.

4.3.2.2 Kinetics

Figure 4.8a and b present the COD evolution as a function of the transferred ozone dose (TOD) and versus contact time for the primary effluents, respectively. Two stages can be clearly identified. The first one takes place during the first 30-70 mg/L of ozone transferred depending on the wastewater sample, a lower ozone transferred dose compared to IOD values of 64 mg/L, 83mg/L , 348 mg/L and 249 mg/L for P1, P2, P3 and P4 respectively. During the first stage, a strong elimination of the COD (30% approximately of COD removal for both P1 and P2, and close to 20% of COD removal for P3 and P4 samples, respectively) is achieved. From this TOD, a second stage with lower kinetics occurs.

The two oxidation stages observed are even more pronounced when COD kinetics curves are evaluated. Applying a pseudo first order kinetic model, pseudo-first order kinetic constants were determined for both regimes (Figure 4.8b). The transition took place after 5 min of contact time and the first kinetic constant was calculated for contact times between 0 and 5 min. Instead, the second stage was calculated from minute 15 and until the end of the reaction. For P1 and P2 effluents, the first kinetic regime can be characterized by a rate constant of 0.031 min⁻¹ and 0.028 min⁻¹, respectively. In the case of P3 and P4, the constants rates for the first kinetic regime

decrease until 0.020 min^{-1} and 0.018 min^{-1} , respectively. In the second regime we found a rate constant of 0.0017 min^{-1} , 0.002 min^{-1} , 0.0016 min^{-1} , and 0.0014 min^{-1} for P1, P2, P3 and P4 respectively. These values suggest that the first stage constant varies according to the wastewater origin when the second stage constants remain rather close. It is important to note that the first kinetic regime occurs under ozone mass transfer limitation within the IOD stage.

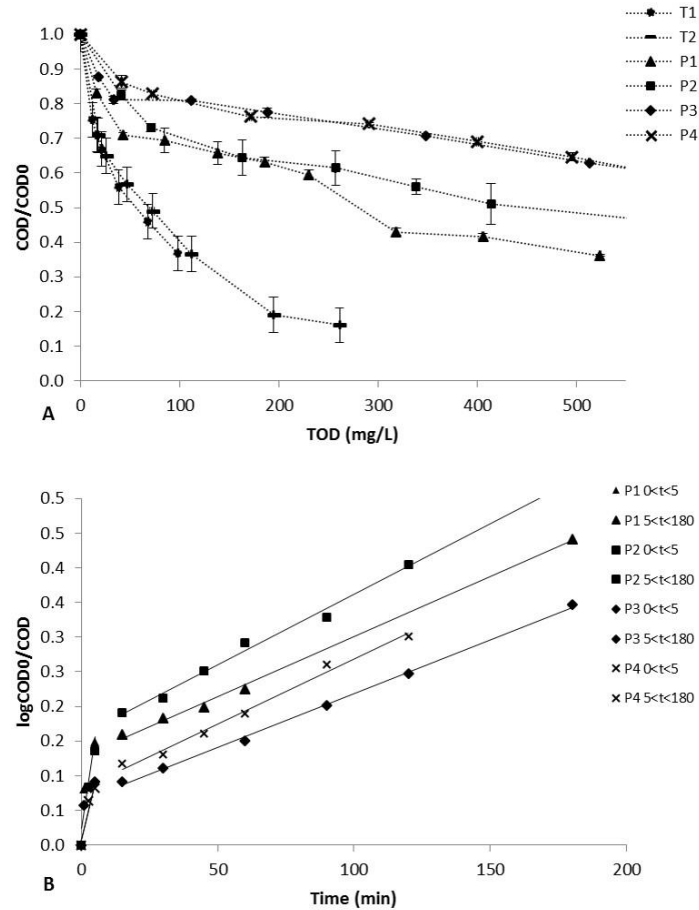


Figure 4.8 A) COD/COD₀ versus transferred ozone dose. B) COD and LN(COD₀/COD) versus contact time, primary effluents.

Table 4.4 COD pseudo-first order kinetic constants.

Samples	First $K_{1,COD}$ m^{-1}	k_d (min^{-1})	Second $K_{2,COD}$ m^{-1}	R^2
P1	0.031	45	0.0017	0.99
P2	0.028	70	0.0020	0.99
P3	0.020	33	0.0016	0.99
P4	0.018	73	0.0014	0.99
T1	0.066	14	0.0076	0.98
T2	0.089	18	0.0105	0.98

The COD rate constants for the first kinetic regime obtained from the ozonation of the bio-treated effluent from the coastal WWTP are higher than the ones obtained for the primary effluent, accordingly ranging from 0.066 to 0.089 min^{-1} . The same ozonation experiment before microfiltration leads to rate constants ranging from 0.14 to 0.16 min^{-1} for the first oxidation stage (Domenjoud 2012). This can certainly partly attributed to the absence of solid and fast reacting organic matter in the micro-filtrated effluent. Indeed, the presence of solid organic matter was

shown to enhance the COD removal kinetic during the first stage of secondary effluent ozonation (Domenjoud 2012) as probably experienced in primary effluents.

The oxidation of the COD observed supports the results of ozone mass transfer observed in Figure 4.2 and Figure 4.3. First, the most reactive compounds towards ozone are oxidized during the first stage and then the resulting products were more recalcitrant to further oxidation by ozone. The transition transferred ozone dose lower than the IOD moreover suggest that fast reacting compounds expressed by COD only counts for a minor part of the IOD (Table 4.4).

UV_{254} parameter is directly linked with the content in unsaturated compounds and notably aromatic substances dissolved in the effluent. Changes in absorbance reflect the behaviour of compounds comprising EfOM. UV_{254} is considered as one of the most promising tools associated with bulk organic matter to supplement existing analytical methods such as liquid or gas chromatography. Several studies have established correlations between ΔUV_{254} and several indicator compounds and microbes. Moreover, strong linear correlations have been found between ozone sensitive compounds and UV_{254} behaviour (Gerrity and Snyder 2011). Its evolution is represented in Figure 4.9 and provides additional information on ozone reactivity during primary effluent ozonation. As observed for the COD evolution, two oxidation stages are also observed in the normalized UV_{254} . At the end of the first stage, a reduction of 40% and 35% is achieved in the case of P3 and P2 respectively, to finally reach at the end of the treatment an overall reduction of 64% and 70%. In the case of P1 and P4 sample, lower eliminations have been observed: a reduction of 20% and 30% during the first stage and a reduction of 40%-45% at the end of the treatment. Furthermore, regarding COD analysis (Figure 4.8A) and UV_{254} analysis lower ozone susceptibility in the case of organic matter from P4 have been detected for P4.

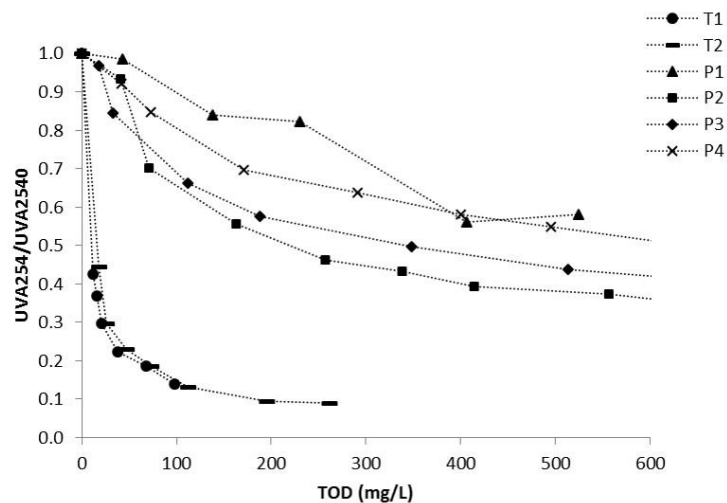


Figure 4.9. UV_{254}/UV_{2540} vs TOD for P1, P2, P3, P4, T1 and T2.

4.3.2.3 Organic matter transformation changes in MW distribution

Ozone attacks the solid organic matter from the first moments of the reaction. Therefore, it has been observed, from the first moments of the reaction, a rapid reduction of solid content evidenced by a rapid decrease of the turbidity Figure 4.10. Turbidity decreases mainly in the first stage of the reaction, when low ozone doses are transferred. Turbidity decreases mainly in the first stage of the reaction with TOD, when low ozone doses under 100 mg/L are transferred, obtaining removals of 80% and 50% for P1 and P2 respectively for example. Particulate matter thus represents a major contribution to IOD.

On the other hand, at the end of the reaction an increase in the turbidity parameter is observed due to a white precipitate.

Similar behaviours were observed in studies related to ozone application to secondary effluents from the same WWTP; accordingly, the removal of COD and UV₂₅₄ according to two well distinct oxidation regimes, the great reactivity of solid organic matter towards ozone, the enhancement of effluent biodegradability with the existence of a maximum (Domenjoud 2012).

Ozone reactivity with organic matter has been extensively studied and it is generally assumed that ozone depicts a great reactivity towards unsaturated compounds and notably aromatic substances (Hoigné and Bader 1983b). These last compounds are mostly more hydrophobic than hydrophilic showing thus a higher propensity to adsorb onto suspended solids. Indeed, it was shown that ozone reacts sequentially with the hydrophobic, transphilic and hydrophilic substances present in urban secondary effluents leading to the formation of hydrophilic and more biodegradable by-products (Domenjoud 2012). The knowledge on ozone reactivity is therefore consistent with the evolutions of the different parameters related to organic matter and suspended solids monitored in this study.

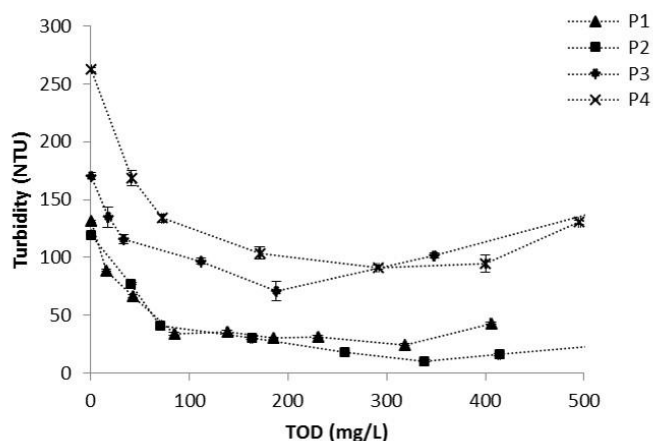


Figure 4.10. Turbidity evolution versus TOD for Primary effluents.

Further investigations on the role of particulate matter were carried out by comparing the behaviour of raw effluents and pre-filtered effluents for P3 and P4 samples with ozonation at low ozone dose transferred. Of interest, IOD values decreased to 220 mg/L and 206 mg/L in P3 and P4 upon filtration from 348 mg/L and 249 mg/L, respectively. The reduction of IOD confirms the predominant role of particulate matter in fast reactions.

Table 4.5. UV₂₅₄ absorbance, turbidity and COD variations for P3 and P4 before and after ozone application.

Samples	TOD mg/L	UV ₂₅₄ m ⁻¹	Turbidity NTU	COD mg/L
P3	0	86.3	136.3	623
	70	78.2	65.3	504
P3 Filtered	0	69.4	1.5	336
	60	67.5	3.5	320
P4	0	76.2	182.0	1191
	24	65.1	158.3	1146
P4 Filtered	0	66.6	11.4	188
	24	62.5	22.1	140

Table 4.5 reports the variations in UV₂₅₄ absorbance, Turbidity and COD parameters in relation with ozone dose transferred much lower than the IOD for raw and pre-filtered effluents. As expected, filtration of the effluents before ozone application results in high decrease in COD and turbidity when UV absorbance is less affected. Particulate matter corresponds to 46 % and 84% COD in P3 and P4 respectively. Ozone impact on all effluents is shown in Figure 4.11. All parameters are reduced upon ozone application in both not-filtered effluents. Of particular interest, turbidity is lowered by more than 20%. In the opposite, in pre-filtered effluents, a turbidity increase was observed when initial values are greatly lowered by filtration. Compared to not-filtered effluents, UV₂₅₄ reduction rates are lower on the filtered sample considered: 10% for non-filtered P3 and 15% for non-filtered P4 and only 3% and 6%, for P3 and P4 respectively. These observations are consistent with the high ozone reactivity towards unsaturated compounds and aromatic substances (Gong et al. 2008, Hoigné and Bader 1983b) that have higher hydrophobic character and high propensity to adsorb onto suspended solids. COD and UV₂₅₄ variation can be less important for P3 or similar for P4.

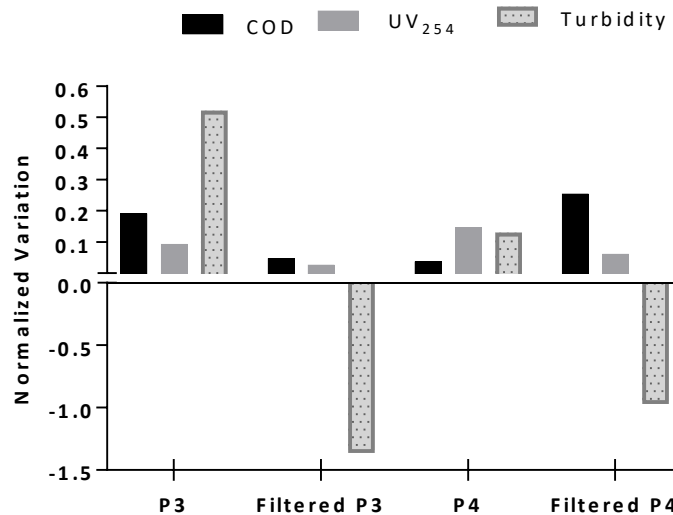


Figure 4.11. Changes in the main water characteristics upon ozonation of raw and pre-filtered wastewaters,

4.3.2.4 Changes in the MW distribution

LC-OCD analysis was applied to eight different samples of P3 and P4 effluents to identify the different subtypes of the pool of organic matter in a municipal primary effluent. So, for each sampling campaign (P3 and P4) we analyzed two samples before ozonation (filtered and non-filtered) and two samples after ozonation (filtered and non-filtered). The identification and quantification have been done into 6 fractions: Biopolymers, Humic Substances, Building Blocks, Low Molecular-weight Acids, Low Molecular-weight Neutrals, and Hydrophobic Organic Carbon. Figure 4.12 shows the different organic matter distribution for the P3 and P4 effluent, before and after ozone application. The transferred ozone dose was 70 mg/L and 24 mg/L, for P3 and P4 respectively. Biopolymers fraction correspond to the hydrophilic compounds with a high molecular weight (MW >20000 g/mol) (Huber et al. 2011b). This fraction slightly increases in the case of P3 sample after ozonation probably due to the solubilization of suspended solids. Moreover, the concentrations in Humic Substances, Building Blocks, LMW Neutrals and LMW Acids concentrations increase as ozone can readily affect the biopolymer and suspended solids fractions. The transition TOD in terms of COD removal was 33 mg/L. This fact can explain the

changes observed in P3. Regarding P4 sample, no change has been observed after ozonation. The transferred ozone dose (24 mg/L) is not sufficient to induce changes on dissolved organic matter distribution. In this last case, the transition TOD for COD removal was determined at 73 mg/L (

Table 4.4).

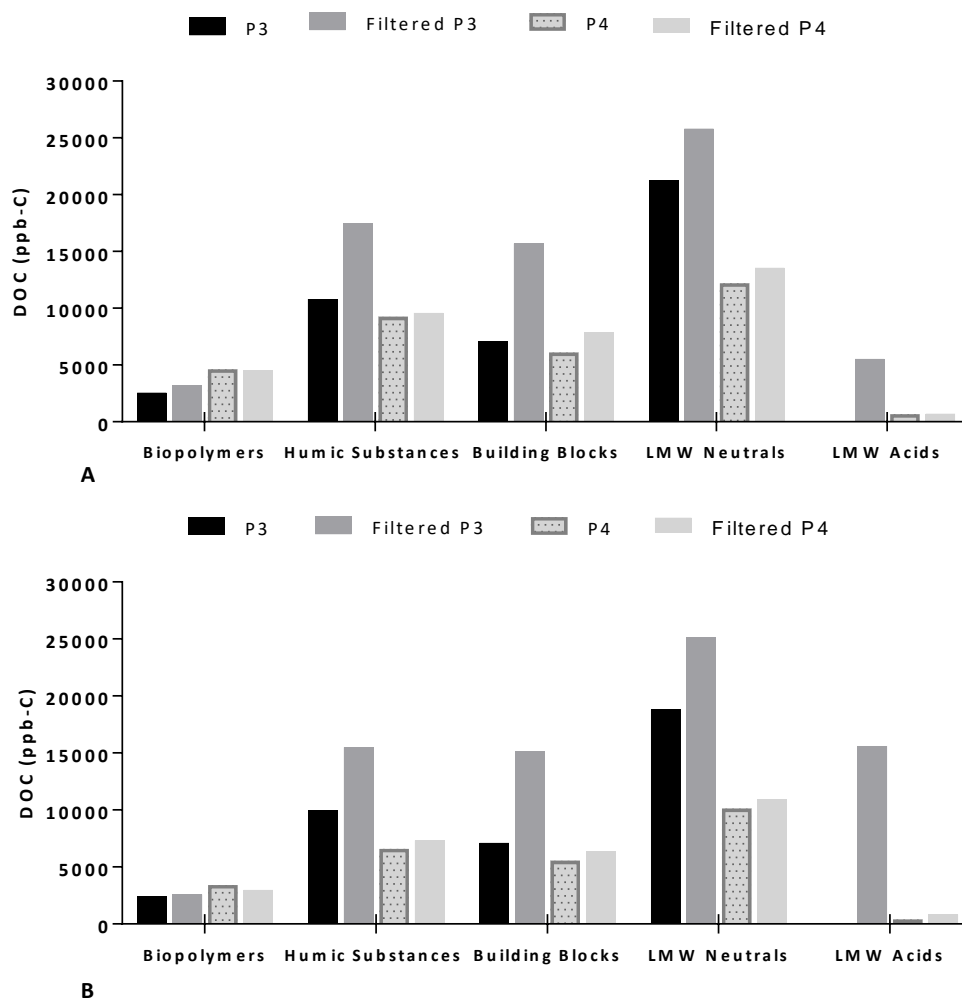


Figure 4.12 A) Organic matter sub-fractions for raw effluents P3 and P4 before and after ozonation. B) Organic matter sub-fractions for effluent P3 and P4 before and after ozonation, both filtered (0.45 μm) before the ozone application.

Comparison of Figure 4.12 A and B highlights the impact of suspended solids. Regarding variations upon ozonation for each family, same tendency has been observed in both series of experiments.

Table 4.6. Impact of ozone dose and filtration before ozonation on the molecular weight distribution. DOC > 20000 g/mol, DOC ~1000 g/mol, DOC ≤ 500 g/L belong to the hydrophilic group.

Samples	TOD	Hydrophobic	DOC >	DOC ~	DOC ≤
	mg/L	DOC	20000g/mol	1000g/mol	500g/mol
		%	%	%	%
P3	0	15.1	5.2	22.0	57.7
	70	25.3	3.5	19.3	51.9
P3 Filtered	0	14.8	5.3	22.2	57.7
	60	14.2	3.0	18.0	64.8
P4	0	11.5	12.4	24.9	51.1
	24	11.3	11.1	23.5	54.0
P4 Filtered	0	17.4	10.8	20.9	50.9
	24	13.2	9.1	22.3	55.4

Table 4.6 shows the molecular weight distribution before and after ozonation. It is important to emphasize that categories DOC > 20000 g/mol, DOC ~1000 g/mol, DOC ≤ 500 g/L belong to the hydrophilic group. Typically, ozone leads to the conversion of the hydrophobic and transphilic substances to hydrophilic substances. Regarding P3 after ozonation (TOD of 70 mg/L), the rate of hydrophobic DOC has increased through the ozone attack on suspended solids. In the case of filtered P3 after ozonation, the percentage of the smaller molecular weight compounds (Building Blocks, LMW neutrals and Acids) has increased. Concerning P4 sample, a small increase has been observed in the lower molecular weight group as a consequence of the ozone application. In the case of the filtered P4 sample, the hydrophobic fraction has decreased as well as biopolymers fraction (DOC > 20000 g/mol) obtaining lower molecular weight compounds.

4.3.3 Ozone impact in micropollutants present in primary effluents

Different micropollutants were tracked for P3, P4, P5, P6 and P7 effluents. 25 Compounds were analyzed, including: Adsorbable Organohalogenes (AOXs), non-ionic and anionic surfactants (Linear alkylbenzene sulfonates (LAS)) and Pharmaceuticals (see section 433.2.10, Table 3.1) . In the case of P7 and P6 effluents, Polycyclic Aromatic Hydrocarbons (PAHs), Polybrominated diphenyl ethers (PBDEs) and Pesticides were also monitored (see section 433.2.10, Table 3.2 and Table 3.3). The main micropollutants monitored are shown in the Table 4.7, below. Concerning pharmaceuticals, different groups were screened: β -Blockers, Antibiotics, anti-inflammatory drugs, analgesics, antifungal agents and antiepileptic drugs. The synthetic and steroidal estrogen ethinyl estradiol was found in lower concentrations than the LOQ, so it was not possible to quantify it for any campaign.

Table 4.7 Initial concentration of Micropollutants for different sampling campaigns: P3, P4, P5, P6 and P7

4.3.4 Removal of AOX in primary effluent

Figure 4.13. AOX Residual Concentration vs TOD for each sampling campaign P3, P4, P5 and P7.

4.3.5 Removal of Pharmaceuticals in primary effluent

Figure 4.14. Removal of B-Blockers and Antibiotics versus the TODs (mg/L)

In the case of anti-inflammatory drugs, the maximum removal achieved was in the case of Diclofenac (73%), after a TOD of 23 mg/L. In the case of ketoprofen, the maximum removal was 29% for a TOD of 15mg/L. For lower or equal doses of 5 mg/L, the removal range is 1-13%.

Figure 4.15. Removal of Anti-inflammatory and analgesic drugs versus the TODs (mg/L)

Figure 4.16. Antifungal (Econazole), Anti-epileptic drug (Carbamazepine) and analgesic (Paracetamol) residual concentrations (%) versus TOD (mg/L)

4.3.6 Removal of Surfactants and PBDEs in primary effluent

Figure 4.17. LAS, Σ non-ionic surfactants, Σ 4-nonylphenol and PBDEs concentration versus TOD (mg/L)

4.3.7 Removal of PAHs and Pesticides contained in primary effluent

Figure 4.18. PAHs (Acenaphthene and Phenanthrene) and Pesticides (Alachlor and Chlorpyrifos) residual concentrations depending on the TODs.

4.3.8 Micropollutant removal overview depending on ozone reactivity.

Table 4.8. Molecular Structure, Classification and reactivity of the monitored compounds

Figure 4.19. Average removals of selected compounds for a $TOD \leq 5\text{mg/L}$ versus $\text{Log } k_{O_3}$.
A. Diclofenac B. Atenolol C. Sulfamethoxazole D. Carbamazepine E. Propranolol F. Ciprofloxacin G. Phenanthrene

4.4 Conclusions

Ozone application to primary effluents displays a positive impact on aggregate parameters; it globally improves the primary effluent quality at ozone doses between 30 mg/L-70mg/L depending on the sample. Applying ozone doses below 30 mg/L, which corresponds to the first stage of ozone reactions, ensures a high enhancement of water quality. For these low doses, an important and fast oxidation of the OM was achieved. Comparison of results from ozonation of primary effluents and biotreated effluents show similar behaviors. For both type of effluents, the ozone consumption can be classically described by two characteristics which are the immediate ozone demand and the subsequent first order rate. These characteristics greatly depend on the water quality. Ozone consumption can be described by IOD in the case of ozone fast reactions and the subsequent first order rate for slower reactions. Average Immediate Ozone Demand values of are 74 mg/L and 7 mg/L were found for primary effluents and for tertiary effluents respectively from the coastal WWTP. In the case of the primary sample P3, P4 from a Municipal WWTP close to Lyon the average value IOD increase until 298mg/L. The IOD completion stage covers the first high rate COD removal stage, fully for primary effluents and partially for tertiary effluents. High variation of the decay kinetic constant, due to further slower

ozone reactions was highlighted within the primary quality type. The evaluation of these process characteristics pointed out the major influence of global organic matter parameters.

Regarding the ozone impact in organic matter, the comparison of variations in COD, UV absorbance and turbidity makes appear the major reaction of particulate matter. Different behaviours were observed for the DOC families depending on the transferred ozone doses. Even though, few changes if any have been observed on dissolved organic matter categories at ozone dose transferred lower than the IOD. The first kinetic stage of organic matter removal covers totally the IOD completion in the case of primary effluents.

4.5 Supplementary Information

Table 4.9. Initial concentration and removal percentages of the monitored pharmaceuticals of P3

0

Table 4.10. Initial concentration and removal percentages of the monitored Surfactants and AOX of P3

Table 4.11. Initial concentration and removal percentages of the monitored pharmaceuticals of P4

Table 4.12. Initial concentration and removal percentages of the monitored Surfactants and AOX of P4

Table 4.13. Initial concentration and removal percentages of the monitored pharmaceuticals of P5

Table 4.14. Initial concentration and removal percentages of the monitored Surfactants and AOX of P5

Table 4.15. Initial concentration and removal percentages of the monitored pharmaceuticals of P6

Table 4.16. Initial concentration and removal percentages of the monitored Surfactants and PBDEs of P6

Table 4.17. Initial concentration and removal percentages of the monitored pesticides of P6

Table 4.18. Initial concentration and removal percentages of the monitored PAHs of P6

Table 4.19. Initial concentration and removal percentages of the monitored Pharmaceuticals of P7

Table 4.20. Initial concentration and removal percentages of the monitored Surfactants, AOX and PBDEs of P7

Table 4.21. Initial concentration and removal percentages of the monitored Pesticides of P7

Table 4.22. Initial concentration and removal percentages of the monitored Pesticides of P7

4.6 Appendix

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Ozonation treatment of urban primary and biotreated wastewaters: Impacts and modeling

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HIGHLIGHTS

- Ozone application to primary effluents displayed a positive impact on water quality.
- Fast oxidation of the organic matter is observed for low ozone transfer doses.
- The IOD completion stage covers the first high rate COD removal stage.

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ABSTRACT

Most of the published studies concerning water and wastewater ozonation for subsequent reutilization or discharge are focused on applying ozone as an advanced treatment process downstream a biological secondary treatment. Ozonation usually shows good performances in improving water quality as shown when monitoring aggregate parameters during ozone treatments. Nevertheless, additional studies related to ozone application on pre-biological treatment stages should be considered for a better understanding of its effects on water quality as well as on the existing process performances. Therefore, the present study investigates the impact of ozone on the organic matter from municipal waste water effluents with the aim to highlight potential benefits depending on the ozone application point. Special focus was made on ozone transfer and kinetics. To do so, aggregate parameters as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), turbidity and absorbance at 254 nm (UV_{254}) were selected to characterize the effluent quality before and after treatment. These parameters provided useful information regarding the extent of oxidation, the changes in aromaticity and in biodegradability of the effluent organic matter (OM). Ozone application to primary effluents displayed a positive impact on aggregate parameters, improving effluent quality. For both type of effluents, the ozone consumption can be classically described by two characteristics which are the immediate ozone demand and the subsequent constant of first order decay. Their evaluation pointed out the major influence of global organic matter parameters.

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5. APPLICATION OF OZONE ON ACTIVATED SLUDGE: MICROPOLLUTANT REMOVAL AND SLUDGE QUALITY

5.1 Introduction

Nowadays, our society is extremely concerned about the exposure to micropollutants occurring in the environment (Ribeiro et al. 2015). The problematic involves not only the variety of these compounds but also the low concentrations of the micropollutants in the environment. These facts generate new challenges for the scientific community (Luo et al. 2014).

Moreover, as previous works have shown, Municipal Wastewater Treatment Plants (WWTPs) are significant ways for the discharge of micropollutants into environment as many of these organic compounds are weakly removed along the treatment (Eggen et al. 2014, Nie et al. 2012, Qiang et al. 2013). Currently, only half of the whole amount of micropollutants is eliminated in the conventional WWTPs, either by removal or by sorption to sludge. There are many compounds with hydrophilic character that do not sorb to the sludge and are persistent or transformed into mostly unknown products. To reduce the negative ecological impact and to improve the quality of the discharged water, some measures should be considered (Eggen et al. 2014).

Activated Sludge is the main process and globally used in the WWTPs (Qiang et al. 2013). However, focusing on the conventional activated sludge (CAS) stage, sludge excess disposal can generate pollution regarding the release to the environment of the pollutants (heavy metals, pathogens, persistent organic pollutants) that are absorbed in the sludge (Zhang et al. 2016). In addition, the excess of sludge generated during the wastewater treatment highly increase the treatment's cost accounting for the 25-60% of the total wastewater treatment cost (Qiang et al., 2013, Saktaywin et al. 2005, Yan et al. 2009, Zhang et al. 2009, Zhao et al. 2007). As a consequence, alternative plans for sludge management have been promoted.

Ozone is a strong oxidant capable to develop cell lysis and disinfection, causing suspended solids (SS) reduction and increasing the soluble COD. In the case of sludge ozonation, the sequential events have been proposed during the process application: 1. Fragmentation of sludge flocs; 2. Solids solubilisation (mainly cells) and 3. Mineralization of soluble organic compounds (Ahn et al. 2002, Chu et al. 2009, Lee et al. 2005). Even though, there are several works bringing up ozone as the suitable option for sludge excess problematic, the effectiveness of ozone greatly depends on the sludge characteristics and structures (Zhao et al. 2007). Besides, many studies have considered ozonation as one of the easiest, quick and rising technology for micropollutant removal and prevention of a subsequent release of these compounds in the environment (Luo et al. 2014, Qiang et al. 2013, Xu et al. 2002, Yan et al. 2009, Zhang et al. 2016). Qiang et al. found ozone treatment to be suitable for degradation of Endocrine Disruptors Compounds present in the activated Sludge and opened the door to do research and expand its application for the removal of other compounds adsorbed into the sludge (Qiang et al. 2013). As a selective oxidant, O_3 reacts rapidly with the rich electron moieties (ERMs) such as phenols, olefins and amines. As a consequence of its oxidative properties, ozone and the $OH\cdot$ radicals generated high removals of micropollutants with low ozone doses (Lee et al. 2012). In addition, the transformation products formed upon direct reaction with ozone or the indirect reaction with $OH\cdot$ radicals are less biologically active than the initial compounds (Lee and von Gunten 2010).

This chapter focuses on the reaction of ozone with constituents of activated sludge liquor with the aim to understand the behaviour of organic micropollutants and to analyse the changes in the mixed liquor sludge matrix. Ozone transfer related parameters as immediate ozone demand (IOD), ozone decomposition kinetic constant (k_d) and ozone mass transfer constant (k_{La}) were also estimated for the sludge as they are important parameters for removal of micropollutants and process design. As higher ozone consumption represents higher operational costs, it is important to determine correctly the required ozone consumption for an effective system operation. Some of the results of this chapter have been submitted for publication in the *Ozone Science & Engineering*.

5.2 Materials and Methods

5.2.1 Sampling at the Wastewater Treatment Plant

Two Wastewater Treatment Plants (WWTP) were chosen to collect the samples for this work. The first one is a coastal WWTP located in the province of Tarragona (Spain) and the second one is a WWTP located close to Lyon (France). Sampling campaigns were performed at the outlet of the sludge recirculation loop of the Conventional Activated Sludge (CAS) system. The sludge samples collected were composed by the whole sludge matrix, mixed liquor. Primary effluent and secondary effluent samples were collected twice as a control for the micropollutant evolution along the treatment chain. Effluent samples were refrigerated at 4°C prior to be use. The sludge sample collected at the WWTP located near Lyon is referenced as S1; whereas S2, S3, S4, S5 and S6 are samples from the coastal WWTP (Spain). The main characteristics are presented in the Table 5.1 below:

Table 5.1. Initial parameters of the CAS sampling Campaigns

Samples	UV ₂₅₄ m ⁻¹	pH	tCOD mg/L	sCOD g/L	DOC mg/L	IC mg/L	TN mg/L	SS g/L	VS g/L
S1	253.1	7.2	6.9	1.0	258.3	62.3	89.3	3.9	3.2
S2	26.5	6.9	3.0	0.1	49.2	55.5	-	0.8	-
S3	14.5	7.3	3.9	0.3	8.5	77.6	9.0	3.3	2.9
S4	32.4	7.0	6.4	0.1	-	57.7	15.9	3.7	3.3
S5	15.2	7.0	4.0	1.8	9.1	75.6	9.5	2.3	2.0
S6	9.8	7.1	3.7	0.01	16.3	78.1	6.6	1.8	1.6

5.2.2 Ozone Treatment

The detailed ozone set up is described in (Marce et al. 2016). Briefly, ozone experiments were performed at lab scale in a 2.5 L jacketed semi-batch reactor with 2L working volume. Experiments were performed without pH adjustment, at 20 °C. Ozone gas was injected at the bottom of the reactor with a glass porous plate. The mechanical mixing ensured the good contact between the liquid and gas phases. Ozone concentrations were measured in the gas phase by the BMT 964 BT (BMT Messtechnik GMBH, Germany) ozone analyzer, up and downstream the reactor, and in the liquid phase thanks to the probe Q45H/64 (Analytical Technology, US) located in a recirculation loop. Two types of different experiments were performed. In order to determine the Initial Ozone Demand (IOD) and the ozone decay, a set of experiments with a sludge dilution of 1:5 was done in milliQ water. For these experiments, the gas flow rate and ozone inlet concentration were kept constant at 60 L/h NTP (0 °C and 1 atm) and 40 mg/L NTP during all the treatment, respectively. The second type of experiments

consisted to apply a range of specific transferred ozone doses to determine the impact in the micropollutants and the sludge parameters. For this set of experiments, the gas flow rate and ozone inlet concentration were kept constant at 25 L/h NTP (0 °C and 1 atm) and 15 mg/L NTP during all the treatment, respectively. Only the reaction time differs. In both cases, 10 ppm of a silicone antifoam agent (Antifoam A Concentrate, Sigma Aldrich, US) polymer was used to avoid the foam generation. As is described in the product information, Antifoam A Concentrate was diluted with 4 parts of propylene glycol (aqueous). To have the complete scheme of operating conditions see Table 5.2.

Table 5.2. Operating conditions

Samples	Reaction Time min	Ozone Concentration in inlet gas,	Gas flow rate L/h NTP
		[O ₃]g,in mg/L NTP	
S1	1; 3.167; 9.5; 18.5	15.15 ± 0.10	26.21 ± 2.0
S2	1; 3.2; 9.8; 17	15.01 ± 0.03	25.96 ± 0.93
S3	1.2; 4.2; 12; 19.8	15.14 ± 0.10	23.92 ± 2.9
S4	240	40.13 ± 0.20	57.2 ± 0.85
S4	1; 3; 9.6; 18	15.00 ± 0.10	25.83 ± 1.7
S5	240	40.13 ± 0.03	59.50 ± 1.9
S5	1; 3.6; 8.4; 16.2; 35	14.84 ± 0.05	24.64 ± 1.0
S6	240	40.08 ± 0.15	57.84 ± 1.2
S6	1; 3; 8.4; 16.2	15.14 ± 0.04	23.72 ± 1.7

Ozone balance was assessed by continuous measurements of ozone concentrations in the gas phase at the inlet and outlet of the reactor and also in the liquid phase. The transferred ozone dose (TOD), which refers to the accumulated ozone transferred to the water sample per unit of sample volume, was calculated by doing an ozone mass balance.

5.2.3 Analysis of micropollutants

All the sludge samples were filtered with a Glass Microfibre Filters 0.7µm (Whatman®, GE Healthcare Life Science, USA) obtaining the aqueous phase and sludge phase. Water phase and solid phase were analyzed separately. Previously to the extraction, the sludge phase was dried at room temperature. In the case of the primary and secondary effluent, the extraction was performed for the whole matrix.

Each group of substances required a specific sample treatment and instrumental analysis. The extraction of the compounds adsorbed onto sludge was carried out by sonication with organic solvents. The extraction of compounds from water phase was performed by liquid-liquid extraction (LLE). The analysis of PAHs, PBDEs, alkylphenols and pesticides were performed by GC-MS/MS (EVOQ GC-TQ, Bruker). For the analysis of pharmaceuticals the analytical extraction procedure was based on the USEPA-Method 1694, consisting in a solid phase extraction (SPE) with HLB cartridge (Waters). The sample treatment for the determination of non-ionic and anionic surfactants was based on the method described by Barco et al (Barco et al. 2003). The identification and quantification of Surfactants and pharmaceuticals have been carried out by LC-HRMS (Orbitrap-Exactive, Thermo Scientific).

Different micropollutants were detected in the samples with concentrations in the range ng/L; µg/L and mg/L. High concentrations were found in the sludge solid phase due to sorption. However, all micropollutants were not found in both phases (supernatant and sludge), because of their inherent chemical properties.

A total of 62 compounds were analyzed in this work. Pharmaceuticals and surfactants (non-ionic and anionic) were analyzed for all the campaigns while PAHs and PBDEs were analyzed for sampling campaigns S4, S5 and pesticides only for the S5.

5.2.4 Further Analysis

Other measurements regarding the effluent quality were performed for all the samples, between them, the Absorbable Organic Halogen Compounds (AOX) determined by combustion and is detected coulombiometrically.

Soluble and total Chemical Oxygen Demand (sCOD and tCOD) were measured following the Standard Methods 5220D procedures. DOC, IC and TN (samples previously filtered through 0.45 µm Polyethersulfone filter (PES)) were measured by means of a Shimadzu TOC-VCS analyzer (SHIMADZU, Japan). Regarding the solids content, Standard Methods 2540 procedures were followed. To analyse COD, the Standard Methods 5220D procedures were followed. Ultraviolet absorbance at 254 nm (UV_{254}) was followed with a spectrophotometer UV-Vis, Lambda 20 (Perkin-Elmer, USA). Turbidity monitoring in a Hach 2100P Turbidimeter was able only for the set of experiments where the sludge was diluted, as it has been mention before. For further details on these techniques see Materials and Methods, section 3.2 Main analytical techniques and instruments.

5.3 Results and Discussion

5.2.5 Ozone impact on organic matter solubilization

A set of long and high transferred ozone doses (TODs) experiments were performed for three of the six sampling campaigns in order to evaluate the effect of ozone application onto sludge. Ozone balance was assessed by continuous measurements of ozone concentrations in the gas phase at the inlet and outlet of the reactor and also in the liquid phase. In Chapter 4, section 4.2.3 Definitions, the equations regarding the ozone balance is described. Furthermore, transferring high ozone doses makes possible the detection of dissolved ozone and thus determination of the IOD. The values of IOD for S4, S5 and S6 are presented in Table 5.3.

Table 5.3. tCOD and sCOD at the specified TOD, after IOD completion.

Sample	IOD gO ₃ / gSS	TOD gO ₃ / gSS	tCOD g/L	sCOD g/L
S4- Feb 2016	0.57	0.65	1.1	1.1
S5- April 2016	1.51	1.77	1.1	1.0
S6- July 2016	0.61	0.67	2.0	1.9

On the other hand, to evaluate the impact on ozone decomposition, the COD solubilization rate has been defined by:

$$e_{\text{COD}} = (\text{sCOD} - \text{sCOD}_0) / \text{tCOD}_0 \quad [33]$$

Where the total initial COD is described by tCOD_0 and the initial soluble COD as sCOD_0 .

In Figure 5.1, the COD solubilization rate (θ_{COD}) is represented versus the TOD per gram of Suspended Solids (SS). The maximum θ_{COD} observed was 24, 21 and 19% for S4, S5 and S6, respectively. Afterward, a slightly decrease (2-9%) was detected matching with the IOD completion shown in the graph by the discontinuous lines for each sampling campaign. The sludge solubilization rate is one of the most important parameters for the sludge ozonation assessment (Chu et al. 2009).

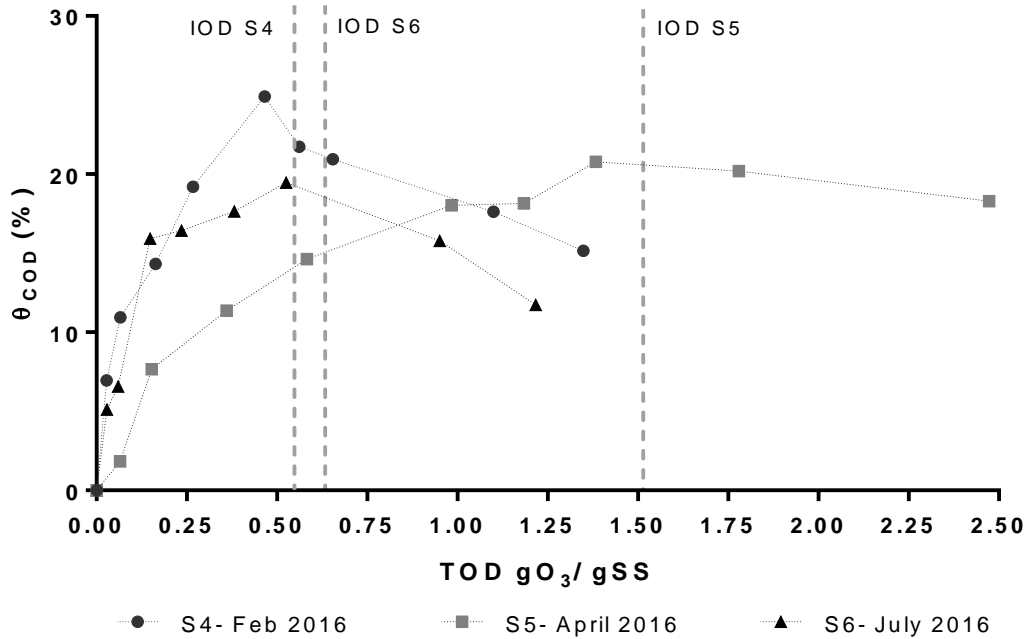


Figure 5.1. COD solubilization rate versus TOD

Changes in the UV absorbance mirrors the OM behavior (Marce et al. 2016). Similar behavior was observed in the case UV_{254} normalized with the initial UV_{254} (UV_{i254}) shown in Figure 5.2. An increase of UV_{254} between 7 to 12 times depending on the sampling campaign, has been detected until the accomplishment of the IOD stage. A stabilization accompanied with a slight decrease is observed for TOD higher than IOD. Ozone attacks part of the SS matter composing the sludge and transforms the solid content into soluble compounds and then, the release of the soluble aromatic components in the supernatant can take place. UV_{254} parameter is often used to monitor the content in unsaturated compounds and aromatic substances.

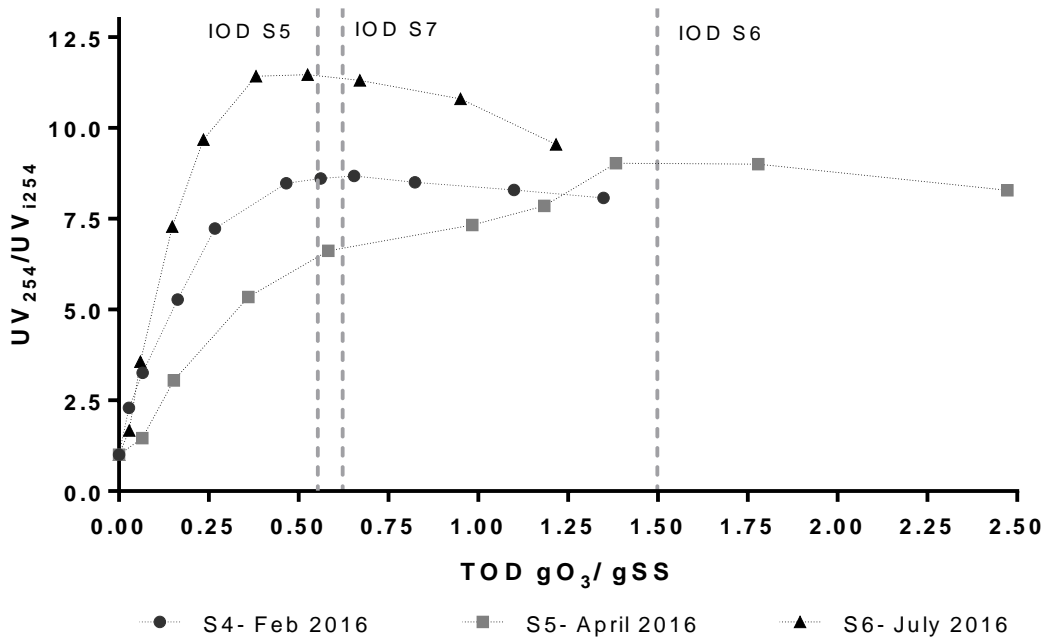


Figure 5.2. UV₂₅₄/UV₁₂₅₄ versus TOD

IC decreases along reaction when TOD increases. This fact might be explained due to the stripping of CO₂ initially present in the sludge and promoted by gas injection. However, in previous works have been reported that mineralization and the subsequent CO₂ stripping result rising the pH value (González et al. 2013, Lee et al. 2009). Nonetheless, as it is shown in Figure 5.4, the pH did not increase but decrease by 3 units during ozone reaction which might indicate the generation of some acidic intermediates. It is important to notice the almost 3 unit depletion in the pH value when the IOD is achieved (Figure 5.4).

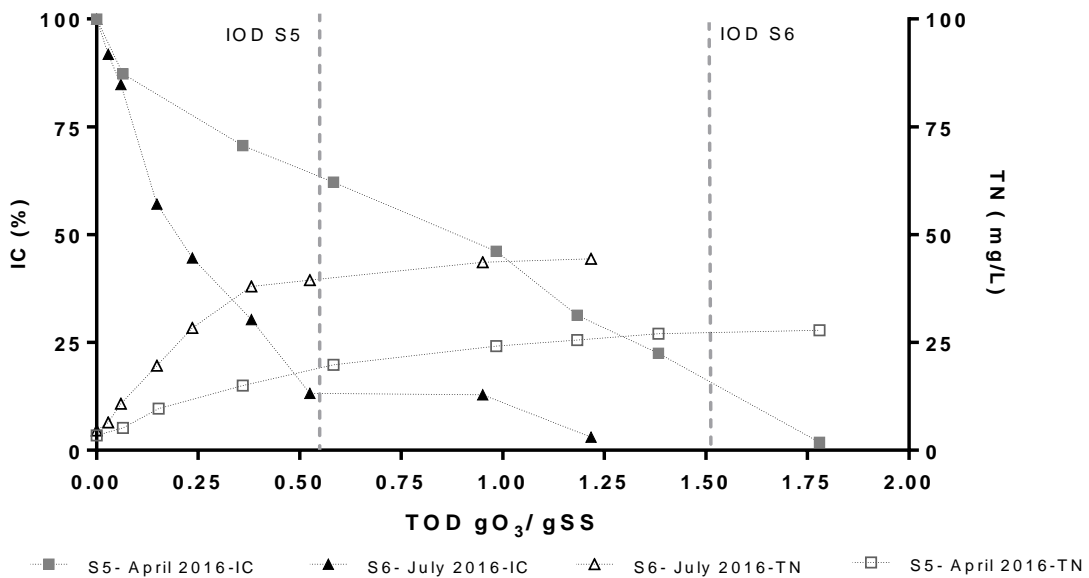


Figure 5.3. Inorganic Carbon (IC) and soluble Total Nitrogen (TN) Evolution versus TOD gO₃/gSS

Ozone is widely known for its oxidant and disinfectant capabilities which can highly alter bacteria. To do so, ozone is able to generate cell damage, especially in the cell wall and deteriorate the zoogloea structures (Zhang et al. 2009). Saktaywin et al. found that phosphorus

solubilization is proportional to the sCOD during sludge ozonation. In addition, Saktaywin et al. detected phosphates indicating the solubilization of phospholipids which are the main component of the cell membrane (Saktaywin et al. 2005). Indeed, when the ozonated sludge reappears in the wastewater treatment process, it can be biologically degraded thanks to the solubilization promoted by the ozone. Sludge ozonation favors SS reduction and generation of sCOD (Saktaywin et al. 2005, Zhang et al. 2009). The soluble Total Nitrogen (TN) evolution is represented in Figure 5.3. Many works have reported that different compounds such as proteins, carbohydrates, nucleic acids, lipids and humic products form the intercellular matrix which ensure the floc attachment. All these compounds are released and solubilized when the cells and flocs are broken (Zhao et al. 2007). As well as θ_{COD} and UV_{254} , TN shows an increase along the reaction as a consequence of the ozone attack to the sludge flocs and the subsequent release of proteins, amino acids and nucleic acids (major components of microorganisms). So, the TN increase is mainly due to the organic nitrogenous (Chu et al. 2009).

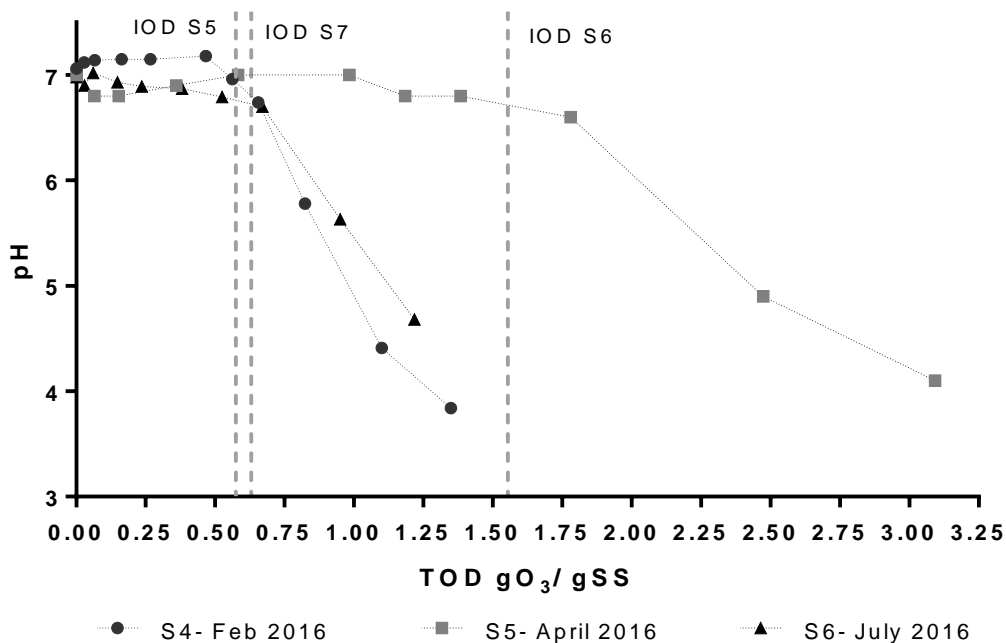


Figure 5.4. pH evolution versus the TOD

Concerning to IOD completion, our results reflect that dissolved ozone increases when the organic content of the sludge is almost completely under soluble form. Table 5.3 presents the tCOD and sCOD for a concrete TOD higher than the IOD. As it can be noticed, the tCOD which indicates the organic particulate content is comparable to the sCOD which expresses the soluble organic matter. The COD values correspond to the first samples collected during ozonation after detection of dissolved ozone in the IOD fulfillment for each sampling campaign. These COD values (soluble and total) remained constant from that point (IOD completion) until the end of reaction. This fact suggests that IOD fulfillment is strongly related with the solubilization of particles found in the sludge.

5.2.6 Impact on the sludge quality

Previous studies have demonstrated that at a dose higher but close to 20 mg/ gSS almost the 80% of the microbial respiration activity is lost (Chu et al. 2008, Yan et al. 2009, Zhao et al. 2007). Nevertheless, for lower doses than 20 mg/ gSS no noticeable modifications to the total sludge DNA were reported (Chu et al. 2008, Yan et al. 2009, Zhao et al. 2007). However, other authors reported that at an ozone dose of 50 mg/ gSS, the inactivation rate for heterotrophic organisms was 97% and 80% for the nitrifying bacteria (Chu et al. 2009). In the present study, set of experiments were performed with ozone doses in the range of 0 to 55 mg/ gSS: 1. to analyze the ozone impact at that low doses and 2. To monitor the ozone impact in the micropollutants found adsorbed in the solid phase or dissolved in the supernatant of the sludge.

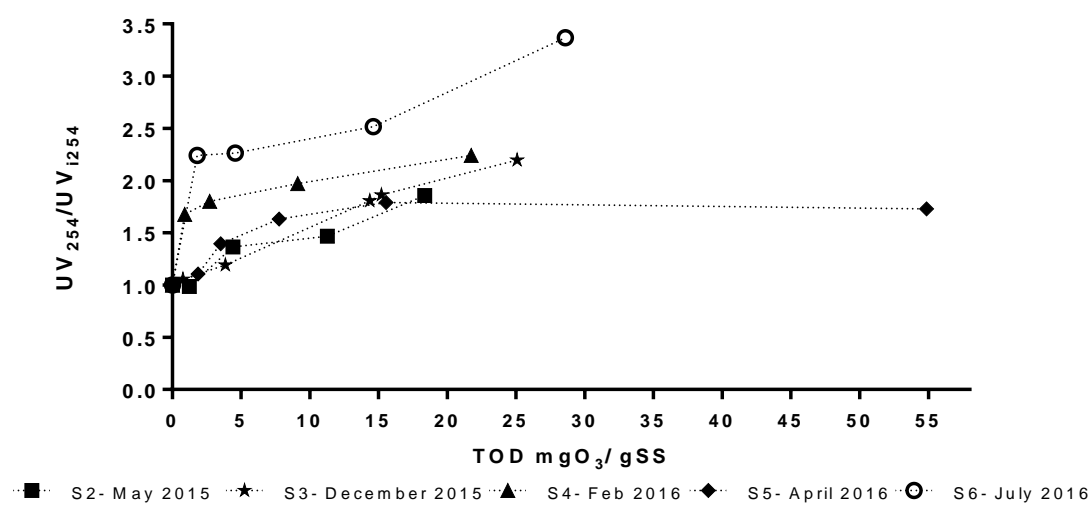


Figure 5.5. Normalized UV_{254} parameter versus TOD for S2, S3, S4, S5 and S6 sampling campaigns.

In general, an increase in the normalized UV_{254} has been found for TODs up to 55 mg/ gSS. Indeed, some changes have been noticed even at the minimum TOD of 1 mg/ gSS, in the case of S4. In Figure 5.5, the normalized UV_{254} evolution value is presented for a range of low TODs, up to 30 mg/L. Moreover, all the sampling campaigns show similar behavior for TODs lower than 20 mg/ gSS, almost doubling the initial UV_{254}/UV_{1254} value in some of the cases.

The SVI was analyzed in order to detect the effect of ozone on the sludge settleability. Zhao et al. found a decrease of almost 40% in the SVI value when the ozone dose was found between 20-60 mgO₃/ gSS (Zhao et al. 2007).

In our case, the studied TODs were selected in a lower range, up to 30 mg/ gSS. For TODs under 10 mg/ gSS, the decrease in the SVI parameter is found in the range 2-45%, depending on the sludge sample. Moreover, when the TOD is in the range 10-20mg/ gSS, the reduction is found between 14-49%. As reported in other studies, ozone is a feasible disinfectant to the filamentous bacteria. Since this type of prokaryotic microorganisms are the scaffolding of sludge flocs, when ozone attacks the sludge, its structure is modified and the intercellular water of sludge flocs is released. The flocs are ruptured into smaller and dispersed particles (Chu et al. 2009, Zhao et al. 2007). These facts promote the reduction on the volume of the particles that are in suspension (Zhao et al. 2007).

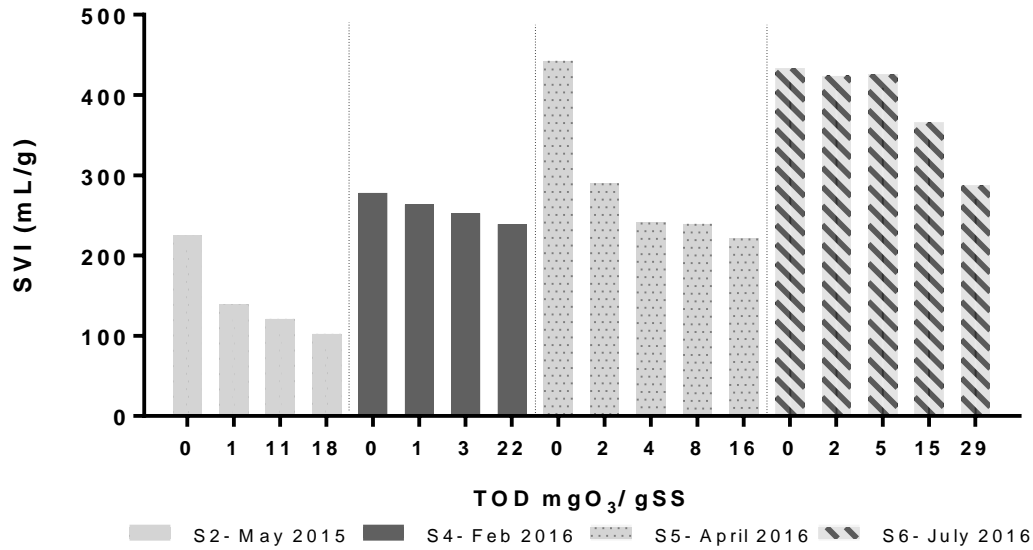


Figure 5.6. Changes in SVI versus TODs

5.2.7 Occurrence of selected compounds and elimination overall treatment

Four sampling campaigns (S1, S2, S3, S4) were performed in order to track different micropollutants. A target list of 25 compounds was analyzed: Absorbable Organohalogenes (AOXs), Non-ionic Surfactants, Anionic Surfactants and Pharmaceuticals. Regarding Pharmaceuticals, the screening included: β -Blockers, Antibiotics, anti-inflammatory drugs, analgesics, antifungal agents and antiepileptic drugs. However, from the 25 target compounds, 3 were not quantified neither in the primary clarifier outlet, secondary clarifier outlet nor the recirculation loop of the Conventional Activated Sludge (CAS) system.

Table 5.4 AOX, Surfactant and pharmaceuticals average concentrations in the outlet of primary clarifier, recirculation loop of CAS and in the outlet of the secondary Effluent. n.q = lower than LOQ

Compound	Primary Effluent	CAS	Secondary effluent	Units
AOX	0.20 \pm 0.05	2.86 \pm 2.02	0.20 \pm 0.06	mg Cl/L
Atenolol	5.81 \pm 4.23	0.63 \pm 0.75	2.49 \pm 1.74	μ g/L
Paracetamol	n.q	n.q	n.q	μ g/L
Ciprofloxacin	47.80 \pm 5.37	7.19 \pm 10.75	13.73 \pm 18.96	μ g/L
Sulfamethoxazole	1.74 \pm 0.90	1.51 \pm 1.51	0.29 \pm 0.18	μ g/L
Propranolol	0.24 \pm 0.32	0.33 \pm 0.08	0.28 \pm 0.38	μ g/L
Econazole	n.q	0.19 \pm 0.22	n.q	μ g/L
Carbamezapine	0.28 \pm 0.21	0.38 \pm 0.21	0.58 \pm 0.46	μ g/L
Ketoprofen	n.q	0.25 \pm 0.10	1.59 \pm 1.46	μ g/L
Diclofenac	2.24 \pm 1.47	1.19 \pm 1.63	2.97 \pm 2.76	μ g/L
Acetylsalicylic acid	n.q	n.q	n.q	μ g/L
Ibuprofen	52.79 \pm 50.95	0.24 \pm 0.24	9.2 \pm 12.94	μ g/L
Ethinylestradiol	n.q	n.q	n.q	μ g/L
Σ 4- Nonylphenol	1.02 \pm 0.36	4.08 \pm 5.39	0.68 \pm 0.06	μ g/L
Σ non-ionic surfactants	3419.8 \pm 4413.9	50.89 \pm 39.51	4.73 \pm 5.98	μ g/L
LAS	537.81 \pm 653.6	166.08 \pm 153.50	0.50 \pm 0.001	mg/L

Different pharmaceuticals, AOX and surfactant average concentrations are presented in Table 5.4. Even after biological treatment, some compounds presented significant concentrations, for example, 14 µg/L in the case of Ciprofloxacin or 9 µg/L for ibuprofene. Moreover, we observed considerable concentrations of these micropollutants in the CAS. Considering that CAS treatment is not always completely efficient to remove some pharmaceuticals and micropollutants, they might persist in the sludge or in the supernatant. Furthermore, due to their physical-chemical properties and slow biodegradations, some of the micropollutants that are absorbed into the sludge could persist even after anaerobic digestion. Thus, if the digested sludge is applied to the soil (Carballa et al. 2007), the micropollutants could persist in the environment.

In addition to the micropollutants mentioned before, 16 different PAHs and 9 PBDEs were screened for S3 and S4. Nonetheless, only 6 PAHs were detected. Finally, a list of 25 pesticides were tracked in S4 but only 8 were detected in our samples. Most of the compounds investigated are defined in the last European Directive (Directive 2013).

5.2.8 Removal of pharmaceuticals contained in sludge

The range of initial concentrations of the pharmaceuticals tracked are presented in Table 5.5. Higher concentrations corresponded to Ciprofloxacin, Diclofenac and Sulfamethoxazole up to 18.6, 18.6 and 2.90 µg/L respectively. On the other hand, concentrations of Acetylsalicylic acid, Paracetamol and Ethinylestradiol were below the LOQ (see section 3.2.10, Table 3.4, Table 3.5 and Table 3.6), so it was not possible to monitor them. All the mass balances and initial concentrations are in found in the Supplementary Information (Section 5.5).

Table 5.5 AOX, Surfactant and pharmaceuticals initials concentrations for CAS. n.q = Lower than LOQ.

µg/ kg Sludge	S1	S2	S3	S4
Atenolol	n.q.	0.02	0.31	1.17
Paracetamol	n.q.	n.q.	n.q.	n.q.
Ciprofloxacin	2.18	1.99	0.39	18.51
Sulfamethoxazole	0.04	n.q.	0.18	0.90
Propranolol	0.27	0.23	0.24	0.33
Econazole	0.23	n.q.	0.02	0.01
Carbamezapine	0.06	0.21	0.15	0.47
Ketoprofen	n.q.	n.q.	0.25	0.14
Diclofenac	0.03	0.01	0.61	2.85
Acetylsalicylic acid	n.q.	n.q.	n.q.	n.q.
Ibuprofene	n.q.	n.q.	0.06	0.33
Ethinylestradiol	n.q.	n.q.	n.q.	n.q.
Σ4-nonlyphenol	0.53	1.91	0.27	9.66
ΣNon Ionic Surfactant	92.52	3620.90	0.83	61.76
Anionic Surfactants	51.08	219.43	356328.11	23.16

Different ozone doses were transferred in a range between 0-30 mg/gSS. The removal has been analyzed in the liquid and solid phase of the sludge samples. As the TODs increased, the removal of pharmaceuticals increased too. Different removals have been observed depending on the pharmaceuticals structure and chemical properties. Two graphs have been plotted with the removal of pharmaceuticals for each sludge sample, in both phases. Figure 5.7 presents the

residual concentrations of β -Blockers (Atenolol and Propranolol) and Antibiotics (Sulfamethoxazole and Ciprofloxacin) found in the samples. High removals have been observed for doses below 5 mg/ gSS. For example, in the case of β -Blockers, Propranolol removal for doses under 5 mg/ gSS is 38-56% and between 60- 76% for Atenolol. Regarding the Antibiotic removal, the range of removal is found between 16-55% for Ciprofloxacin and 20-70% for Sulfamethoxazole. Significant differences in the removal are found depending on the campaign probably due to the matrix differences.

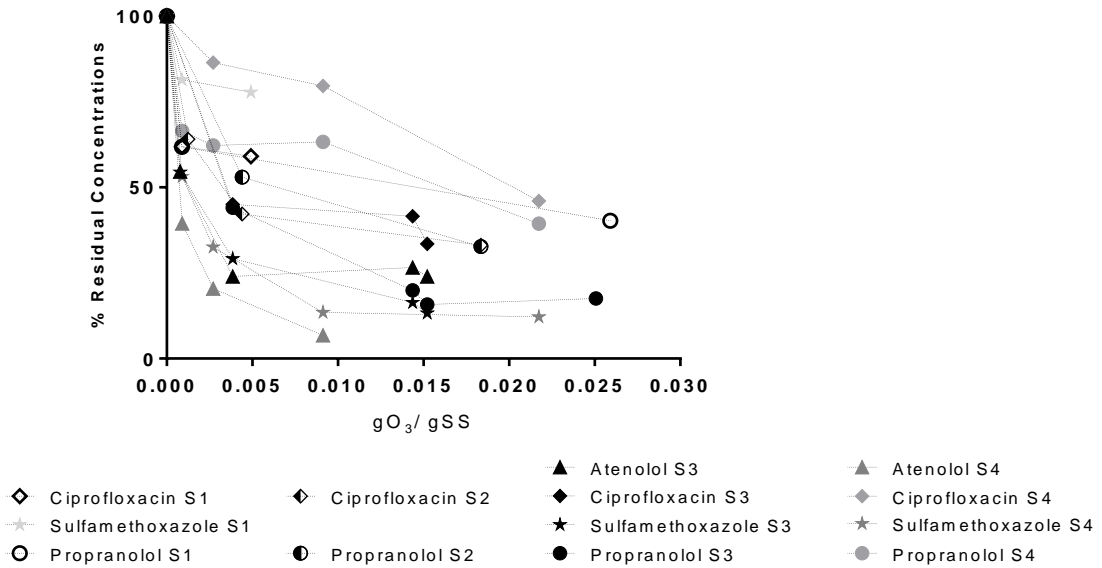


Figure 5.7. Removal of B-Blockers and Antibiotics versus the TODs in CAS matrix

Important removals are also observed in the case Anti-inflammatory, Antifungal and Anti-epileptic drugs. As it is shown in Figure 5.8, for TODs under 0.005gO₃/ gSS, the removals observed are in the range of 45-65% in the case Econazole (antifungal); 37-68% in the case of Carbamazepine (anti-epileptic); 35-90% in the case of Diclofenac (Anti-inflammatory) and 35%-45% in the case of Ibuprofen.

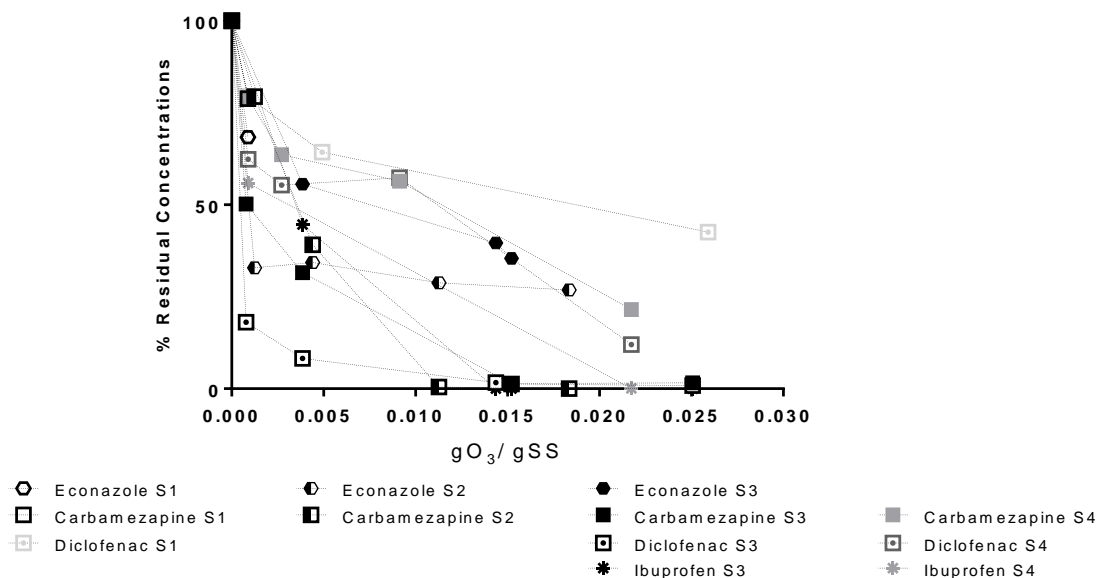


Figure 5.8. Removal of Anti-inflammatory, Anti-fungal and Anti-epileptic drugs versus the TODs in CAS matrix

Ozone reactivity towards micropollutants can be estimated by means of the compound molecular structure and pKa which turns into a determined apparent second order rate constant k_{O_3} (Kovalova et al. 2013). Moreover, three degrees of reactivity can be differentiated: high reactivity when $k_{O_3} > 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$; intermediate reactivity when $10 \text{ M}^{-1} \text{ s}^{-1} < k_{O_3} < 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and low reactivity when $k_{O_3} < 10 \text{ M}^{-1} \text{ s}^{-1}$ (Sonntag and Von Gunten 2012). In Chapter 4, Table 4.8, is presented for each compound, the k_{O_3} obtained in literature and the expected reactivity towards ozone. Moreover, a positive trend is found when the average removal rate (TOD range 10-20 mg/gSS) is represented versus $\log k_{O_3}$ Figure 5.9). Thus, removal efficiencies (for both phases) equal or higher than 80% were achieved for the compounds with higher k_{O_3} (Sulfamethoxazole, Diclofenac, Atenolol, Carbamazepine). Removal yields of 65% and 61% were achieved by Propranolol and Ciprofloxacin, respectively. In the case of Econazole, k_{O_3} was not available in literature, but intermediate reactivity was expected and its removal corresponds to the 70%. Despite the low value of Ibuprofen k_{O_3} , 99% of removal yield was obtained for the same TODs range. As previous studies have pointed out before, ozone is not highly reactive towards the functional groups of the ibuprofen molecule and its removal varied significantly during ozonation (Nakada et al. 2007). Moreover, the second order rate constant with the Hydroxyl Radical is $7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, significantly higher compared to the k_{O_3} (Huber et al. 2003). So, this fact suggest that in the case of Ibuprofen the radical pathway gained importance and for this reason is not presented in Figure 5.9.

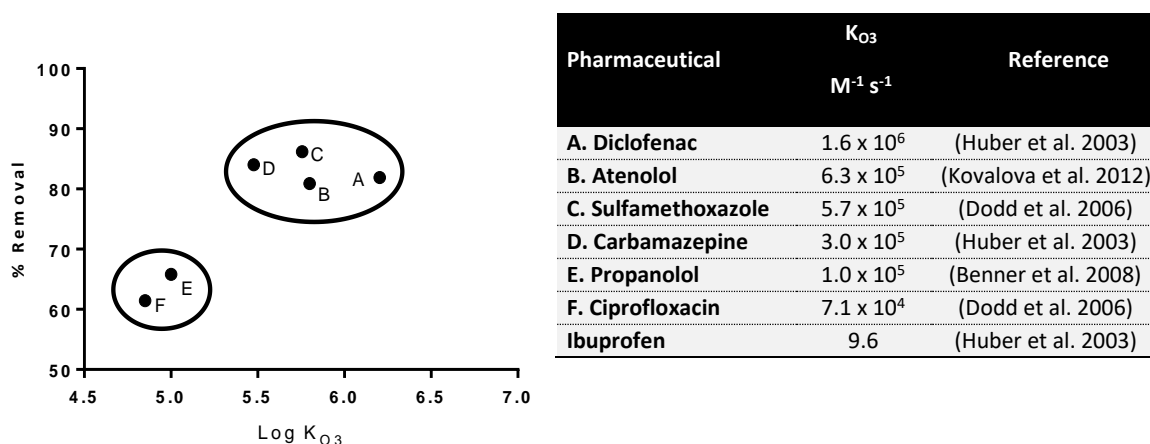


Figure 5.9.(Left) Pharmaceutical average removals for a range of TOD= 10-20 mg/gSS versus $\log K_{O_3}$, (right) K_{O_3} of the presented compounds.

Concerning the applied TODs, great removal efficiencies were achieved by using TODs in the range of 10 to 20 mg / gSS but even for TODs below 10 mg/ gSS, the removals rates were significant. In section 5.5 Supplementary Information, the concentrations of the pharmaceuticals are presented with the corresponding removals for each phase and treatment.

Table 5.6. Log K_{ow} for the studied pharmaceuticals.

Compound	Log K_{ow}	Reference
Atenolol	0.43	(Kovalova et al. 2013)
Paracetamol	0.91	(Kovalova et al. 2013)
Ciprofloxacin	0.28	(Takács-Novák et al. 1992)
Sulfamethoxazole	0.68	(Nam et al. 2014)
Propranolol	2.58	(Kovalova et al. 2013)
Econazole	5.61	(Villain et al. 2016)
Carbamazepine	2.77	(Kovalova et al. 2013)
Ketoprofen	3.12	(Tsantili-Kakoulidou et al. 1997)
Diclofenac	4.26	(Kovalova et al. 2013)
Acetylsalicylic acid	1.19	(Ni et al. 2002)
Ibuprofen	3.97	(Avdeef et al. 1999)
Ethinylestradiol	4.15	(Vega-Morales et al. 2010)

Regarding separately both phases, the majority of pharmaceuticals were found only in one phase or the other, sludge or liquid phase. Only two compounds were found in both phases in all four sampling campaigns: Carbamazepine and Propranolol. S3 and S4 were chosen in Figure 5.10 to represent the evolution in each phase along the different TODs applied. Table 5.6 presents the different Log K_{ow} which provides information about the compound hydrophobicity. Even though, Carbamazepine has a moderated hydrophobicity (Log K_{ow} = 2.77), it was mainly detected in the water phase, while propranolol (Log K_{ow} = 2.58) showed higher sorption in the sludge (principally in S3). By means of the obtained data, neither desorption from sludge to supernatant nor adsorption from supernatant to sludge was detected in the case of these two compounds. Thus, the carbamazepine percentage range for S3 was found between 96 and 100% of the total percentage (100%) in the aqueous phase: the initial value was 98% and the final value for the highest dose was 100%, being almost constant. In the case of S4, the carbamazepine range for the aqueous phase was found between 95 and 98 %, being totally removed for the highest doses. The range of Carbamazepine in the aqueous phase was found between 86 and 94% for S1 and 86 to 93% for S2. Furthermore, when the highest dose was applied to S1 and S4, the total amount of carbamazepine remains in the aqueous phase (99.6 and 100%, respectively). Regarding Propranolol, different percentages are found between campaigns. In the case of S3, the range in the aqueous phase was found between 89 and 79%, achieving the 100% for the highest TOD (total elimination of carbamazepine in the sludge phase). Lower percentage of propranolol was found in the aqueous phase of the initial sample, 62 % and the range achieved with the different ozone doses corresponded to 62-78% of the 100%. Similar results were obtained for Propranolol in S2, measuring a range between 63 and 73% of Propranolol in the aqueous phase. Finally, in S1, higher sorption of propranolol onto sludge was detected, being the range in the aqueous phase equal to 15-20% of the total percentage (100%).

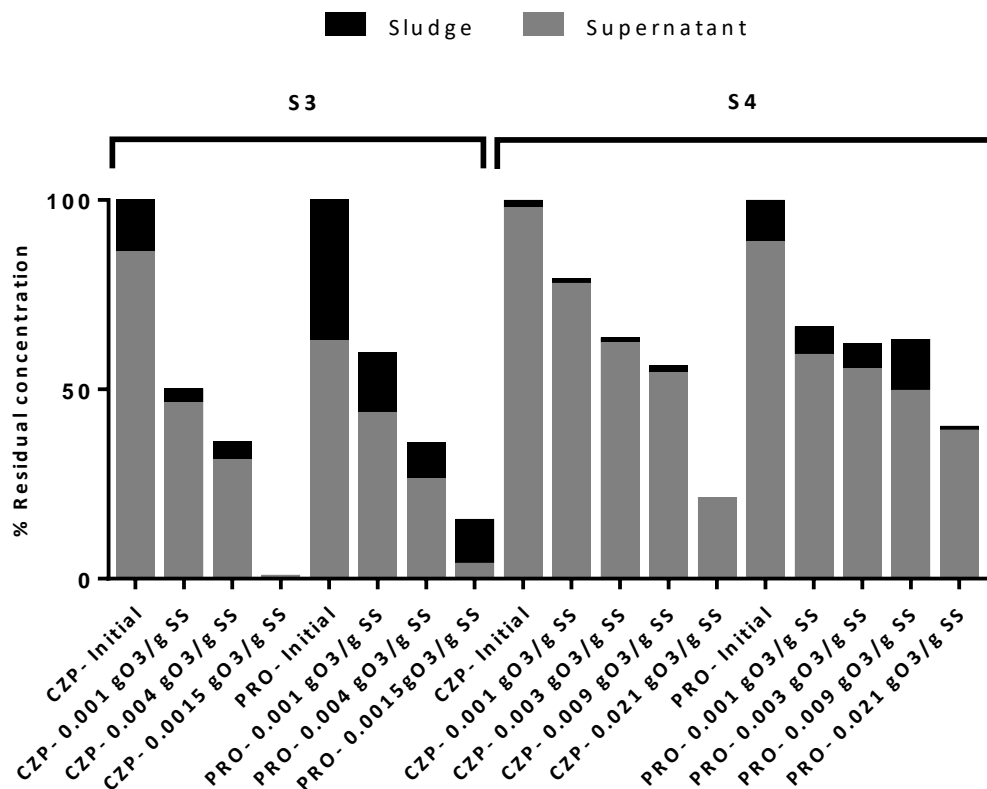


Figure 5.10. CZP= Carbamazepine; PRO= Propranolol. Initial and residual Concentrations of CZP and PRO in sludge and supernatant phases for S3 and S4 sampling campaigns.

On the other hand, Ibuprofen and Econazole were detected in the sludge phase due to their hydrophobicity profile, $\text{Log } K_{ow} = 3.91$ and 5.61 , respectively. However, no desorption was possible to detect along the different TODs applied. The other analyzed pharmaceuticals showed different behavior depending on the campaign, for instance, Diclofenac was detected in both phases for S1 and S4, but only in the supernatant in the case of S2. Diclofenac can also be distributed as a sodium or potassium salt, depending on the country, with a $\text{Log } K_{ow} = 0.7$ according to (Jones et al. 2002). This fact may explain its solubility depending on the campaign. Moreover, a correlation has been observed between Atenolol distribution and its K_{ow} (0.43) since it has been detected 100% in the supernatant in all the campaigns where it has been measured. Even though, Ketoprofen K_{ow} is moderately high, it was detected in the aqueous phase in all the campaigns. Finally, Ciprofloxacin was mainly detected in the aqueous phase except for S4 campaign, and Sulfamethoxazole was completely detected in the aqueous phase which correlates with their octanol-water partition coefficient.

5.2.9 Non- ionic and anionic Surfactant Degradation by ozone application

Figure 5.11. Persistence of Surfactants versus the TOD (gO₃/ gSS)

5.2.10 PAHs and PBDEs removal efficiencies and ozone dosage in CAS effluents

After the evaluation of the pharmaceutical removals by means of ozone, the next step was to evaluate the impact of ozonation in the removal of PAHs. These compounds are originated from anthropogenic and natural sources. However, the anthropogenic origin is the main pathway of PAHs entry into the environment, as represents 90% of the PAHs emission. Moreover, as a result of their toxicity and carcinogenesis, they have been considered priority pollutants in the European Directive 2013/39/EU(Directive 2013) and for The United States Environmental

Protection Agency (EPA). Different remediation technologies have been used (Thermal, Physical and Biological treatments), over them chemical oxidation through ozonation is a promising technology (Russo et al. 2010). PAHs can react towards ozone either via molecular ozone or hydroxyl radicals (Masten and Davies 1997).

5.12

Figure 5.12. PAHs concentration (%) versus the TOD (gO₃/gSS)

5.2.11 Ozone impact on Pesticides

Figure 5.13. Pesticides removal through 3 TODs : 0.001; 0.003 and 0.02 gO₃/ gSS in S4. * n.a: non available

5.4 Conclusions

This study focuses on the reaction of ozone with constituents of activated sludge liquor with the aim to understand the behaviour of organic micropollutants and to analyse the changes in the mixed liquor sludge matrix.

A correlation has been observed between the sludge solubilization and IOD stage completion, concerning COD, TN, pH and UV₂₅₄. Moreover, even at low doses, this solubilization takes place and it is related with an improvement of the sludge settleability.

On the other hand, the presented results show that ozone might quickly and selectively react with the studied pharmaceuticals present in solid and/or liquid phases despite the fact that the working matrix is a complex sludge matrix presenting a high ozone demand. By applying ozonation to secondary effluents for removal of pharmaceuticals and PPCPs, Nakada et al. suggested that oxidation by means of the ozone molecular pathway seemed to be the main pathway, especially when low dosages were transferred (Nakada et al. 2007).

. Other studies have proposed that ozone may firstly attack the soluble portion of the sludge and then react the particulate matter (Cesbron et al. 2003). However, regarding the removal rate presented in this work for some micropollutants adsorbed onto the sludge and the solubilization degree, we can consider that depending on the conditions, ozone attack would rather occur on the particulate matter at the beginning of the reaction. Different behaviors were observed between campaigns in terms of pharmaceutical sorption and solubility. Only two pharmaceuticals were found in both phases in all the sampling campaigns: carbamazepine and propranolol. Neither sorption nor desorption was observed after the ozone application. However, high removals were observed for these compounds.

5.5 Supplementary Information

Table 5.7 Mass balance for the studied pharmaceuticals of S1. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available data; n.q.= below the limit of quantification.

Table 5.8 Mass balance for the studied surfactants of S1. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification

Table 5.9 Mass balance for the studied pharmaceuticals of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification.

Table 5.10 Mass balance for the studied pharmaceuticals of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification.

Table 5.11 Mass balance for the studied surfactants of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification.

Table 5.12 Mass balance for the studied surfactants of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification.

Table 5.13 Mass balance for the studied pharmaceuticals of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal.n.a =non available; n.q.= below the limit of quantification.

Table 5.14 Mass balance for the studied pharmaceuticals of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a = non available; n.q.= below the limit of quantification.

Table 5.15 Mass balance for the studied surfactants of S2. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification.

Table 5.16 Mass balance for the studied surfactants of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q.= below the limit of quantification.

Table 5.17 Mass balance for the studied PAHs of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q . = below the limit of quantification.

Table 5.18 Mass balance for the studied PAHs of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q .= below the limit of quantification.

Table 5.19 Mass balance for the studied PBDEs of S3. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q .= below the limit of quantification.

Table 5.20 Mass balance for the studied pharmaceuticals of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a = non available; n.q .= below the limit of quantification.

Figure 5.21. Mass balance for the studied pharmaceuticals of S4 For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a = non av

Table 5.21. Mass balance for the studied surfactants of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q .= below the limit of quantification.

Table 5.22. Mass balance for the studied PAHs of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q .= below the limit of quantification.

Table 5.23 Mass balance for the studied PBDEs of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a =non available; n.q .= below the limit of quantification.

Table 5.24. Mass balance for the studied pesticides of S4. For each TOD is described the compound % in the sludge phase, the compound % in the water phase (supernatant), the % of residual concentration after the TOD application and the % of removal. n.a = non available; n.q .= below the limit of quantification.

6. PROCESS COMBINATION: OZONE AND BIOLOGICAL PROCESSES.

6.1 Introduction

Nowadays, the need to find the best configuration for the wastewater treatment and to obtain energy from the wastewater cycle suppose major challenges for companies and institutions working on the wastewater management field.

Biological treatments have shown to be economic and reliable systems (Marco et al. 1997) even though, currently, it is known that conventional biological treatments do not remove completely the wide spectrum of micropollutants and toxic substances present in wastewater. For this reason the combination of advanced processes (based on radical pathways) and ozonation with biological treatments seems to be a promising solution.

Indeed, one potential option is to apply AOP's technologies as a pre-treatment to convert the more recalcitrant compounds into more biodegradable substances which can be followed by the biological treatment gaining efficiency and reducing the cost (Sarria et al. 2002). Thus, the main objective of the chemical oxidation is the partial degradation instead of the complete mineralization. Therefore, two configurations can be proposed for the chemical oxidation: 1. before the biological treatment as a pre-treatment or 2. after the biological treatment as a post-treatment. The last mentioned option has as first objective, the elimination of biodegradable matter by biological treatment and secondly, the degradation of the refractory matter (Oller et al. 2011).

Anaerobic digestion it is a necessary step to reduce sludge: this process can reduce the sludge production by about 40-50%. Moreover, the production of biogas as a process result makes this process profitable (Bougrier et al. 2006). Incineration is the other alternative for sludge treatment, even though it is being questioned for its environmental impact (Weemaes et al. 2000). Hydrolysis, acidogenesis and methanogenesis constitute the different stages of anaerobic digestion. Hydrolysis is the rate-limiting step in the case of sludge from Municipal WWTPs as a consequence of the particulate matter and low biodegradability (Carballa et al. 2007). To enhance Hydrolysis step, pre-treatments should be considered (Bougrier et al. 2006, Carballa et al. 2007, Carrère et al. 2010). An improvement in hydrolysis could be translated in a better anaerobic performance and for instance, an increase on the biogas production (Bougrier et al. 2006). Ozone is considered a good option as a chemical pre-treatment since no oxidant residues are formed and no increase in salt concentration occurs (Carballa et al. 2007). In this case, ozonation is understood as a process to increase the hydrolysis and to produce partial oxidation, but it is not considered for complete mineralization (Carballa et al. 2007). Bougrier et al. found that ozone could enhance the anaerobic digestion with a consumed dose of 0.15 gO₃/ gTS (Bougrier et al. 2006).

This chapter is divided in two main sections associated to each main objective. The first one corresponds to a study of the possible benefits of ozone application as a pre-treatment of the biological treatment. So, a comparison was performed at the organic matter and micropollutant level between ozonated primary effluent, biotreated effluent feed with ozonated primary effluent and ozonated secondary effluent. For this purpose, a biological treatment was simulated at the laboratory level intending to evaluate the combination of ozonation with biological treatment and the enhancement of the quality of the obtained wastewater. This fact could promote the wastewater reclamation. Moreover, acute toxicity was tested in order to

analyze the impact of ozone in the toxicity evolution. On the other hand, the second objective was to couple sludge ozonation and anaerobic digestion in order to increase the biogas production. Several authors have exposed the benefits of the application of ozone on sludge: reduction in sludge excess (Chu et al. 2009), improvement of settleability (Zhao et al. 2007), degradation of EDCs (Qiang et al. 2013) and other micropollutants also covered in Chapter 5. So, in addition to these mentioned advantages, the second objective of this chapter was to evaluate if the ozone application on sludge could increase the biogas production. This fact could change the wastewater/sludge scenario promoting ozone as a profitable technology.

6.2 Materials and methods

The experimental set up related with this chapter is described in Sections 3.1.2 and 3.1.3.

6.2.1 Wastewater and sludge characterization

For this study, samples of wastewater effluents and aerobic sludge mixed liquor were collected from a costal WWTP (WWTP-A) located in the province of Tarragona (Spain). Sampling campaigns were performed at the outlet of the primary treatment, at the outlet of the sludge recirculation system and at the outlet of the secondary treatment. For this set of experiments, samples were kept at 4°C prior to be use. Moreover, the inoculum for the anaerobic experiments was collected from a costal WWTP (WWTP-C) located in the province of Barcelona. Samples from the primary effluents collected during different campaigns from the coastal WWTP (Spain) are referenced as P6 and P7; while S5 and S6 are the aerobic sludge mixed liquor samples. S5 was used as a substrate for the anaerobic experiments and S6 as a biomass (aerobic inoculum) for the experiments simulating aerobic biological treatment. The secondary effluent is referenced as B1 and the inoculum as I1.

Table 6.1. Initial water quality parameters

Samples	UV ₂₅₄ m ⁻¹	SUVA L/(mg·m)	pH	tCOD mg/L	DOC mg/L	IC mg/L	TN mg/L	SS mg/L	Turbidity NTU	BOD ₅ /COD mg/L	Alkalinity mgCaCO ₃ /L	Conductivity μS
P6	36.2	0.70	7.6	253	52	80	37	110	70	0.30	369	1945
P7	40.7	0.53	7.3	398	62	75	24	161	144	0.34	415	1948
B1	19.1	0.76	7.7	27	8	88	27	47	4.2	0.22	-	1820

Table 6.2. Initial quality of sludge samples from aerobic (S5,S6) and anaerobic (I1) biological treatment.

Samples	UV ₂₅₄ m ⁻¹	pH	tCOD g/L	sCOD g/L	DOC mg/L	IC mg/L	TN mg/L	SS g/L	VS g/L	TS g/L	Alkalinity mgCaCO ₃ /L
S5	15.2	7.0	4.0	1.8	9	76	10	2.3	2.0	-	387
S6	9.8	7.1	3.7	0.01	16	78	7	1.8	1.6	5.8	420
I1	73.7	7.7	26.9	-	349	1029	106	23.2	16.6	29.2	7050

Moreover, the ion content was checked by ion chromatography (section 2.2.6 Materials and methods) for some sampling campaigns. Thus, the ammonium content was monitored for the anaerobic batch test.

6.2.2 Operating Conditions

All the ozone experiments were performed before IOD fulfillment stage. For these experiments, the gas flow rate and ozone inlet concentration were kept constant between 30 to 40 L/h NTP (0 °C and 1 atm) and 15 mg/L NTP during all the ozone treatment for primary effluents, respectively. In the case of the secondary effluent (B1), the gas flow rate and ozone inlet concentration were kept constant at 34.5 L/h NTP (0 °C and 1 atm) and 10 mg/L NTP during all the ozone treatment, respectively. Finally, the dedicated experiments for sludge biodegradation were performed at 25 L/h NTP (0 °C and 1 atm) and with an inlet concentration of 15 mg/L NTP (Table 6.3).

Table 6.3. Operating conditions for ozone experiments.

All the details for the aerobic and the anaerobic experiments are described in Section 4.2, Materials and methods.

6.2.3 Specific analysis and measurements during biological tests.

The dissolved oxygen content was monitored during the aerobic experiments with the Waterproof Portable Dissolved Oxygen and BOD meter H198193 (Hanna, Italy).

Biogas composition was determined by a Shimadzu GC-2010+ gas chromatograph equipped with a capillary column Carboxen 1010 Plot (0.53mm ID; 30 m length) and a thermal conductivity detector (TCD). The composition was given as percentage of methane and carbon dioxide. The analysis program consisted in: hold 6 min at 40°C, increase to 230°C at a rate of 25 min⁻¹ and hold 2 min at this temperature. Injector and detector temperature was set at 200°C and 230°C, respectively. The carrier gas was helium at 47 mL min⁻¹ and 20.4kPa.

Volatile Fatty Acids (VFAs) were analyzed by a Shimadzu GC-2010+ gas chromatograph equipped with a capillary column Nukol (0.53mm ID; 15m length) and a flame ionization detector (FID). The analyzed acids were: acetic, propionic, butyric, valeric, hexanoic and heptanoic. The chromatograph program comprised: an increase from 85°C to 110°C at a rate of 10 min⁻¹, increase to 145°C at 15 min⁻¹, increase to 190 °C at 20 min⁻¹ and hold 10 min. Injector and detector temperature was set at 280°C and 300°C, respectively. Carrier gas was helium at 36.9 mL min⁻¹ and 17.6 kPa.

6.2.4 Definitions

Toxicity units can indicate the toxicological level and are calculated as it is shown below:

$$TU = Toxicity Unit = \frac{100}{EC_{50}} \quad [34]$$

Where EC₅₀ is the effective concentration that reduces the bioluminescence to 50%. Moreover, toxicity removal efficiency was determined as:

$$E(\%) = \frac{TU_i - TU_{TOD}}{TU_i} \times 100 \quad [35]$$

Furthermore, a toxicity range can be established depending on toxicity units calculated by the equation [35] (Miralles-Cuevas 2015):

Table 6.4. Toxicity levels regarding TU values

Toxicity Level	TU values
Negligibly toxic	< 1.99
Weakly toxic	2-2.99
Moderately Toxic	3-3.99
Toxic	4-4.99
Highly Toxic	>5

One of the most important parameters for the correct operation of the biological treatment is the substrate to inoculum ratio (SIR). The inoculum provides the system with the initial microbial population, which will then participate to the reactions constituting the degradation of the the organic matter present in the substrate (Pellera and Gidarakos 2016). The SIR can be calculated by means of the VSS or COD of both substrate and inoculum:

$$SIR_{VSS} = \frac{VSS \text{ Substrate (mg/L)}}{VSS \text{ Inoculum (mg/L)}} \quad [35]$$

$$SIR_{COD} = \frac{COD \text{ Substrate (mg/L)}}{COD \text{ Inoculum (mg/L)}} \quad [36]$$

6.3 Results and Discussion

6.3.1 Ozone treatment coupled to aerobic biological treatment- impact to organic matter.

The aerobic biological experiments were performed in order to simulate the biological treatment and to check the possible benefits of the ozone application as a pre-treatment in the primary effluents at the level of quality parameters and micropollutants. Moreover, this study pretends to perform a comparison between the secondary effluent from the WWTP and the effluent biotreated and obtained at lab scale. To do so, ozone was applied to P6 and P7, transferring two different doses for each effluent.

Figure 6.1. Evolution of sCOD/sCOD₀ and UV₂₅₄/UV_{254,0} during the biological treatment for all the samples of P7 effluent.

6.1

6.2

Table 6.5 Residual concentration (%) of DOC, sCOD, UV₂₅₄ achieved after the biological treatment for P6 an P7.

Figure 6.2. Evolution of normalized inorganic carbon and dissolved organic carbon during biological treatment.

6.3

6.3

6.3

Figure 6.3. Overall residual concentrations (normalized) of soluble COD (sCOD) and UV_{254} treatments for P6 (A) and P7(B).

Table 6.6. Values of different parameters for initial, ozone treatment and ozone treatment coupled with biological aerobic treatment for P6 and P7, as well as, the parameters for B1 for ozone treated and untreated sample.

Figure 6.4 Determined OUR for all the samples of P7 versus time (min)

6.3.2 Ozone treatment coupled to aerobic biological treatment – impact on micropollutants.

Different groups of micropollutants were tested: pharmaceuticals, non-ionic and anionic surfactants, pesticides, polycyclic aromatic carbons (PAHs) and PBDEs. As in the other chapters of this thesis, most of the micropollutants screened were found in the list of the last European Directive (Directive 2013).

Figure 6.5. Removal of anionic surfactants (LAS), octylphenol, Nonylphenol, total amount of PBDEs and non-ionic surfactants for each performed treatment. A) Presents the results detected in sampling campaign P6 and B) presents the results for sampling campaign P7.

Figure 6.6. Removal of the pesticides (Alachlor and Chlorpyrifos) for sampling campaign P6 (A) and P7 (B).

Figure 6.7. Removal of pharmaceuticals for sampling campaign P6 (A) and P7 (B).

Figure 6.8. Removal of PAHs for sampling campaign P6 (A) and P7 (B,C).

Figure 6.9. Residual concentrations of Pharmaceuticals (A) and Pesticides (B), initial and after two different transferred doses in secondary effluent, B1.

6.9

6.10

Figure 6.10. Residual concentrations of PAHs, initial and after two transferred doses for secondary effluent, B1.

6.3.3 Acute Toxicity and Biodegradability

This section pretends to evaluate the acute toxicity of the primary effluent and secondary effluent: untreated and after two TODs, as well as the relation with their biodegradability. The samples used for these experiments were collected in the WWTP- A and are the ones referenced as P7 and B1.

Table 6.7. Pharmaceuticals and Surfactants analyzed in P7 and B1; n.q = non quantified and X= quantified

Categorie	Compound	P7	B1	LOQ	Units
AOX		x	x	0.03	mg Cl/L
Pharmaceuticals	Atenolol	x	x	0.01	µg/L
	Paracetamol (Acetaminophen)	x	x	0.20	µg/L
	Ciprofloxacin	x	x	0.02	µg/L
	Sulfamethoxazole	x	n.q	0.01	µg/L
	Propranolol	x	x	0.01	µg/L
	Econazole	n.q	n.q	0.01	µg/L
	Carbamezapine	x	x	0.01	µg/L
	Ketoprofen	x	x	0.30	µg/L
	Diclofenac	x	x	0.01	µg/L
	Acetylsalicylic acid	n.q	n.q	0.20	µg/L
	Ibuprofen	x	x	0.05	µg/L
Ethinylestradiol	n.q	n.q	0.50	µg/L	
Non Ionic Surfactants: alkylphenols and alkylphenol ethoxylates	nonylphenol polyethoxylated	n.q	n.q	0.50	µg/L
	polyethoxylated alcohol C10	x	x	0.50	µg/L
	polyethoxylated alcohol C11	x	x	0.50	µg/L
	polyethoxylated alcohol C12	x	x	0.50	µg/L
	polyethoxylated alcohol C13	x	x	0.50	µg/L
	polyethoxylated alcohol C14	x	x	0.50	µg/L
polyethoxylated alcohol C15	x	x	0.50	µg/L	

	polyethoxylated alcohol C16	x	x	0.50	µg/L
	polyethoxylated alcohol C17	x	x	0.50	µg/L
	polyethoxylated alcohol C18	x	x	0.50	µg/L
Anionic surfactants	linear alkylbenzene sulphonates	x	x	0.001	mg/L

Table 6.8 PBDEs and PAHs analyzed in P7 and B1; n.q = non quantified and X= quantified

Categories	Compound	P7	B1	LOQ	Units
Polybrominated diphenyl ethers (PBDEs)	BDE-28	x	x	0.01	ng/L
	BDE-47	x	x	0.02	ng/L
	BDE-99	x	x	0.01	ng/L
	BDE-100	x	x	0.01	ng/L
	BDE-153	x	x	0.01	ng/L
	BDE-154	x	x	0.01	ng/L
	BDE-183	x	x	0.01	ng/L
	BDE-197	x	n.q	0.01	ng/L
	BDE-209	x	x	0.03	ng/L
Polycyclic aromatic hydrocarbons (PAHs)	Naphtalene	x	x	8.54	ng/L
	Acenaphthene	x	x	0.33	ng/L
	Fluorene	x	x	0.75	ng/L
	Acenaphthylene	x	x	0.09	ng/L
	Phenantrene	x	x	1.64	ng/L
	Anthracene	n.q	n.q	0.12	ng/L
	Fluoranthene	x	x	0.36	ng/L
	Pyrene	x	x	0.47	ng/L
	Benz[a]anthracene	x	x	0.05	ng/L
	Chrysene	x	n.q	0.07	ng/L
	Benzo(b)fluoranthene	x	x	0.04	ng/L
	Benzo(k)fluoranthene	x	x	0.03	ng/L
	Benzo(a)pyrene	x	x	0.03	ng/L
	Indeno(1,2,3-cd)pyrene	x	x	0.05	ng/L
	Benzo(g,h,i)perylene	x	x	0.05	ng/L
Dibenzo[a,h]anthracene	n.q	n.q	0.03	ng/L	

Table 6.9 Pesticides analyzed in P7 and B1; n.q = non quantified and X= quantified

Categories	Compound	P7	B1	LOQ	Units
CPesticides	Isoproturon	x	x	0.08	ng/L
	Dichlorvos	n.q	n.q	0.62	ng/L
	Diuron	x	x	1.54	ng/L
	DEA	n.q	x	0.19	ng/L
	Trifluralin	n.q	n.q	0.09	ng/L
	Dimethoate	n.q	x	2.66	ng/L
	Simazine	n.q	x	0.14	ng/L
	Atrazine	n.q	n.q	0.14	ng/L
	Tebuthylazine	n.q	x	0.04	ng/L
	Diazinon	n.q	n.q	0.17	ng/L
	Alachlor	x	x	0.14	ng/L
	Heptachlor	n.q	n.q	0.03	ng/L
	Terbutryn	x	x	1.33	ng/L
	Metolachlor	x	x	0.02	ng/L
	Chlorpyrifos	n.q	n.q	0.09	ng/L
	4,4-dichlorobenzophenone	n.q	x	0.04	ng/L
	Heptachlor epoxide B	x	x	0.03	ng/L
	Chlorphenvinfos	x	x	0.08	ng/L

Cybutrine	n.q	x	0.42	ng/L
α-Endosulfan	n.q	n.q	0.05	ng/L
β-Endosulfan	n.q	n.q	0.19	ng/L
Aclonifen	n.q	n.q	0.11	ng/L
Endosulfan sulphate	n.q	n.q	0.10	ng/L
Quinoxifen	n.q	n.q	0.21	ng/L
Dicofol p,p'	n.q	n.q	1.01	ng/L
Cypermethrin	x	n.q	2.90	ng/L
1,2,3 Trichlorobenzene	n.q	x	0.14	ng/L
1,2,4 Trichlorobenzene	n.q	x	0.13	ng/L
1,3,5 Trichlorobenzene	n.q	x	0.22	ng/L
Hexachlorobutadiene	n.q	n.q	0.35	ng/L
Pentachlorobenzene	n.q	x	0.05	ng/L
Hexachlorobenzene	x	x	0.05	ng/L
α-HCH	x	x	0.05	ng/L
β-HCH	x	x	0.02	ng/L
γ-HCH	x	x	0.05	ng/L
δ-HCH	x	x	0.02	ng/L
o,p'-DDE	x	n.q	0.07	ng/L
p,p'-DDE	x	x	0.05	ng/L
o,p'-DDD	x	x	0.03	ng/L
p,p'-DDD + o,p'-DDT	x	x	0.05	ng/L
p,p'-DDT	x	n.q	0.05	ng/L
Aldrin	n.q	n.q	0.01	ng/L
Isodrin	n.q	n.q	0.01	ng/L
Dieldrin	n.q	n.q	0.05	ng/L
Endrin	n.q	n.q	0.04	ng/L

Table 6.10. Toxicity of primary effluent P7 expressed as Effective Concentration that reduces bioluminescence 50% (EC₅₀), Toxicity Units (TU) and toxicity removal efficiency.

Figure 6.11. EC₅₀ and BOD₅/COD ratio vs TOD for primary effluent, P7.

6.3.4 Anaerobic digestion of Ozone pre-treated Sludge

6.3.4.1 Concept

Anaerobic digestion is a biochemical treatment performed in the absence of oxygen to stabilize organic matter while producing biogas, a mixture formed mainly of methane and carbon dioxide (Mata-Alvarez et al. 2014). The conversion of the organic matter into biogas is a process which involves several reactions and different groups of microorganisms (bacteria and archaea) (Basset 2015). The anaerobic digestion process may be subdivided into the following four phases (Figure 6.12):

1. **Hydrolysis:** complex organic matter is decomposed into simple soluble organic molecules.
2. **Fermentation or acidogenesis:** dissolved compounds present in cells of fermentative bacteria are converted into simple compounds (VFA, alcohols, lactic acid, CO₂, NH₃, H₂ and H₂S).
3. **Acetogenesis:** the fermentation products are converted into acetate, H₂ and CO₂.
4. **Methanogenesis:** Acetate and H₂/CO₂ are converted into methane (CH₄) and CO₂.

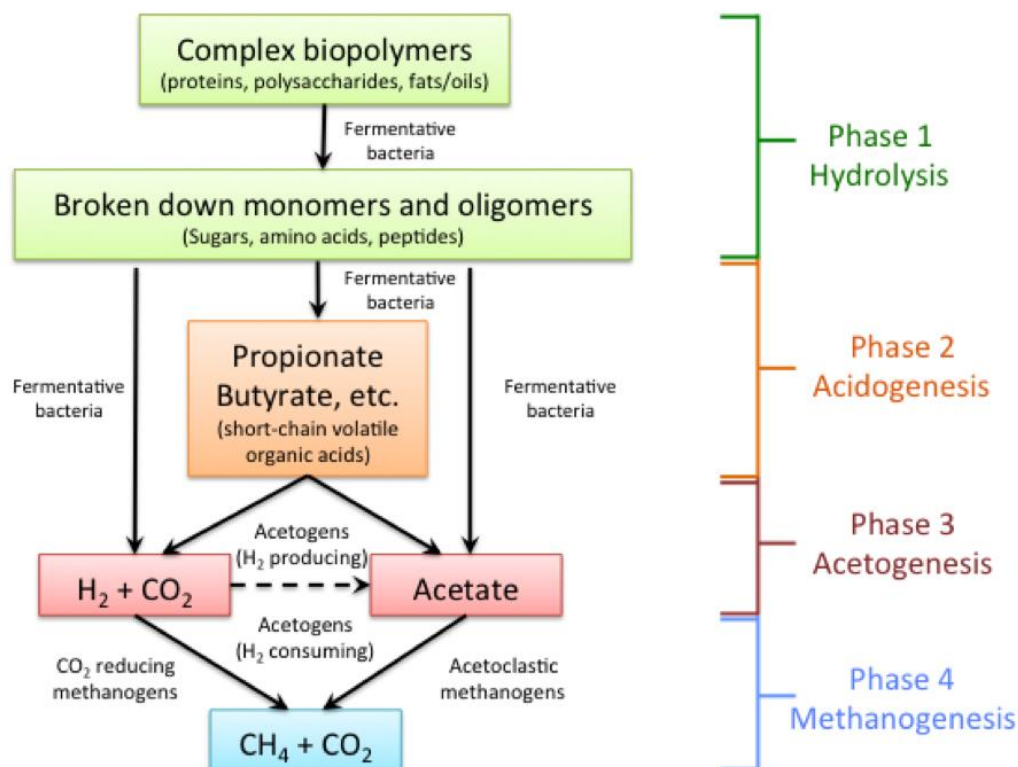


Figure 6.12. Phases of anaerobic digestion and biogas production. Source: Biobased Energy Education Materials Exchange System (BEEMS) - Modul B7

The anaerobic degradation is a slow process since waste activated sludge is mainly composed of biomass (Tanaka et al. 1997). Hydrolysis step is the rate-limiting step and for this reason, different studies have pointed out the importance to find an adequate pretreatment (Bougrier et al. 2006, Müller et al. 1998). In chapter 5, it has been shown that ozone application leads to partial sludge solubilisation. As a consequence of this solubilization, the biogas production increases and for instance, different studies suggested ozone as a possible suitable pretreatment (Bougrier et al. 2007, Weemaes et al. 2000). Moreover, these works proposed optimal ozone doses of: 0.1gO₃/g COD (Weemaes et al. 2000), 0.2 gO₃/ gSS (Yeom et al. 2002) and 0.15 gO₃/gTS (Bougrier et al. 2007). Indeed, the present work pretended to investigate if lower transferred doses (lower doses compared to the studies mentioned above) could promote an enhancement of the biogas production.

6.3.4.2 Sludge ozonation

Figure 6.13

Figure 6.13. (Left) Residual Total COD elimination (%), residual SVI (%) and θ_{COD} (%) versus TOD. (Right) Percentage of total COD removal for each TOD.

6.3.4.3 BMP test

The Biomethane potential test was performed in order to investigate the impact of ozone in the anaerobic digestion, methane production and to see which ozone dose is the more appropriate for the treatment.

Figure 6.14. Methane production along anaerobic treatment. A) Methane production represented considering the amount of volatile suspended solids (VSS) added and B) considering the amount of COD added.

On the other hand, during the acidogenesis stage the soluble compounds from the hydrolysis stage are transformed to VFA and to simple compounds (see Figure 6.12) by fermentative bacteria. Indeed, these volatile fatty acids (VFA) will be the precursors of the acetate product during the acetogenesis step. Since there are two major pathways for the methanogenesis (phase 4): one from H_2/CO_2 and the other from the acetate breaking down to CO_2 and CH_4 , named acetoclastic, the amount of VFA is significantly related with the methane production.

Table 6.11. Total VFA concentrations at the end of the batch experiment for each transferred dose.

Table 6.12. Biogas enhancement, methane content and methane production (accumulated at the end of the test)

6.4 Conclusions

After the benefits observed in ozone application on primary effluent (Chapter 4) and ozone application on sludge (Chapter 5), this chapter pretended to study the possible benefits of ozone application in subsequent possible biological steps of the treatment chain at the level of lab scale. To do so, ozone treatment has been applied to primary effluent and CAS which has been afterwards combined with biological (aerobic and anaerobic) treatment. All this chapter aimed to evaluate a possible synergetic between both chemical and biological oxidation. Thus, aerobic and anaerobic treatment have been used at lab scale as a biological treatments. Moreover, acute toxicity was tested by Microtox[®] toxicity test using luminescent *Vibrio Fischeri* bacteria in order to assure that ozone application do not increase the acute toxicity.

A new strategy consisting in ozone application on the primary effluent after the primary clarifier (inlet effluent of CAS) followed by a biological treatment with activated sludge has been tested to degrade micropollutants. In chapter 4, the benefits of ozone application in primary effluent have been presented. However, in this chapter the main objective was to analyze if the combined processes (chemical and biological) have a synergetic effect. To do so, different groups of micropollutants were analyzed: pharmaceuticals, surfactants, pesticides, PBDEs and PAHs.

6.5 Supplementary Information

Table 6.13. Initial concentration and removal percentages of the monitored pharmaceuticals of P6

Table 6.14. Initial concentrations and removals of anionic surfactants, alkylphenols and PBDEs for P6.

Table 6.15. Initial concentrations and removals of pesticides for P6.

Table 6.16. Initial concentrations and removals of PAHs for P6.

Table 6.17. Initial concentrations and removals of Paracetamol (pharmaceuticals) for P7.

Table 6.18. Initial concentrations and removals of anionic surfactants, alkylphenols and PBDEs for P7

Table 6.19. Initial concentrations and removals of pesticides for P7

Table 6.20. Initial concentrations and removals of PAHs for P7

Table 6.21. Initial concentrations and residual concentrations of screened Pharmaceuticals for B1

Table 6.22. Initial concentrations and residual concentrations of monitored pesticides for B1

Table 6.23. Initial concentrations and residual concentrations of monitored PAHs for B1.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

Looking back to the main objectives proposed for this thesis, the benefits of ozone application in non-conventional ozone application points have been tested in order to mitigate the micropollutant issue between others. The presented work was looking to assess the suitability of ozone in the water quality improvement. Moreover, technical aspects as ozone demand and organic matter evolution have been determined for the different matrices. These work aimed to investigate if application of ozone in non-conventional points of the treatment line could increase the benefits compared to the conventional ozonation at the end of the wastewater treatment. Hence, ozone has shown a great capability for micropollutant removal and organic matter degradation in different complex wastewater matrices. Ozone demand, micropollutant removal and water quality parameters have been studied for primary effluents obtaining positive results. Promising results were also obtained when ozone was applied in the activated sludge matrix both in the micropollutant removal and in the treatment of sludge excess and settleability. At the end of the thesis, it was investigated if the combination between ozone application in primary effluent followed by an aerobic biological treatment at lab scale promoted a positive synergetic effect. Good apparent removal has been obtained for the coupled treatment : ozonation followed by biological treatment. Moreover, once the ozone doses were selected for the desired variations on the primary effluent, acute toxicity was tested in order to have an indication on the ecotoxicological impact. A decrease on the acute toxicity for the primary effluent was observed at low TODs and no toxicity was observed for the secondary effluent. Finally, the project aimed to check if extra benefits were derived from sludge ozonation. Therefore, the combination of sludge ozonation and anaerobic digestion was tested to check if the process can improve the biogas production.

Even though the specific conclusions are given at the end of each chapter, the main conclusions are summarized in the following paragraphs.

- Thus, from Chapter 4 which is related to ozonation of primary effluent it can be pointed out:
 - ✓ Ozone application to primary effluents displays a positive impact on aggregate parameters (UV_{254} , tCOD and turbidity); it globally improves the primary effluent quality at ozone doses between 30 - 70mg/L depending on the sample.
 - ✓ For primary and biotreated effluents, the ozone consumption can be classically described by two characteristics which are the immediate ozone demand and the subsequent first order rate. Similar behaviors were observed in both effluents in terms of ozone consumptions and dissolved ozone profiles.
 - ✓ Average values are 298, 74 and 7 mg/L for Primary effluent from MWWTP close to Lyon, primary effluent from coastal MWWTP and biotreated effluent front coastal MWWTP, respectively. A positive trend has been detected between the IOD and the organic content.
 - ✓ The IOD completion stage covers the first high rate COD removal stage, fully for primary effluents and partially for tertiary effluents.
 - ✓ Regarding the ozone impact in organic matter, the comparison of variations in COD, UV absorbance and turbidity makes appear the major reaction of particulate matter. An

- important and fast oxidation was achieved for doses below 30 mg/L which enhances the water quality.
- ✓ Different behaviours were observed for the DOC families depending on the transferred ozone doses. Even though, few changes if any have been observed on dissolved organic matter categories at ozone dose transferred lower than the IOD.
 - ✓ The first kinetic stage of organic matter removal covers totally the IOD completion in the case of primary effluents.
-
- From Chapter 5 where ozone is applied to CAS (mixed liquor), it can be concluded:
 - ✓ COD, TN, pH and UV_{254} parameters described sludge solubilization upon CAS ozonation and a correlation was found between solubilization and IOD stage completion.
 - ✓ Even at low doses (under 10 mgO₃/ gSS), solubilization takes place and it is related with an improvement of the sludge settleability reducing the SVI between 2 and 45%.
 - ✓ Depending on the conditions, ozone attack would rather occur on the particulate matter at the beginning of the reaction.
 - ✓ Ozone might quickly and selectively react with the studied pharmaceuticals present in solid and/or liquid phases despite the fact that the working matrix is a complex sludge matrix presenting a high ozone demand. Regarding the results, ozone reacts simultaneously to both phases. Moreover, for low ozone doses (0 – 0.03 g/gSS) high pharmaceutical removal was observed achieving in some cases an elimination of 100% (Carbamazepine).
 - ✓ Regarding micropollutants that are absorbed in the sludge phase and supernatant phase (carbamazepine and propranolol), neither absorption nor desorption were observed but elimination in both phases.

 - ✓ In summary, ozone application on sludge improves sludge quality and limitates not only the micropollutant discharge on the water effluents but the micropollutants discharge via sludge deposition for reuse.
-
- In Chapter 6, the combination of ozone oxidation and the subsequent biological treatment was analyzed to evaluate a possible synergetic effect. In this case, it can be highlighted:

✓

7.2. Recommendations

8. RESUM EN CATALÀ

8.1. Breu introducció i objectius

La nostra societat formada per diferents cultures i realitats esta organitzada principalment en ciutats i àrees residencials. Des de fa anys, el sistema de tractament d'aigua i de sanejament d'aquestes ciutat ha estat estudiat i planificat per proporcionar una millora en la qualitat de vida dels habitants i promoure ciutats netes i organitzades.

Els avenços econòmics, tecnològics i socials han promogut la millora en l'estil de vida però a la vegada han posat sota pressió als recursos hídrics. Aquest fet genera repte per la nostra i les futures generacions.

Els darrers anys, una major consciència col·lectiva del medi ambient esta imposant-se, fet que es tradueix en un major enteniment dels riscos i conseqüències de l'impacte ecològic de les ciutats. Respecte aquest fet, actualment, hi ha una ambició col·lectiva per reduir l'impacte ecològic i per transformar les ciutats en ciutats més sostenibles. En aquest escenari, es necessari millorar el sistema de tractament d'aigües, per facilitar el reus i per minimitzar el seu consum.

La millora dels sistemes de tractaments d'aigua impliquen modificacions a gran escala. Tot i així, per fer-ho possible, diferents estudis a escala pilot i de laboratori han de realitzar-se prèviament. Al final, els diferents resultats obtinguts a petita escala participen en la millora del sistema de sanejament. Per tant, aquest treball pretén participar en aquest procés d'investigació i millora.

Extensos treballs d'investigació han estat realitzats aplicant ozó al final de la línia de tractament d'aigües, especialment en el tractament terciari i a les plantes potabilitzadores. L'ús d'aquest oxidant en altres punts de la cadena de tractament, sovint ha generat dubtes i una certa reticència. Tot i així, el treball que es presenta té com a objectiu trobar els possibles beneficis de la aplicació d'ozó en punts no convencionals de la línia de tractaments d'aigües.

Diferents estudis s'han realitzat i es realitzen en el marc de la Unió Europea respecte factors mediambientals. L'Eurobaròmetre de l'any 2012 va mostrar que el 68% de la població consideraven com problemes importants els problemes relacionats amb l'aigua (EU-Comission 2012). Mirant enrere, durant la dècada dels anys noranta, la pressió per un reformulació de la política relacionada amb l'aigua va augmentar. Així, a l'any 2000, com a resultat de les pressions dels anys anteriors, la Directiva 2000/60/EC va ser publicada amb l'objectiu d'identificar substàncies perilloses per l'ecosistema aquàtic (Directive 2000, Ribeiro et al. 2015). Uns anys després, a l'any 2008, la Directiva 2008/105/EC va ser presentada, establint els estàndards de qualitat mediambiental per 33 substàncies considerades de prioritat, i 8 contaminants (Directive 2008, Ribeiro et al. 2015). A l'any 2013 es va presentar la darrera directiva europea amb l'objectiu d'establir accions preventives, la Directiva 2013/39/EU. Aquesta, es basa en el reconeixement de les causes de la contaminació, intentant actuar en els punt d'abocament del contaminants, desenvolupant tecnologies alternatives i assequibles pel tractament d'aigües (Directive 2013, Ribeiro et al. 2015). Actualment la Directiva Marc de l'Aigua inclou 45 substàncies amb els seus respectius estàndards de qualitat mediambiental. La darrera directiva també es fixa en la ecotoxicitat produïda per aquests compostos. En aquest escenari, la importància de les tecnologies d'oxidació avançada i la recerca relacionada amb aquestes augmenta com a tecnologies alternatives.

Així els objectius generals del treball presentat són:

- Com a objectiu global, analitzar els possibles beneficis d'aplicar ozó en punts no convencionals de la línia de tractament d'aigua.
- Avaluar l'impacte de l'ozó en la qualitat dels efluent principalment en l'eliminació de microcontaminats i matèria orgànica present als efluent
- Per tant, la recerca realitzada també pretén estudiar la viabilitat del procés d'ozó per la millora de la qualitat de l'aigua.

A continuació, es presenten els objectius concrets de la Tesi Doctoral:

- Aplicació de l'ozó en efluent primaris: anàlisi d'aspectes relacionats amb la demanda d'ozó, la reactivitat d'aquest oxidant amb la matèria orgànica present, evolució dels paràmetres de qualitat de l'aigua i els microcontaminants. A més, d'analitzar com influeix l'aplicació de l'ozó amb els canvis en els diferents grups de la matèria orgànica.
- En segon lloc, es pretén analitzar l'impacte de l'ozonització en els fangs provinents del tractament biològic, i així estudiar com afecta l'ús d'ozó en la qualitat i el comportament dels fangs. D'altra banda, s'ha investigat com afecta l'aplicació d'ozó en la eliminació i comportament dels microcontaminants.
- Finalment es pretén investigar la combinació de l'ozonització amb processos biològics, per tal d'examinar les possibles millores produïdes per l'ozó com a pretractament. Així s'ha combinant l'ozonització a baixes dosis amb tractaments biològics aeròbics i anaeròbics. En el cas del tractament anaeròbic s'ha volgut estudiar si l'aplicació d'ozó pot produir un increment en la producció de biogàs.
- Comparació de l'ozonització en l'efluent primari i en l'efluent secundari.
- Estudi de la toxicitat aguda dels efluent abans i després de l'aplicació de l'ozó i la relació amb la seva biodegradabilitat.

Així considerant els punts ja esmenats, l'aplicació de l'ozó en aquesta tesi ha estat focalitzada en el punt 1. i el punt 2. de la Figura 1 per tal d'investigar quin dels dos tractaments es més genera més beneficis.

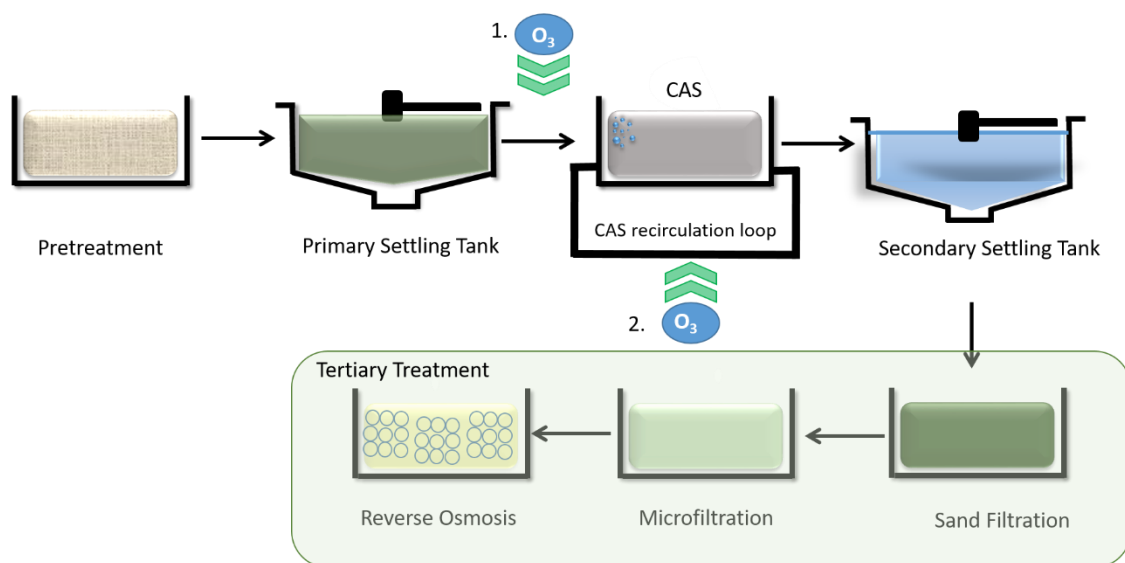


Figura 1. Estratègia en l'aplicació de l'ozó

8.2. Introducció

La recerca s'ha dut a terme en el marc del Projecte TRIUMPH (Projecte ACQUEAU) en col·laboració directe amb Degremont SAS.

Importància de l'aigua, perspectives i desenvolupament sostenible

L'aigua és químicament el resultat de dos enllaços entre l'oxigen i dos àtoms d'hidrogen. A més de la seva importància biològica, l'aigua es el centre del nostre desenvolupament. Així un sistema de tractament d'aigües col·lectiu i sostenible, les infraestructures relacionades amb el tractament de l'aigua i la qualitat d'aquesta tenen un rol important en els estàndards de qualitat de vida, en el creixement econòmic i la cohesió social (WWAP 2016).

La disponibilitat de l'aigua i la seva distribució depèn principalment en el cicle continu d'evaporació, precipitació i escorrentia. Tot i així, les accions humanes interfereixen amb el cicle natural de l'aigua i per tant han de ser considerades quan s'analitza el cicle globalment.

Diferents situacions col·loquen els recursos hídrics sota pressió: el creixement poblacional, els canvis en els patrons de consum i el canvi climàtic són alguns exemples (WWAP 2015, 2016). A més podríem classificar l'escassetat de l'aigua en tres nivells: escassetat física, escassetat econòmica i escassetat institucional.

En aquest escenari on la problemàtica recau tant en la qualitat de l'aigua com en la quantitat a nivell global, la recerca i el desenvolupament han generat noves tecnologies emergents les quals poden promoure l'ús de recursos d'aigua alternatius. En alguns països, el reus d'aigües municipals residuals representa el 35% del total d'aigua utilitzada (WWAP 2016). Per tant, avui en dia, es pot afirmar que l'aigua utilitzada té un valor afegit. La recuperació de recursos i l'anàlisi de possibles riscos relacionats amb el reus d'aigües residuals estant guanyant importància si ens fixem en el context econòmic i mediambiental. Així, accions importants estant sent considerades per tal d'agilitzar la innovació i el desenvolupament, establint ,en molts casos, enllaços entre la recerca, les opcions de mercat, opinió pública, les institucions i el medi ambient.

Reutilització de les aigües residuals

El reús d'aigües residuals pot representar una opció real per recuperar una quantitat d'aigua que permetria cobrir una part de la demanda d'aigua existent. Aquesta aigua podria ser utilitzada per la irrigació d'àrees urbanes o d'agricultura, per usos recreatius, com sistemes de refrigeració i per enriquir les aigües subterrànies (Bixio et al. 2006, Rizzo et al. 2013). Tot i així, diferents mesures s'ha de dur a terme per tal d'impulsar l'ús d'aigua reutilitzada, entre elles:

1. Modificació de la legislació relacionada amb la reutilització d'aigua
2. Intensificació de la col·laboració entre les diferents parts encarregades de la gestió de l'aigua.
3. Definició de protocols per el reús de aigües residuals
4. Promoure el seu ús mitjançant compensacions econòmiques
5. Fer divulgació i fer créixer el seu suport social.

En aquest àmbit, el repte es aconseguir la qualitat i quantitat suficient mitjançant el processos més sostenibles. A més, cal definir diferents nivells de qualitat per diferents usos i trobar diferents tecnologies per assegurar que s'arriba als límits acordats. Per exemple, l'aigua reutilitzada que es dediqui a la agricultura i la irrigació urbana, cal que compleixi uns estàndards mínims ja que els contaminants es poden bioacumular en plantes i organismes (Fatta-Kassinos et al. 2016).

A més la toxicitat és un aspecte que també s'ha de considerar quan es vol trobar nous usos a l'aigua residual reutilitzada. De fet, es necessari realitzar un ventall de bioanàlisis per tal de detectar qualsevol impacte en els diferents nivells d'organismes. Efectes adversos han estat detectats al nivell de ng/L en el cas d'exposicions cròniques i de µg/L en el cas de la toxicitat aguda (Fatta-Kassinos et al. 2016).

Característiques de les aigües residuals

Les característiques de les aigües residuals varien molt en funció de cada comunitat. Les aigües residuals es podrien definir com la combinació de residus líquids i transportats per l'aigua provinents de residències, institucions, àrees comercials i industrials i generalment barrejades amb aigües subterrànies i superficials (Tchobanoglous and Burton 1991).

Es important ser conscient de la composició de l'aigua residual ja que pot ser útil per entendre les interaccions entre els compostos orgànics e inorgànics presents (Shon et al. 2006). Així definim matèria orgànica de l'efluent a la matèria orgànica que es troba present en aigües residuals. Aquesta matèria orgànica està caracteritzada principalment per 3 components:

1. La matèria orgànica natural: originada de la descomposició de les plantes i dels microorganismes, es troba també en sòls i sediments.
2. Els compostos orgànics sintètics: en aquesta categoria trobem des de els contaminants orgànics convencionals fins als emergents, en general han estat introduïts en el medi ambient a causa de l'acció de l'home.
3. Els productes microbians solubles: són substàncies polimèriques extracel·lulars. Es generen biològicament a partir del metabolisme d'un substrat durant el creixement de la biomassa i s'alliberen a través de la membrana cel·lular o excretats.

D'altra banda, la matèria orgànica dissolta és un dels majors components de la matèria orgànica de l'efluent, ja que pot arribar a contribuir amb un 86% de la DQO (Shon et al. 2006).

Plantes convencionals de Tractament de les aigües residuals municipals i els microcontaminants

En general les plantes de tractament d'aigües residuals urbanes estan organitzades en quatre etapes principals que inclouen processos físics, químics i biològics. La primera etapa sovint conté un sistema de cribratge de major a menor amb un seguit de reixes i tamisos i té com a objectiu la eliminació dels sòlids. En segon lloc, el tractament primari pretén eliminar els sòlids suspesos mitjançant un conjunt de decantadors i sedimentadors. El tractament biològic secundari té com a objectiu degradar la part biodegradable de la matèria orgànica, sovint present en forma dissolta. Finalment trobem un tractament terciari addicional que inclou diferents etapes de filtració i desinfecció. D'altra banda, és important optimitzar el consum d'energia que es necessita durant el tractament d'aigües residuals. Així, dintre dels objectius futurs podem definir:

- Minimització de l'energia necessitada pel tractament d'aigües residuals
- Reducció de l'impacte ecològic
- Promoció de la autosuficiència de les plantes de tractament.

Tot i així, efectes ecològics s'han observat a les sortides de les plantes de tractament d'aigües residuals, probablement a causa de la eliminació únicament parcials dels contaminants per part de les plantes de tractament convencionals (Margot et al. 2015). L'anàlisi i la comprensió del

comportament del contaminants en les plantes de tractament convencionals és imprescindible per crear mesures i reduir la descarrega d'aquest al medi.

Hi ha diferents mecanismes que poden afectar els microcontaminats durant el procés de tractament. Entre ells: adsorció en els fangs o en la matèria particulada, la transformació biològica, la volatilització i en menor mesura la degradació abiòtica.

A més, podem classificar els microcontaminants en diferents grups: tensioactius, fàrmacs, hormones esteroïdal, productes d'ús personal com ambientadors, cremes per la protecció del solar, repel·lent d'insectes o desinfectants; pesticides, hidrocarburs policíclics aromàtics i retardants de flama.

Processos d'oxidació avançada i l'ozonització

En aquest escenari de contaminació aquàtica, els processos d'oxidació avançada sorgeixen com a possible alternativa per tractar els compostos que són biològicament persistents millorant la qualitat de l'aigua i per tant restaurant el ecosistema aquàtic. Aquests processos, degraden els microcontaminants mitjançant la formació de radicals hidroxils els quals són altament reactius i no selectius (Glaze et al. 1987). Avui en dia, també es poden considerar altres tipus de radicals com els radicals sulfat (Anipsitakis and Dionysiou 2003, De Luca et al. 2016). Els processos d'oxidació avançada, poden oxidar i mineralitzar diferent compostos orgànics, però aquests processos estan considerats com processos cars i actualment, la tendència es utilitzar-los com a pretractament per convertir els microcontaminants persistents en productes més biodegradables.

Així, per l'aplicació de cada procés, experiments a escala de laboratori han de ser considerats per identificar tots els possibles efectes de l'efluent: formació de intermediaris més recalitrants, falta de selectivitat en les fraccions més recalitrants o excés en la dosis d'oxidant.

L'ozó s'utilitza en el tractament d'aigües residuals, desinfecció i tractament de l'aire per tal de minimitzar la contaminació. Aquest tractament té dos punts forts: el primer es el gran potencial oxidant i el segon, el fet que no generi residus. D'altra banda, també cal considerar que quan l'ozó pot generar radicals hidroxils quan aquest es descomposa. Els radicals hidroxils tenen un potencial oxidant major que l'ozó molecular però són menys selectius.

Per tant, l'ozó pot reaccionar de dues maneres diferents:

- Via directa: quan reacciona molecularment, aquesta via es caracteritza per la alta selectivitat
- Via indirecta : quan reacciona mitjançant el radical hidroxil, són reaccions ràpides i poc selectives.

Inicialment, la formació de subproductes a partir de la ozonització com aldehids, bromats i N-nitrosodimethylamines no es va considerar important. Tot i així, actualment, l'ús d'aquestes tecnologies es pot aplicar per obtenir aigua pel consum humà i per tant aquest fet resulta crucial i s'ha de seguir estudiant i analitzant.

Durant aquests darrers anys, l'ozó s'ha utilitzat en diferents aplicacions: aigua pel consum, en el tractament d'aigües residuals, aigües de piscines i aigües industrials.

8.3. Materials i Mètodes

En aquesta secció es presenten tant les instal·lacions utilitzades, les condicions dels experiments i la metodologia utilitzada pels anàlisis realitzats.

Instal·lació d'Ozó

Els experiments d'Ozó es van dur a terme a escala de laboratori en un reactor semi continu de 2.5L amb un volum de treball de 2L. Els experiments es varen dur a terme sense ajust de pH i la temperatura es va mantenir constant a 20 °C. L'ozó es produeix a partir d'oxigen pur (Linde, Alemanya) mitjançant el generador d'Ozó Sander Labor 301.7 (Sander, Alemanya). L'ozó gas va ser injectat per la part baixa del reactor amb un difusor en forma de plat i de vidre porós. L'agitació mecànica va assegurar el bon contacte i transferència entre el líquid i el gas. Diferents velocitats d'agitació van ser aplicades en funció de l'efluent: 750 rpm pels fangs i 1000 rpm per l'efluent primari.

Per tal de determinar la dosis transferida d'ozó, s'ha de realitzar un balanç. Per aquest motiu, les concentracions d'ozó van ser mesurades en la fase gas i la fase líquida gràcies a tres analitzadors. La concentració d'entrada es va mesurar amb l'analitzador BMT 963 BT(BMT Messtechnik GMBH, Alemanya) i la concentració de sortida amb el BMT 964 BT (BMT Messtechnik GMBH, Alemanya). En el cas de la fase aquosa, l'ozó va ser mesurat mitjançant el sensor Q45H/64 (Analytical Technology, US) col·locat en la recirculació. Totes les dades dels experiments es van emmagatzemar en la memòria DaqPRO™ (Fourtec Fourier Technologies, USA).

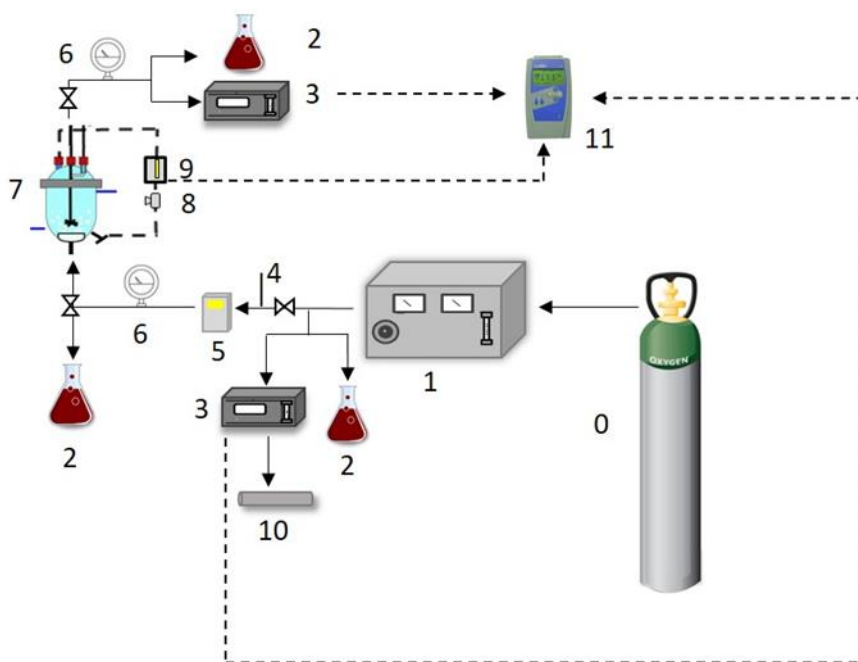


Figura 2. Instal·lació pels experiments d'ozó

0. Bombona d'Oxigen; 1. Generador d'ozó; 2. Solució de KI ; 3. Analitzador d'ozó per la fase gas; 4. Termòmetre; 5. Cabalímetre; 6. Manòmetre; 7. Reactor; 8. Bomba peristàltica; 9. Sensor per la mesura de l'ozó dissolt; 10. Destructor Químic d'ozó; 11. Datalogger.

Experiments biològics aeròbics

Els experiments biològics van ser duts a terme a escala de laboratori i en reactors discontinus de 5L amb un volum de treball de 4.5L. Els tres reactors van funcionar en paral·lel a temperatura

ambiental i durant 4 hores: un va ser omplert amb efluent primari sense ozonitzar i els altres dos amb mostres d'efluent primari pretractades amb ozó. La relació de la DQO entre el substrat i la biomassa va ser de 0.24. Tres agitadors magnètics van ser utilitzats per homogenitzar els reactors biològics (300 rpm). L'oxigen dissolt es va monitoritzar amb el Mesurador d'Oxigen Portable HI98193 (Hanna instruments, USA). Els reactors van ser coberts amb paper d'alumini per evitar la proliferació d'algues a conseqüència de la incidència de la llum.

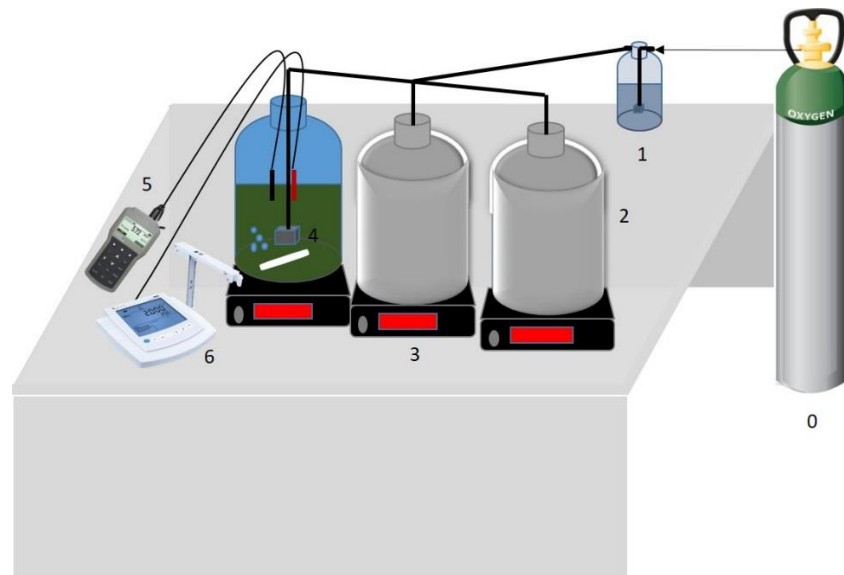


Figura 3. Instal·lació pel tractament biològic aeròbic

Experiments biològics anaeròbics- Test BMP

El test BMP per la mesura del biogàs es va realitzar en unes ampolles de 115mL tancades amb un septum fixat amb segellat amb un tap d'alumini. Les ampolles van ser omplertes amb 15mL de l'inòcul, establint una relació de 0.5 entre la DQO del substrat i de l'inòcul. El volum de treball va ser ajustat a 80mL mitjançant aigua desionitzada. Abans de segellar les ampolles, es va bombollear nitrogen (1 min, 3L/min) en el contingut de cadascuna. La sobrepressió generada durant la primera hora va ser eliminada. La temperatura es va mantenir constant en condicions mesòfiles, a 37°C. Els reactors van ser agitats en un agitador orbital i el test es va dur a terme durant 28 dies. La producció de biogàs va ésser mesurada utilitzant el mesurador de pressions Ebro-VAM 320. El contingut de metà acumulat en cada ampolla va ser mesurat per cada mostra amb un Cromatògraf de gasos. El test es va dur a terme per triplicat.



Figura 4. Material per dur a terme el Test BMP

Anàlisis realitzats

Diferents anàlisis s'han dut a terme per tal de mesurar els canvis i els valors de la matèria orgànica. Entre ells, la determinació del carboni orgànic dissolt, el carboni inorgànic i el nitrogen total. Aquests paràmetres s'han mesurat amb el Shimadzu TOC 5055 analyzer (Shimadzu, Japó) i la mostra s'ha hagut de filtrar prèviament. D'altra banda també s'ha mesurat la demanda química d'oxigen (DQO), i la demanda biològica d'oxigen per tal de tenir informació de la matèria oxidable tant biològicament com químicament. També s'ha mesurat el grau d'aromaticitat mitjançant absorbància UV i el contingut iònic amb el cromatògraf iònic 861 Advance Compact IC (Metrohm, Switzerland). L'alcalinitat de les mostres va ser mesurada mitjançant el titrador automàtic CRISON pH Burette 24 (CRISON, Spain). La toxicitat aguda es va mesurar en el cas d'algunes mostres amb el Microtox® Toxicity Test. El contingut en sòlids: sòlids suspesos totals, sòlids suspesos volàtils, sòlids totals i sòlids totals volàtils van ser mesurats seguint els protocols dels Standard Methods 2540.

D'altra banda, els anàlisis dels microcontaminants es van realitzar en col·laboració amb el Laboratori d'espectroscòpia de masses del IDAEA/CSIC.

A més, altres anàlisis en relació a la matèria orgànica es van realitzar en col·laboració amb el laboratori DOC-Labor –Dr.Huber. D'aquesta manera es va poder separar la matèria orgànica en diferents fraccions en funció de la mida de la molècula.

Origen i característiques de les mostres d'aigües residuals

El mostreig es va realitzar principalment en dues plantes de tractament d'aigües municipals. La primera, WWTP-A, es troba en una àrea costanera de la província de Tarragona. Aquesta és una planta de tractament convencional que utilitza com a tractament biològic fangs activats i que conté un tractament terciari. El tractament terciari es gestionat per un club de golf que té com a objectiu reutilitzar l'aigua per irrigació. El tractament terciari consisteix en filtració de sorra seguida per microfiltració i osmosis inversa. La segona WWTP-B, en canvi, es troba localitzada prop de Lyon. Esta constituïda per dos línies: una amb fangs activats i l'altre amb reactors de biofilm de llit mòbil (MBBR) com a tractament biològic. Tot i així, totes les mostres recol·lectades per aquest estudi corresponen a la línia de fangs activats.

En la següent figura, estan presentat els tres punts de mostreig utilitzats en aquesta tesi. De totes maneres, la mostra recol·lectada en el decantador del efluent secundari és va col·lectar per recolzar l'estudi de l'impacte de l'ozó en l'efluent primari. Per tant, les campanyes de mostreig més significatives son les de la sortida del decantador primari i les de la recirculació dels fangs activats.

A continuació es descriuen els rangs dels paràmetres de qualitat de l'aigua per les diferents campanyes de mostreig. Així el rang de la dqo en el cas dels fangs activats es de 3.0-6.9 g/L i per l'efluent primari es 0.27-0.89 g/L. El carboni orgànic dissolt es va trobar en un rang de 9 a 260 mg C/L per els fangs activats i entre 69 i 110 mgC/L per l'efluent primari. L'aromaticitat descrita pel UV_{254} va ser entre 27-96 m^{-1} per l'efluent primari i 10-253 m^{-1} pels fangs activats.

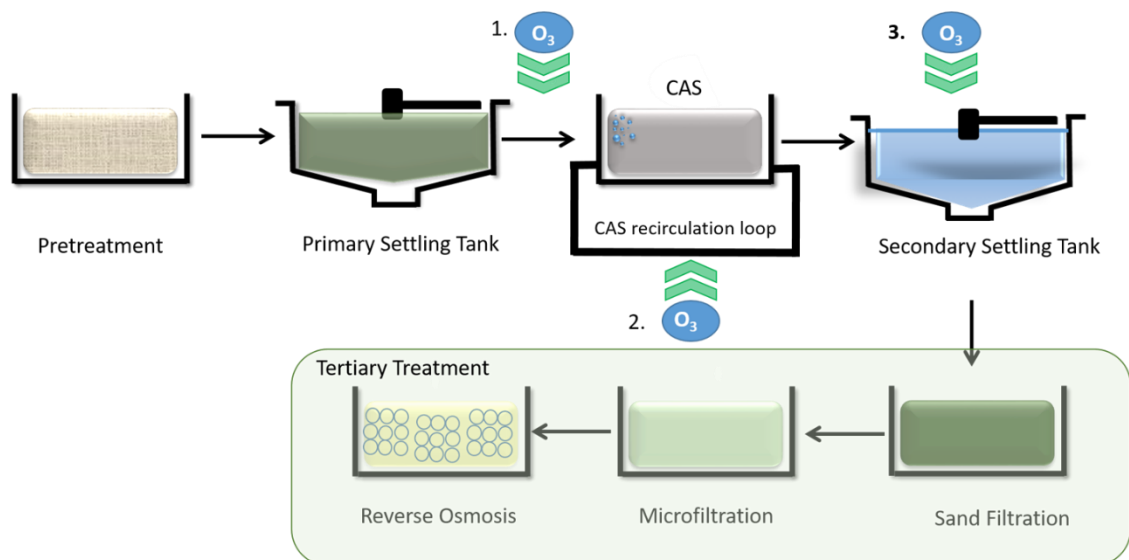


Figura 5. Punts de mostreig a la Planta de Tractament d'Aigües residuals.

8.4. Resultats

Aplicació de l'ozó en l'efluent primari

La reactivitat de l'ozó està altament relacionada per la manera i la cinètica de la descomposició de l'ozó. Així, en aquest capítol es va decidir investigar i determinar la constant de descomposició de l'ozó (k_d), el coeficient de transferència de massa (K_{La}) i la demanda inicial d'ozó (IOD). La demanda inicial d'ozó es defineix com la mínima quantitat d'ozó transferida a l'efluent que permeti detectar ozó dissolt en la fase aquosa.

Taula 1. Valors de k_d , K_{La} i IOD pels diferents tipus d'effluents.

Mostres	K_{La} (min^{-1})	k_d (min^{-1})	IOD mg/L
P1	0.83	0.80	64
P2	0.76	0.19	83
P3	0.50	0.66	348
P4	0.79	0.30	249
T1	1.89	0.08	5
T2	0.67	0.10	10
D1	1.97	0.08	3
V1	3.94	0.09	3

En la Taula 1 es presenten els resultats de la k_d , K_{La} i IOD per quatre efluents primaris (P1, P2, P3 i P4), dos efluents terciaris (T1, T2), una mostra d'aigua de l'aixeta (V1) i una mostra d'aigua embotellada (D1). En el cas de l'efluent primari, els valors de la constant de descomposició, k_d , són majors que en els altres efluents mostrant l'efecte d'un contingut major en matèria orgànica. A més, els valors de la IOD, també estan correlacionats amb el contingut de matèria orgànica, observant valors més elevats en el cas de l'efluent primari, seguit de l'efluent terciari i trobant amb els valors menors a l'aigua embotellada i de l'aixeta. A més, les diferències trobades en els valors d'aquests paràmetres es poden atribuir a la natura i la càrrega de contaminació dels efluents. Aquest fet també es pot observar representat a la Figura 6, on es

diferencien 3 zones en funció del efluent i del seu contingut en matèria orgànica. Així a la zona 1 hi trobem els efluent amb baixa càrrega orgànica com l'aigua embotellada, l'aigua de l'aixeta i l'efluent terciari. En canvi, a la zona 2, hi trobem els valors corresponents a l'efluent primari amb més baix contingut de matèria orgànica (P1 i P2). Finalment, a la zona 3 trobem els valors corresponents als efluent primaris amb una càrrega major de matèria orgànica, P3 i P4.

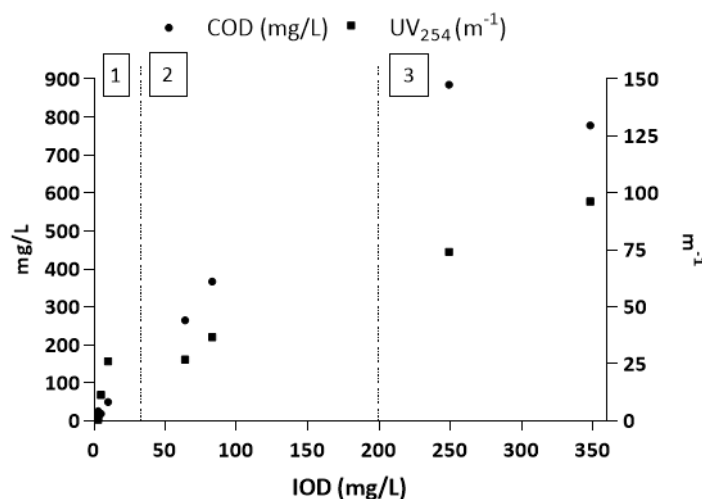


Figura 6. DQO (eix esquerre) i UV₂₅₄ (eix dret) vs IOD per P1, P2, P3, P4, T1, T2, D1 i V1.

A continuació, l'evolució dels paràmetres analitzats en les aigües residuals es van investigar en relació amb la TOD i la IOD (Figura 7A). Així, quan ens fixem en les corbes de DQO, dos etapes poden ser clarament diferenciades. Les dues fases d'oxidació encara s'observen més pronunciades quan la corba cinètica es evalua (Figura 7B). Els resultats suggereixen que la constant cinètica relacionada amb la primera etapa, varia en funció de l'origen de l'aigua residual i per tant, de la composició d'aquesta. En canvi, en el cas de les constant cinètiques de la segona etapa, són similars en tots els casos. La transició entre una fase o l'altre es va produir després de 5 minuts de temps de contacte, i per tant la constant cinètica relacionada amb aquesta fase es va calcular entre els temps 0 - 5 minuts. Comportaments similars es van detectar entre efluent primaris i terciaris.

L'absorbància UV₂₅₄ es un paramtre directament enllaçat amb el contingut the compostos insaturats i substàncies aromàtiques dissoltes en els efluent. Tot i que no es mostra la gràfica en aquest resum, en el cas de l'absorbància UV₂₅₄, un ràpid decreixement es va observar abans d'arribar a la IOD. Aquest esdeveniment encaixa amb el fet que la majoria dels compostos que absorbeixen a la longitud d'ona de 254nm, són compostos orgànics amb dobles enllaços i sistemes aromàtics el quals estan relacionats amb l'ozó. A la vegada també concorda amb els resultats obtinguts en referència a la evolució de la DQO i per tant dues fases també poden ser diferenciades.

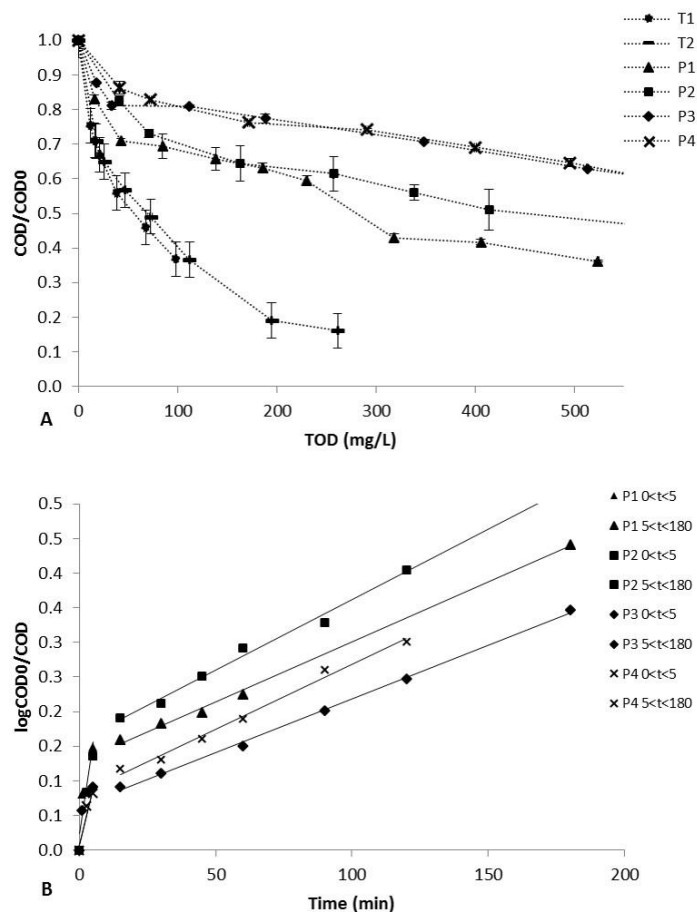


Figura 7. A) DQO/DQO0 versus la dosis transferida d'ozó (TOD). B) LN(COD0/COD) versus el temps de contacte per efluents primaris.

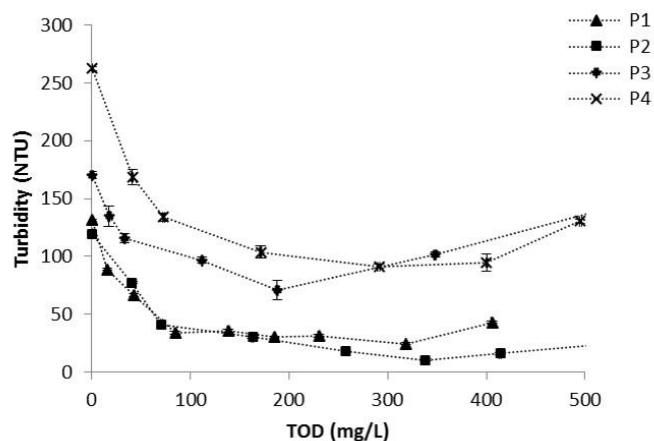


Figura 8. Evolució de la terbolesa versus la dosis d'ozó transferida (TOD) per efluents primaris

Com s'ha presentat a les gràfiques anteriors, l'ozó ataca la matèria orgànica sòlida des del primer moment de la reacció. Per tant, s'ha observat una reducció des de l'inici de la reacció del contingut en sòlids i un decreixement de la terbolesa. La Figura 8 presenta la variació de la terbolesa a mesura que avança la reacció amb l'ozó. Un decreixement ràpid s'observa a l'inici de la reacció, quan dosis baixes d'ozó han estat transferides. Per tant, hi ha una influència significativa del contingut de partícules en els valors de IOD. D'altra banda, un precipitat blanc s'observa al final de la reacció, fet que comporta un augment de la turbidesa.

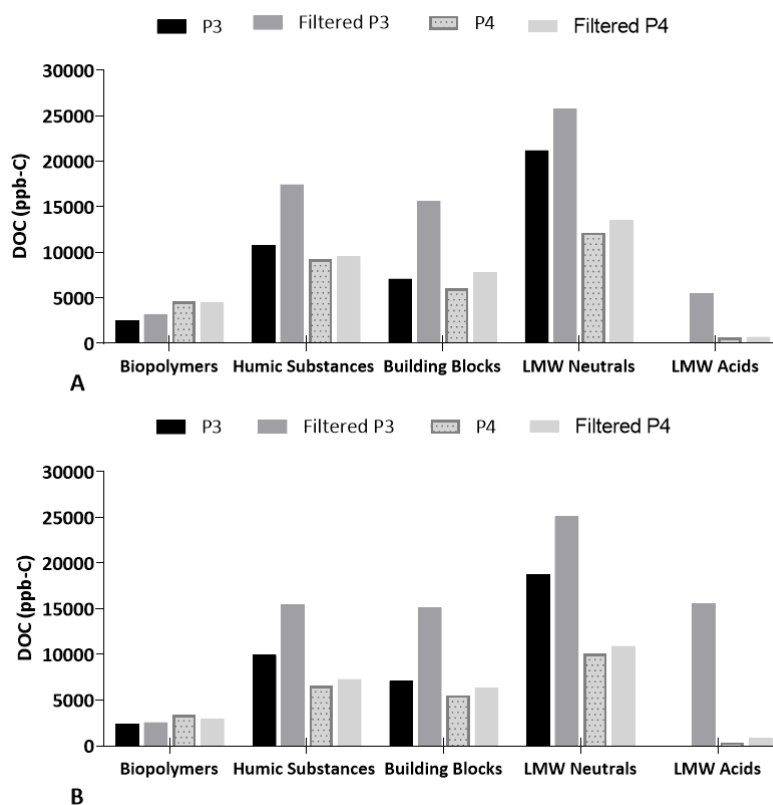


Figura 9. A) Fraccions de matèria orgànica per P3 i P4 abans i després de l'ozonització. B) fraccions de matèria orgànica per P3 i P4 abans i després de l'ozonització, amb la mostra prèviament filtrada.

Altres experiments es van realitzar per tal d'analitzar la funció i/o l'impacte dels sòlids durant l'ozonització d'efluents primaris. Durant aquests experiments, es van analitzar canvis en les diferents fraccions de matèria orgànica en efluents primaris de procedència urbana. Les fraccions que es van estudiar són: els biopolímers, la substàncies húmiques, els "Building blocs", els compostos de baix pes molecular neutres i àcids. Aquests experiments es van realitzar amb l'effluent prèviament filtrat i sense filtrar per tal de comparar l'impacte dels sòlids. Tot i així, no es van observar canvis significatius en les diferents famílies de matèria orgànica com es pot observar en la Figura 9.

Finalment es va comprovar quin impacte té l'ozó sobre els microcontaminants presents en l'effluent primari. Un dels objectius era investigar si l'ozó atacaria a la matèria orgànica i als microcontaminants o bé únicament a la matèria orgànica. 25 compostos van ser analitzats, incloent: halurs orgànics, tensioactius no-ionics i aniònics i fàrmacs. En el cas dels fàrmacs diferents grups van ser analitzats: Antibiotics, anti-inflamatoris, analgèsics, fungicides, antiepilèptics i β - blocadors. A més, les diferents dosis d'ozó transferides van ser inferiors a 25 mgO_3/L

Figura 10. Eliminació de fàrmacs anti-inflamatoris i analgesics versus TODs (mg/L)

Aplicació de l'ozó en els fangs activats del tractament biològic convencional

L'aplicació de l'ozó en els fangs activats del tractament biològic pot aportar beneficis tant en la quantitat com en la qualitat dels fangs: millores en la decantació, sedimentació dels fangs i la reducció de l'excés de fangs i eliminació de contaminants presents en els fangs.

Respecte els fangs, en primer lloc es va analitzar l'impacte de l'ozó en la solubilització de la matèria orgànica. Per poder dur-ho a terme es va mesurar la DQO soluble i particulada, el carboni inorgànic (IC), l'absorbància UV (a una longitud d'ona de 254 nm) i el nitrogen total (TN).

Com es mostra a la figura 11, la màxima solubilització (θ_{COD}) observada va ser 24, 21 i 19% per S4, S5 i S6. Després d'aquest màxim, es produeix un lleu decreixement que coincideix amb la obtenció de la IOD, i per tant a partir d'aquest moment ja es pot detectar ozó en la fase aquosa. Comportaments similars van ser observats en el cas del nitrogen total, el carboni inorgànic i la UV_{254} .

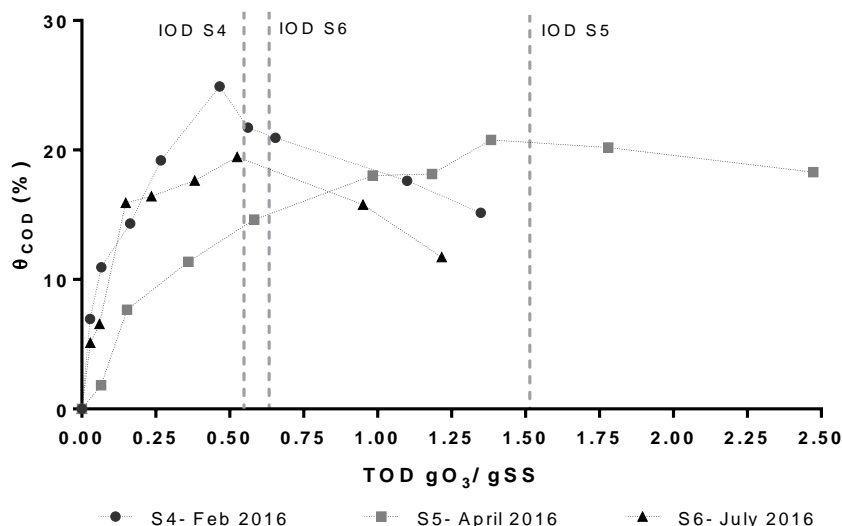


Figura 11. Solubilització de la DQO versus la dosi d'ozó transferida (TOD)

L'ozó ataca una part de la matèria sòlida i suspesa que componen els fangs i transforma el contingut sòlid en compostos solubles i per tant, hi ha un increment de compostos aromàtics solubles. Aquesta solubilització de compostos aromàtics es tradueix en augments del seu UV_{254} d'entre 7 i 12 vegades en funció de la campanya de mostreig i abans d'acomplir la IOD.

Taula 2. DQO total i DQO soluble a les TOD especificades, després de la IOD

Mostra	IOD gO_3/gSS	TOD gO_3/gSS	DQO _{total} g/L	DQO _{soluble} g/L
S4- Feb 2016	0.57	0.65	1.1	1.1
S5- April 2016	1.51	1.77	1.1	1.0
S6- July 2016	0.61	0.67	2.0	1.9

Pel que fa a la IOD, els nostres resultats reflecteixen que l'ozó dissolt incrementa quan el contingut orgànic dels fangs es troben pràcticament completament sota una forma soluble. La Taula 2, presenta la DQO total i soluble per dosis transferides d'ozó més grans que la demanda d'ozó inicial. Com pot ser observat en la taula, la DQO total que indica el contingut orgànic particulat es comparable a la DQO soluble el que expressa la matèria orgànica soluble. Aquest fet suggereix que l'obtenció de la IOD està fortament relacionada amb la solubilització de les partícules trobades en el fang. Els valors de la DQO corresponen a les primeres mostres recol·lectades després de la detecció de ozó dissolt (obtenció de la IOD). Els valors obtinguts i presentats a la Taula 2 es mantenen constants des de l'obtenció de la IOD fins al final de la reacció.

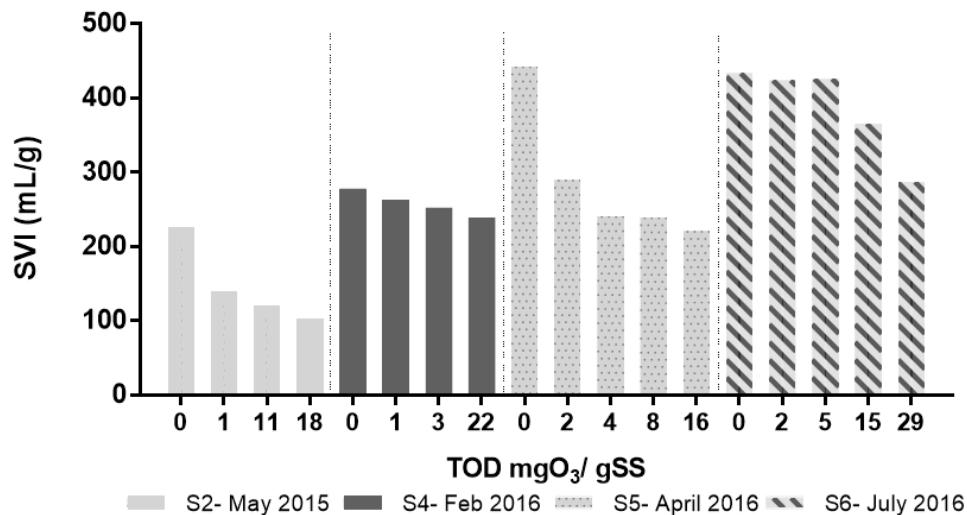


Figura 12. Canvis en la sedimentació dels fangs versus la dosi d'ozó transferida

D'altra banda, també es va investigar l'efecte de l'aplicació de l'ozó en la sedimentació dels fangs. Així va mesurar l'índex del volum dels fangs (SVI) que ens descriu l'efecte en la sedimentació dels fangs. En la Figura 12 es presenten els diferents resultats obtinguts. Així, es pot observar que per dosis d'ozó transferides inferiors a 10mg/L, la disminució en el paràmetre SVI es troba en un rang de 2 al 45%. Com s'ha determinat en estudis previs, l'ozó és un desinfectant de les bactèries filamentosos. Com aquest tipus de microorganismes formen part de la estructura que forma els flocs dels fangs, quan l'ozó ataca el fang, l'estructura es modifica i l'aigua intercel·lular es alliberada. Aquest fet, promouen la reducció en el volum de les partícules que es troben en suspensió (Chu et al. 2009, Zhao et al. 2007).

Figura 13. Concentració residual de PAHs (%) versus la dosi d'ozó transferida

D'altra banda, només dos fàrmacs es van trobar en les dues fases: aquosa (sobrenedant) i sòlida (Fangs), aquest són: Carbamazepine i Propanolol (Figura 14). Els altres fàrmacs, en canvi, es trobaven en una de les dues fases únicament. Amb les dades obtingudes ni desorció dels microcontaminants des dels fangs als sobrenadants ni adsorció des del sobrenedant als fangs s'ha observat.

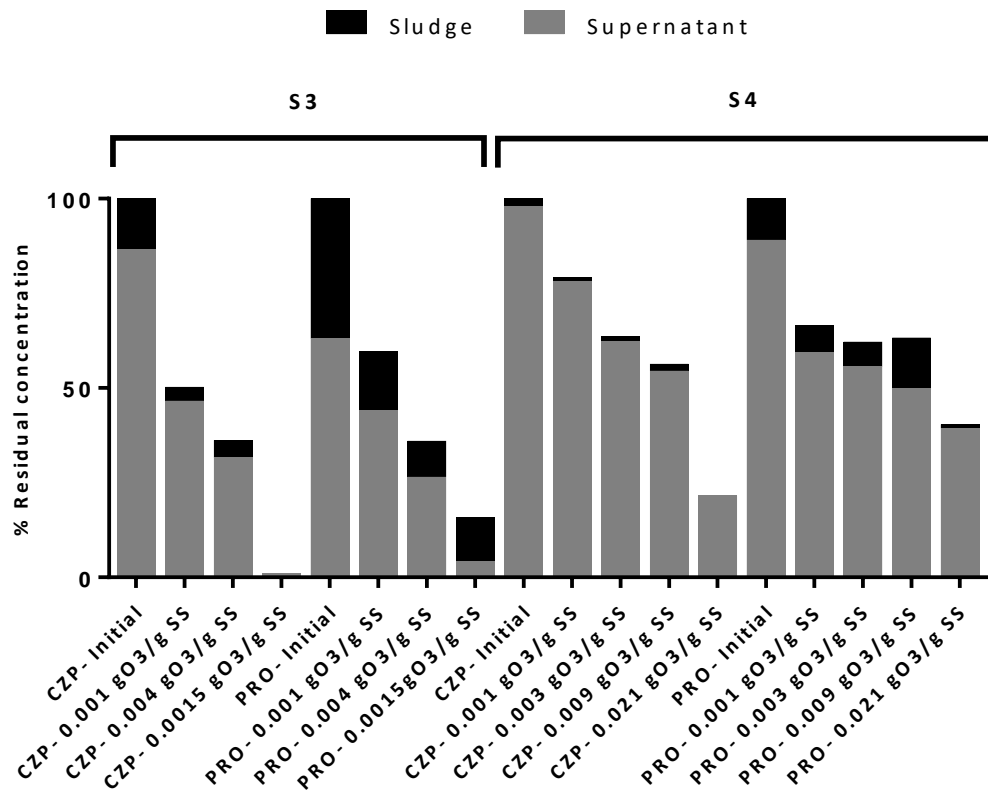


Figura 14. CZP= Carbamazepine; PRO= propranolol. Concentracions inicials i residuals del CZP i PRO en els fangs i el sobrenedant per S3 i S4.

També en aquest cas una correlació es va observar entre les estructures moleculars de la majoria de fàrmacs i la la seva reactivitat amb l'ozó.

Combinació de processos: ozó i processos biològics aeròbics

Figura 15. Evolució de la DQO soluble (sCOD) i la UV₂₅₄ durant el tractament aeròbic per P7.

Figura 16. Eliminació dels pesticides (Alachlor i Chlorpyrifos) per les mostres P6 (A) i P7(B).

Toxicitat Aguda i biodegradabilitat

Figura 17. EC50 i ratio DBO5/ DQO (BOD/COD) versus TOD pel effluent primari, P7

Combinació de processos: ozó i processos biològics anaeròbics

Figura 18. Producció de metà durant el tractament anaerobic

8.5. Conclusions i recomanacions

Si ens fixem en els objectius proposats en aquesta tesi, els beneficis de l'aplicació de l'Ozó en punts no convencionals de la línia de tractament d'aigües han estat estudiats. L'Ozó mostra una gran capacitat per l'eliminació de microcontaminants i degradació de matèria orgànica en diferents matrius complexes. Així, la demanda d'Ozó, l'eliminació de microcontaminants i els paràmetres de qualitat de l'aigua han estat estudiats per l'efluent primari observant resultats positius. També es van obtenir bons resultats quan l'ozó va ser aplicat en els fangs activats del tractament secundari, a nivell d'eliminació de microcontaminants i del tractament de l'excés dels fangs. A la darrera part d'aquesta tesi, es va estudiar l'aplicació de l'ozó en l'efluent primari combinat amb un tractament biològic que va mostrar resultats positius i sinèrgics. A més, es va obtenir una disminució en la toxicitat aguda de l'efluent primari quan s'aplicaven baixes dosis d'ozó. En canvi, no es va observar toxicitat aguda en el cas del efluent secundari. Finalment, s'ha presentat un estudi que es basava en l'aplicació de l'ozó aplicat als fangs convencionals seguits d'un tractament biològic anaeròbic, per tal de analitzar si amb el pretractament d'ozó es millorava la producció de biogàs. Així les principals conclusions de cada capítol es troben resumides a continuació.

- Del Capítol 4 es important remarcar:
 - L'aplicació d'ozó en efluents primaris té un impacte positiu en els paràmetres de qualitat de l'aigua, millora la qualitat de l'efluent primari en dosis d'ozó transferides de 30-70 mg/L depenent de la mostra.
 - Per efluents primaris i per efluents resultants del tractament biològic, el consum d'ozó es descriu mitjançant dues característiques que són la demanda inicial d'ozó i la constant cinètica de primer ordre.
 - La culminació de la IOD cobreix la primera etapa d'eliminació de la demanda química d'oxigen (DQO), totalment en el cas de l'efluent primari i parcialment en el cas dels efluents terciaris.
 - Si ens fixem en l'impacte de l'ozó en la matèria orgànica, la comparació de variacions en la DQO, absorbància UV i terbolesa s'observa que l'ozó ataca les partícules sòlides principalment.
 - Les diferents famílies en base al COD tenen diferents comportaments en funció de la dosis d'ozó transferida. Tot i així, s'han observat pocs canvis en les diferents categories de la matèria orgànica per dosis d'ozó inferiors a la IOD.

- Al capítol 5 es va investigar l'aplicació de l'ozó en els fangs del tractament biològic. Així, es pot concloure:
 - Si ens fixem en els paràmetres COD, TN, pH i UV₂₅₄, una correlació es pot establir entre la solubilització dels fangs i la culminació de la IOD.
 - Fins i tot a baixes dosis d'ozó, la solubilització dels fangs té lloc i esta relacionada amb una millora de la decantació dels fangs. Així, per dosis inferiors a 10 mg/gSS trobem reduccions en l'índex de decantació de 2-45%.
 - L'Ozó reacciona de manera ràpida i selectiva amb els fàrmacs estudiats presents a la fase líquida i sòlida dels fangs, tot i que la matriu de l'efluent es complexa i presenta una alta demanda d'Ozó.
 - En el cas dels microcontaminants que es troben tant en la fase sòlida com en el sobrenedant dels fangs, no s'observa adsorció ni desorció d'aquests després de l'aplicació d'ozó (Carbamazepine i Propanolol).

 - Hi ha un avantatge clar en la ozonització dels fangs, ja que a més d'evitar la descarrega al mediambient dels microcontaminants presents en la fase aquosa, evitem la possible contaminació deguda a la deposició dels fangs contaminats al mediambient.
- Respecte la combinació de l'ozó amb tractament biològic (Capítol 6):

Recomanacions

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