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Feasibility of Catalytic Ozonation for the Removal of Pharmaceuticals and Hormones in Wastewater Streams

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and

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Abstract

Micropollutants in surface water and wastewater streams is a topic of rising concern. Solving the problem at the entry side with chemical compounds, where environmental harm stands in direct competition with human health, is controversial. Pharmaceuticals, such as painkillers, antibiotics and hormones are not easily replaceable with less concerning materials. The worldwide number of publications on the topic of emerging compounds (ECs) in environmental water bodies and their removal with so called advanced oxidation processes (AOPs) has drastically risen in the last two decades. Some full scale wastewater treatment plants (WWTPs) in operation utilize an additional stage after mechanical, biological and possibly chemical treatment, to remove ECs from wastewater. Some examples are adsorption on active carbon (AC) or ozonation. The negative effects of these treatment steps are the often high energy or chemical consumption and the possible formation of toxic byproducts

Within this study, five different wastewater streams of the province of Gipuzkoa, Spain were analysed for the presence of ECs. 21 out of 41 investigated compounds could be quantified, including the painkiller diclofenac (DCL) and the antibiotic erythromycin (ERY).

The preparation and characterisation of catalytic materials has resulted in powdered AC impregnated with 10 wt% cerium oxide (CeO_2) to be the most promising material for catalytic ozonation experiments. The experimental campaign includes adsorption, basic ozonation and catalytic ozonation for the removal of four target compounds. These compounds are included in the current or former EU watch list. The three processes were carried out on synthetic water and real wastewater samples, spiked with ECs. The applied concentrations were 500 and 50 µg/l respectively, whereas catalytic ozonation has mostly been studied on elevated concentrations of single compounds in mg/l range before. Full removal of all ECs could be achieved with adsorption and both ozonation processes from synthetic water and wastewater.

The focus of this study lies on the removal of a mix of compounds in concentrations close to those present in real wastewater streams. The minimum EC concentration for experiments was defined by the limit of detection (LOD) of the analytical equipment and the minimum feasible ozone dose.

The removal of the natural and the synthetic hormones, 17-beta-estradiol (E2) and 17-alpha-ethinylestradiol (EE2), with catalytic ozonation was significantly higher than with basic ozonation. On synthetic water a 20 % higher removal could be achieved. On wastewater the same removal could be reached with a lower specific ozone consumption of one third when comparing catalytic ozonation to basic ozonation.

For DCL and the antibiotic tetracycline (TTC), no significant improvement of removal could be determined with catalytic ozonation over basic ozonation. Regarding all four target compounds, double the removal could be achieved with synthetic water compared to real wastewater when applying the same specific ozone dose.

Kurzfassung

Mikroverunreinigungen im Abwasser gerieten in den letzten zwei Jahrzehnten vermehrt in den Fokus der Wissenschaft. Die ausgehenden Umweltgefahren der Komponenten stehen in in direkter Konkurrenz zur Erhaltung der menschlichen Gesundheit. Pharmazeutische Stoffe, sowie Schmerzmittel, Antibiotika und Hormone können selten mit weniger umweltschädlichen Substanzen ersetzt werden. Die Anzahl an Publikationen, zum Thema Mikroverunreinigungen ist weltweit steigend. Sogenannte vierte Reinigungsstufen sind zur Eliminierung von Pharmazeutischen Stoffen bereits in Betrieb. Diese Reinigungsstufen werden den regulären mechanischen, biologischen und chemischen Reinigungsschritten nachgeschalten. Beispiele für betriebliche Verfahren sind die Adsorption an Aktivkohle (AC), sowie die Ozonierung. Diese Verfahren weisen oft Nachteile, wie hohen Energie- und Chemikalienbedarf und die Formierung toxischer Nebenprodukte auf.

Im Zuge dieser Arbeit, wurden fünf verschiedene Abwasserströme der Provinz Gipzkoa in Spanien auf das Vorkommen von pharmazeutischen Stoffen untersucht. 21 der 41 gemessenen Komponenten, unter anderem das Schmerzmittel Diclofenac (DCL) und das Antibiotikum Erythromycin (ERY) konnten quantifiziert werden.

Als Katalysator wurde pulverförmige Aktivkohle mit Cerium Oxid (CeO_2) imprägniert. Während der Herstellung und Charakterisierung verschiedener (CeO_2) Beladungen, stellte sich heraus, dass sich eine Beladung von 10 wt% am besten eignet. Die Experimente Adsorption, Ozonierung und katalytische Ozonierung wurden zur Beseitigung von vier Zielkomponenten durchgeführt. Diese Komponenten sind oder waren in der „EU Watchlist“ beinhaltet. Die verwendeten Konzentrationen der Komponenten in den Versuchen waren 500 µg/l beziehungsweise 50 µg/l. Wohingegen in vorhergehenden Studien katalytische Ozonierung hauptsächlich and erhöhten Konzentrationen im mg/l Bereich einzelner Modelkomponenten durchgeführt wurde. Alle Zielkomponenten konnten mit den drei Prozesstypen, Adsorption, Ozonierung und katalytische Ozonierung, erfolgreich eliminiert werden. Alle Experimente wurden mit synthetischem Wasser und dotiertem Abwasser durchgeführt.

Das Augenmerk dieser Studie liegt auf der Beseitigung von Komponenten in einer Matrix mit Konzentrationen, nahe an den real vorkommenden Werten. Die minimale zulässige Konzentration zur Experimentdurchführung wurde hingegen durch die Detektionslimits der Analysegeräte und die minimal erreichbare Ozondosis bestimmt.

Eine signifikant höhere Entfernung des natürlichen Hormons 17-Beta-Estradiol (E2) und des synthetischen Hormons 17-Alpha-Ethinylestradiol (EE2) konnte mit der katalytischen Ozonierung, verglichen zur Ozonierung, erzielt werden. Die Eliminierung von synthetischem Wasser war um 20 % höher. Bei der Versuchsdurchführung mit Abwasser konnte mit den beiden Ozonierungsprozessen eine ähnliche Eliminierung erreicht werden, dabei wurde in der katalytischen Ozonierung um ein Drittel weniger Ozon konsumiert.

DCL und das Antibiotikum Tetracyclin (TTC) zeigten keinen signifikanten Unterschied in den beiden Prozessen. Eine zufriedenstellende Entfernung konnte sowohl mit Ozonierung als auch mit katalytischer Ozonierung erreicht werden. Bei der Betrachtung aller Komponenten, wurde festgestellt, dass im Allgemeinen bei gleichbleibender Ozondosis in synthetischem Wasser die doppelte Eliminierung, verglichen zu Abwasser, erreicht werden konnte.

List of abbreviations

AC	Active Carbon
AD	Adsorption
AOP	Advanced Oxidation Process
BO	Basic Ozonation
BSE	Back Scattered Electron
CAT	Catalyst
CO	Catalytic Ozonation
COD	Chemical Oxygen Demand
DCL	Diclofenac
DOC	Dissolved Organic Carbon
E2	17-beta-Estradiol
EC	Emerging Compound
EE2	17-alpha-Ethinylestradiol
ERY	Erythromycin
HPLC	High Performance Liquid Chromatography
IFAS	Integrated Fixed Film Activated Sludge
LOD	Limit Of Detection
MFC	Mass Flow Control
MS	Mass Spectrometry
PNEC	Predicted No Effect Concentration
SD	Standard Deviation
SE	Secondary Electron
SEM	Scanning Electron Microscope
TKN	Total Kjeldahl Nitrogen
TSS	Total Suspended Solids
TTC	Tetracycline
VSS	Volatile Suspended Solids
WWTP	Wastewater Treatment Plant

Contents

1 Introduction

Typical wastewater treatment plants (WWTPs) today efficiently remove organic carbon, nitrogen, phosphorus and other biodegradable substances as well as chemicals and industrial byproducts. It is now well known that a certain mix of micropollutants leaves regular WWTPs unaffected and enters water bodies via different pathways. The cocktail consists of substances like pesticides, personal care products, pharmaceuticals, and also bacteria and viruses, only to name a few. With the technical progress, the ever increasing diversity of chemicals and fields of application, new substances are added to this cocktail on a daily basis. The expanding world population and the water scarcity in many regions often lead to the need for water reuse. Micropollutants are threatening drinking water quality and environmental water basins and soils, due to for example wastewater irrigation. The expanding of modern WWTPs to the removal of harmful trace compounds is an essentially growing topic [1].

The awareness for the problem started to rise in the 1990s when analytical devices were able to detect substances that harm the ecological system even in very low concentrations. Antibiotics will contribute to the development of resistances, whereas hormones can lead to a decrease of fertility in fish populations and other aquatic organisms. Micropollutants can be toxic, mutagenic or act as endocrine disruptors once they enter a living organism. Especially water recycling can cause their presence in drinking water. By now, the awareness of the problem has reached politics and decision makers on EU level [2].

To solve this problem different approaches are considered. Legislation can prohibit the use of certain substances or decrease the consumption of chemical products on an industrial and a domestic scale. This can be a solution for pesticides or personal care products. In the case of pharmaceuticals the situation is more complicated, as the immediate human health has a higher priority than the protection of environmental water bodies. This sounds controversial on a long term, but pharmaceuticals can not be easily replaced by less harming substances. At the same time, due to the huge variety of substances, there is still a lack of studies proving the actual harm of each emerging compound (EC) on the human organism and the environment. The number of publications on advanced treatment technologies of mostly pharmaceuticals has increased drastically and Switzerland installed the first full scale plants about ten years ago [3].

Advanced oxidation processes (AOPs) are promising treatment steps. A wide range of processes with the goal to mineralize harmful persistent organic compounds has been investigated and removal efficiencies of ECs can reach up to 100 % [4]. The effectiveness of different processes depends on the mixture of target pollutants, which can change within hours in the case of wastewater. Potentially harmful secondary products or other undesired byproducts can be produced. Simultaneously, the energy or chemical consumption of the processes can be uneconomic and process safety is not entirely secured.

Ozonation is a well studied and applied method in the field of drinking water disinfection amongst others. Subsequently catalytic ozonation is an innovative process to improve ozonation application. On the surface of the solid catalyst, oxidants with less selective properties, compared to ozone, are produced, which can widen the range of target pollutants [5]. In this study adsorption, as an essential step of catalytic ozonation, ozonation and catalytic ozonation experiments of synthetic water and real wastewater spiked with four model compounds were carried out.

2 Theory and Background

The importance of the micropollutant issue, especially pharmaceuticals, and their threat to the environment and the human health, is validated by the following theoretical aspects. WWTP effluents are one of the main pathways for pharmaceuticals, as many harmful substances cannot be sufficiently eliminated in regular plants. The legal situation in Europe, effluent limitations and future strategies on political level are presented subsequently.

Some possible treatment methods exist in full scale today, like ozonation and adsorption on AC. Amongst different technologies, AOPs are the most promising ones. Many processes are currently tested on pilot scale with the capacity of efficiently removing ECs. Some of these processes are explained and there advantages and disadvantages are pointed out. Full scale as well as pilot scale treatment faces two major problems: high electrical or chemical treatment costs and the formation of toxic byproducts or secondary compounds. Catalytic ozonation is expected to be one of the most valuable methods for reducing process costs, regarding lower ozone input and moreover reducing toxicity of the treated water. So far only a few studies have been carried out, investigating the removal of single model compounds in elevated concentrations with catalytic ozonation on synthetic water.

Related to the experiments carried out in this study the process basics are explained and and the target compounds used for removal experiments are described chemically and their possible harm to the environment is identified.

2.1 Presence and Effects of Emerging Compounds in the Environment

In the 1965s estrogen was found in wastewater streams for the first time. Since then the development of more sensitive analytic instruments lead to an advanced knowledge about EC occurrence in the environment. Pharmaceuticals and hormones have been detected worldwide in water bodies like urban wastewater, surface water, drinking water and groundwater [6]. Discharges from WWTPs, hospital effluent, landfill leachate and sludge reuse are some of the main contributors. Industrial wastewater including the production of pesticides, PPCPs and pharmaceutical add micropollutants to water bodies as well as agricultural runoff, wastewater irrigation, livestock and aquaculture.

Studies have shown that pharmaceuticals were detected in water bodies on all continents. Concentrations are steadily increasing due to population growth, changes in disease burdens, increasing accessibility to medication and the human and veterinarian use of medication. Aus der Beek et al. [7] estimates a global pharmaceutical consumption of 100.000 metric tons per year. The study reports that 631 out of 713 measured compounds were detected all across the world and are mostly measured downstream of WWTPs and densely populated areas. Germany and Spain, representing the leading countries regarding investigation of EC concentrations, report over 100 substances in water bodies and over 30 in tap water. In France, trace compounds were found in bottled water. 16 substances, such as DCL and TTC, were found in all worldwide regions. Certain pharmaceuticals show higher consumption and detection trends in different continents. The number of publications on environmental concentrations has to be taken into consideration as it ranges from almost 100.000 in central Europe to 1000 in Africa. Generally, the highest amounts of antibiotics are reported in Africa. Asia reports the highest concentrations of estrogen, whereas eastern

Europe is leading in analgesics. Most pharmaceuticals are detected in µg/l and hormones in ng/l range. The maximum pharmaceutical concentrations are reported in Asia and Eastern Europe, close to production sites, where concentrations in the range of mg/l were detected [7].

A significant increase of pharmaceutical production sites with an annual growth of 10-15 % in countries like India, where effluents are poorly regulated, is a matter of concern. Wastewater irrigation makes up 100 % of produce irrigation in countries like Ghana and 80 % in Vietnam. Moreover, it was reported that China, Korea as well as South American and Middle Eastern countries use wastewater for irrigation [8].

Regarding Spain, studies have been conducted on the Ebro river amongst others, where Silva et al. [9] and Mandaric et al. [10] report the detection of up to 60 substances with the highest concentrations close to Zaragoza. Dilution and flow rates in rivers highly affect final concentrations and the distribution of occurrences in water and sediment should not be neglected.

The negative effects of pharmaceuticals in water bodies include accumulation persistence, ecotoxicity, antimicrobial resistance and toxicity for aquatic biota, like fish and invertebrates. In addition, potentially additive or synergistic effects within mixtures of different contaminants or chemical elements can appear in terms of toxicity or they can inhibit each others removal in certain processes [11].

Archer et al. [12] states the necessity of eco-toxicological assessment of the fate and the sublethal effects of parental compounds and their metabolites or conjugates on water bodies. Some regularly used ECs may act as endocrine disrupting compounds and have negative effects on wildlife reproduction and on thyroid systems.

High toxic hazards to algae could be reported by Wang et al. [13] with a mixture of environmental concentrations of antibiotics in µg/l range in Chinese lakes, including TTC.

A significant change in river biota could also be observed by Quinlan et al. [14] by applying 0.5 µg/l TTC over a 7 day period to a river stream. Changes in antibiotic resistance and algae biomass, as well as bacteria productivity and organic biomass could be observed.

These studies prove the hazard that derive from a mixture of ECs in environmental water bodies and that the investigation of single compounds is not sufficient. Except for the specific case like the vulture extinction due to veterinary DCL use in India and some proofs of direct impact on aquatic organisms, the effect of the individual concentrations in freshwater sources are lower than those causing direct negative effects on humans [15].

The understanding of pollutant pathways is an important step towards the avoidance of ECs reaching environmental water bodies. The main sources are black water, grey water, leeching from landfill, commercial and industrial effluent, storm water, urban run off, agricultural, horticultural and aquacultural effluent. All water bodies are receiving these pollutants, in which the dilution factor is an important parameter in terms of negative effects. WWTP effluents are the most studied and dominant EC source in urban regions, whereas pharmaceutical production sites, hospitals, agricultural areas, especially in areas with wastewater irrigation are dominant locally.

2.2 Legal Situation and EU Regulations

Up to date there are no legal limits to the discharge of pharmaceuticals into wastewater in Europe. Due to the lack of data on the environmental impact, it is difficult for governments to control the utilisation of these compounds and no decisions on regulation of limit implementations are expected within the next year [16].

Hernando et al. [17] compared comprehensive risk assessment studies and states that associated risk is not sufficiently described for different pharmaceuticals. Since 2006, a comprehensive environmental risk assessment has been required for all new marketing authorisation applications for human medicinal products in the European Union. The European Medicine Evaluation Agency (EMA) applies a method where the predicted environmental concentration (PEC) is compared to to the worst case predicted no effect concentration (PNEC). As long term tests for all drugs are problematic, regulatory concepts of ERA are often based on short term ecotoxicological studies [17].

As the concern about the environmental threat of ECs was rising, in 2000 the EU released the first European Water Policy Directive 2000/60/EC to set up a strategy to define and prioritise high risk substances. In 2001 a list of priority substances, including a variety of micropollutants was published. The discharge of substances from this list can be prohibited or is limited by the European Parliament. The current list, Annex II of Directive 2008/105/EC, includes 33 substances, such as selected existing chemicals, plant protection products, biocides, metals and others. So far no pharmaceuticals are included in the priority list.

In 2015, the EU released the first watch list for pharmaceuticals in the EU Decision 2015/495. The listed ECs should get in the focus of international and national research. The substances on the second and currently valid EU watch list, approved by the EU Decision 2018/840, are listed in Table 1. Compared to the first watch list from 2015, octinoxat, butylhydroxytoluol, oxadiazon, triallate and DCL were replaced by metaflumizone, amoxicillin and ciprofloxacin. The new substances in Table 1 are written in blue letters.

hormones	macrolide antibiotics	neonicotinoids	other substances
17-alpha-Ethinylestradiol	Acithromycin	Imidacloprid	Metaflumizone
17-beta-Estradiol	Clarithromycin	Thiacloprid	Amoxicillin
Estrone	Erythomycin	Thiametoxam	Ciprofloxacin
		Clothianidin	Methiocarb
		Acetamiprid	

Table 1: Substances of the current watch list of the EU Commission Decision 2018/840; blue substances are new compared to the watch list 2015/495 [18]

The EU watch list installed by the European Water Framework Directive, is an instrument to monitor EU wide prioritisation pharmaceutical substances which pose significant risk to river basins all across the EU. Member states must monitor these substances on a minimum number of monitoring sites, set up in places fulfilling specific criteria, and with a minimum sampling frequency. Substances can remain on the watch list for up to four years until enough high quality data could be achieved. They can be removed if they are found not to pose risk on EU level but for example on regional level. If the obtained data poses certain risk, the substance will be moved to the priority list. PNEC is a parameter used to define maximum concentrations without posing harm. This tool is used among a few others. The watch list itself should be updated every 24 months, however the update from the first to the second watch list took 36 months [19].

Each year the current watch list is reviewed like in the report by Loos et al. [19]. In this report, all currently included substances are reviewed and it will be investigated if they can be taken off the watch list. New substances of emerging concern are proposed to be included in the next watch list. The criteria for the inclusion of new substances from a technical view are the availability of sufficient monitoring data, appropriate analysis methods and reliable PNEC values. The availability of appropriate analysis methods is essential, as sometimes the PNEC can be found to be below the limit of quantification. Some substances are not included due to the lack of data proving their hazard, therefore these substances will be reviewed again in the next round. A substance can be taken off the watch list, if there is enough EU wide high quality monitoring data to assess the risk emerging from this specific substance. Another criteria is the availability of quantified data. In the case of qualitative data only, the limit of detection (LOD) must be at least half of the PNEC [19].

In Switzerland, a new water protection act started in January 2016 with the objective to improve surface water quality by reducing the load of micropollutants from WWTPs. Within the next 20 years, about 100 of the 700 existing Swiss WWTPs will have to implement an advanced treatment step for micropollutant removal. There are four main criteria considered within this concept. These include that large WWTPs have to significantly reduce their load. Furthermore, WWTPs in the catchment of lakes and rivers with a high fraction of wastewater are of special concern to protect ecosystems. Especially WWTPs discharging to surface waters, which serve as drinking water resources, must update their treatment systems [3].

The United States Environmental Protection Agency (USEPA) is updating a contaminant candidate list yearly [20]. This list is comparable to the EU watch list and is, up to date, not subjected to any regulations. Contaminants listed may require future regulation under the Safe Drinking Water Act, which also means that the concerns are focused on drinking water and do not include environmental concerns, like in the EU watch list [21]. The contaminates listed are prioritised in future research and data collection.

2.3 Removal of Emerging Compounds

Processes for the removal of ECs from wastewater are currently mainly implemented as third or fourth treatment step in WWTPs, after the regular mechanical and biological treatment. Therefore most studies on new technologies are carried out on the ”purified” effluent stream from WWTPs. Some studies consider implementing this treatment step directly in the effluent of hospital wastewater streams [22].

Jelic et al. [23] reported that WWTP effluent concentrations vary with the hydraulic retention time in the WWTP, where a longer retention time leads to higher removal rates of certain ECs. This confirms the degradamibily of certain ECs in regular WWTPs. It, however, simultaneously confirms the phenomena of ”negative removal” can occur in WWTPs when metabolites or transformation products convert back into the original substance or are released from feces particles during biological treatment. Therefore further treatment is essential.

AOPs represent a certain group within a broader variety of final treatment stages in WWTPs. Physical and chemical treatment for the removal of ECs include for example processes such as adsorption on AC, the application of hydrogen peroxide (H_2O_2) and light driven processes [1].

As the scope of this study is to investigate catalytic ozonation over adsorption and basic ozonation, firstly background knowledge for ozone gas and its reaction mechanisms is given. The main mechanisms of ozonation, adsorption and catalytic ozonation are explained and the utilized catalyst material and its expected positive properties for catalytic ozonation are presented.

2.3.1 Ozone

The molecular structure of the ozone gas can be seen in Figure 1, where the two resonance forms of the dipole molecule can be seen. Ozone occurs naturally in the ozone layer of the stratosphere about 10 to 50 km above the surface of the earth, with a concentration of approximately 2 - 8 ppm. Ozone gas is toxic to the human organism, fortunately the limit of odour is approximately 0.02 ppm and lies well below the toxic dose. Ozone gas has a specific smell which some refer to the smell of rain. This origins from the corona discharge that produces ozone during a storm.
For working environments maximum admitted concentrations of 0.06 ppm (8 h/day) and 0.3 ppm (maximum 15 min) have been established. The gas causes irritations of the mucous membranes and lungs and a long term exposure (> 30 min) at > 50 ppm might be fatal.

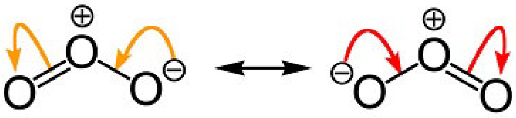


Figure 1: Ozone exists in two resonance structures

The natural process for ozone generation is called Chapman cycle and starts with the photolysis of molecular oxygen, as shown in the mechanism in Equations 1 to 3. Technically, ozone can be produced from oxygen by ultra violet radiation or corona discharge, which most generators use. The energy intensive process takes place in the corona discharge-element or Siemens-generator, which consists of a tube, an oxygen source, dust filters, gas dryers, ozone generator, contacting unit and a torch destruction. The electrical charge, provided by the corona discharge element destructs the oxygen molecule into two oxygen radicals. Each radical bounds with an oxygen molecule to form ozone.

$$O_2 + \text{photon} \longrightarrow 2\,O\cdot \tag{1}$$

$$O\cdot + O_2 \longrightarrow O_3 \tag{2}$$

$$O_3 \longrightarrow O\cdot + O_2 \tag{3}$$

radiation $\lambda < 240$ nm $\Delta H = +142$ kJ/mol $O\cdot$ = free radical

Ozone is a strong oxidizer with an oxidising potential of 2.07 V. It is mostly used as disinfectant for drinking water and the treatment of industrial waters containing phenols and cyanides, leakage from landfill, exhaust air washing water and for the production of ultra clean water. The lifetime in water is up to ten times shorter than in air. The decomposition of ozone can be explosive at elevated temperature and in presence of metals [24].

When dissolved in water ozone is mainly transformed into secondary oxidants. The most important and reactive secondary oxidant is the $OH\cdot$. Other forms like hyperperoxyl radicals, carbonate radicals, hypobromite, permanganate and other radicals depend on the composition of the water matrix and the pH [25].

Ozone itself is an electrophile and is highly selective. The reaction rates of ozone are enhanced by electron donating groups and reduced by electron withdrawing groups. The second order rate constant of direct ozone reaction kinetics varies over a magnitude of ten orders. Whereas the reaction of $OH\cdot$ is almost diffusion controlled [26].

The ozone stability in water ranges from seconds to hours and depends on the pH, the natural organic matter and the alkalinity of the water matrix. The fast initial decrease is followed by a first-order decomposition reaction. The reaction kinetics depend on the pH, as OH^- ions act as reaction initiator. The correlation between ozone stability in water in a basic milieu can be seen in Figure 2. Decomposition steps of ozone and the formation of $OH\cdot$ in water can be seen in reaction Equations 4 to 8 [27].

$$OH^- + O_3 \longrightarrow HO_4^- \tag{4}$$

$$HO_4^- \longrightarrow HO_2\cdot + O_2\cdot^- \tag{5}$$

$$O_2\cdot^- + O_3 \longrightarrow O_2 + O_3\cdot^- \tag{6}$$

$$O_3\cdot^- \longrightarrow O_2 + O\cdot^- \tag{7}$$

$$O\cdot^- + H_2O \longrightarrow \cdot OH + OH^- \tag{8}$$

2.3.2 Ozonation

Ozonation is a process which has been used for drinking water disinfection and the removal of microorganisms like pathogens for almost a century. Ozone is up to date the most efficient chemical disinfectant and is used in drinking water purification across the globe. Often high ozone exposures for disinfection purposes are required, which might lead to potentially human carcinogen byproduct formation [26].

On the other hand oxidation of micropollutants with ozone got into the focus of investigation in the last two decades. The oxidation process with ozone functions in two different ways, directly via ozone and through transformation into secondary oxidants such as $OH\cdot$. While in the disinfection process ozone is the dominant reactant, the oxidation process functions via both oxidants, ozone as well as $OH\cdot$. Based on kinematic studies Gunten et al. [26] states that the influence of $OH\cdot$ on the disinfection process can be neglected. Therefore, a balance between disinfection via direct ozone reactions and the oxidation of ozone resistant compounds via $OH\cdot$ is necessary in ozonation processes to reach optimal disinfection and EC oxidation while decreasing byproduct formation.

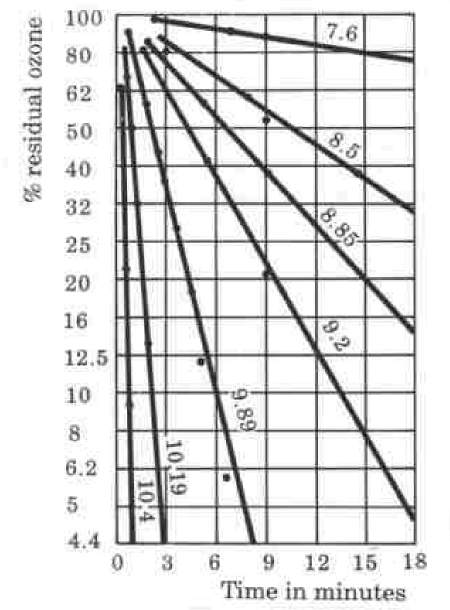


Figure 2: Effect of pH on the decomposition of ozone in water at a temperature of 15 °C [28]

The direct reaction of ozone occurs selectively mainly with double bonds in olefines, phenols and polyaromatic hydrocarbons. Furthermore, amines and sulfides as well a sulfite and nitrite ions react directly with ozone. Ions like nitrite act as ozone scavengers and react to the less toxic compound nitrate. The reactions of these chemical structures happen within seconds, if homogeneous ozone distribution can be assumed. The rate law of direct ozone reaction with organic molecules can be assumed to be a first order and ozone distribution via mixing and mass transfer becomes the rate limiting step, in case of ozone being quickly consumed [25].

Ozonation of large organic molecules usually does not result in full mineralization but in transformation products with usually lower biological activity. These transformation products are often biodegradable and can be decomposed in a sand filtration unit after the ozone treatment [29]. Undesired ozonation byproducts, which are not biodegradable can also be formed, such as bromate and brominated organic compounds, when bromide and dissolved organic carbon (DOC) is present. Permanganate can be formed when Mangan is present. These reactions are much slower than the above mentioned reactions with olefines etc. Aldehydes, organic acids and carbonyl compounds can derive from DOC reacting directly with ozone. Substances like chloride, benzene, toluene and saturated hydrocarbons were found not to react with molecular ozone [25].

In the process of ozonation, ozone is required in excess, as the reaction with organic compounds is not stoichiometric. Additionally, ozone is unstable in water with a half-life time reaching from a few seconds to 30 min. The half-life time of ozone at different pH can be seen in Figure 2.

Direct oxidation of the ozone molecule can occur in three different ways. Electron-transfer reactions with superoxide ion and hydroperoxide anions and ozone form the highly reactive ozonide anion and can be seen below. Reactions which lead to the formation of molecular oxygen are initiated by OH^- as well as other ions like bromide, iodide, iron(II) and nitrite, see reaction Equation 9 to 14.

$$O_2^- + O_3 \longrightarrow O_2 + O_3^- \tag{9}$$

$$HO_2^- + O_3 \longrightarrow HO_2\cdot + O_3^- \tag{10}$$

$$Fe^{2+} + O_3 \longrightarrow FeO_2^+ + O_2 \tag{11}$$

$$NO_2^- + O_3 \longrightarrow NO_3^- + O_2 \tag{12}$$

$$Br^- + O_3 \longrightarrow BrO^- + O_2 \tag{13}$$

$$I^- + O_3 \longrightarrow IO^- + O_2 \tag{14}$$

The third mechanism of ozone addition reactions in Figure 3 and 4 shows the selective ozone reaction with the double bonds of alkenes and with amines.

Most of the molecular ozone in water is transformed into secondary oxidants. The radical formation is strongly influenced by pH, alkalinity and presence of DOC or active carbon (AC) surface. It occurs due to the decomposition of ozone in water, see Chapter 2.3.1. The initiated radical chain reactions are accelerated by OH· are more reactive and less selective than ozone. These radicals are controlling the reaction kinetics of ozone based AOPs. OH· react with organic micropollutants and lead to a great diversity of oxidized compounds. They can also lead to the formation of further undesired byproducts which are, due to the different reaction mechanism of ozone and OH· distinct to the once produced by ozone reactions.

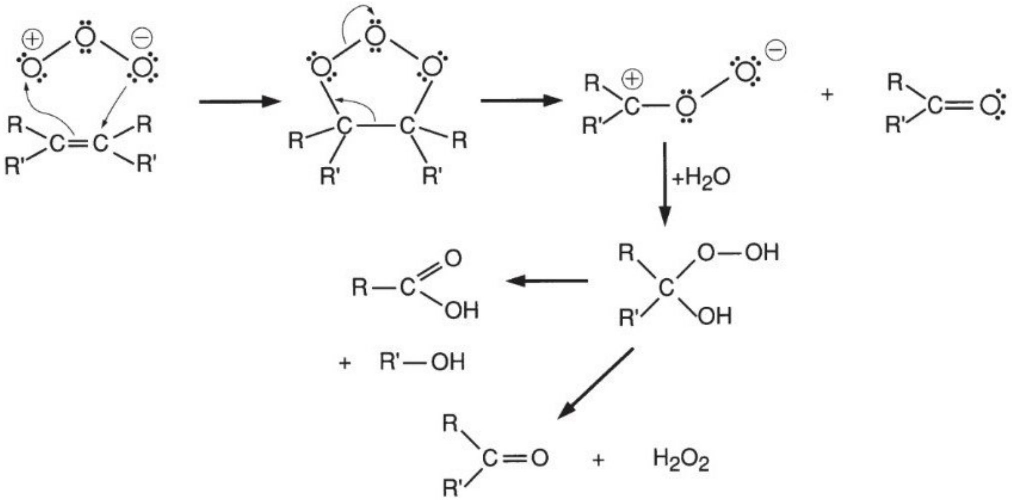


Figure 3: Ozone addition reaction on the double bond of an alkene based on the Criegee mechanism [25]

The OH· can abstract an electron from ions and reduce to OH^- or yield H_2O by abstracting H-atoms from organic molecules. OH· addition reactions are possible and different radicals can form spontaneously. The great variety of radicals may lead to a broad variety of species, when the reaction is terminated by radical - radical combinations.

The reaction kinetics of OH· are studied by Hoigne et al. [25] and he concludes that OH· reactions are much less selective than direct ozone reactions. Primary OH· reactions are first order with respect to target molecule concentrations, as ozone is added in excess. Moreover, the rate constant for OH· increases the more C-H bonds are present in a molecule. For organic compounds with a high molecular mass this means, that OH· react with them quickly and the reaction is nearly diffusion controlled. For compounds of low molecular mass the abstraction of H-atoms and the electron transfer reaction occurs relatively slow. The compounds competing for reaction with OH· in water samples might either be pollutants or scavengers.

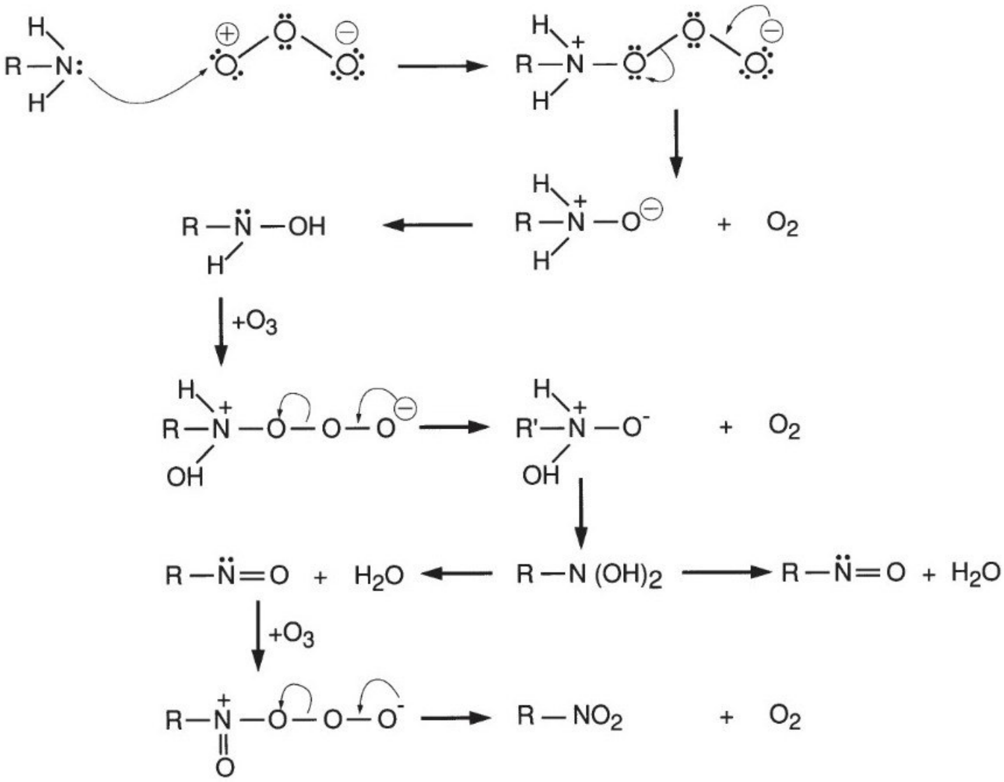


Figure 4: Ozone addition reaction to an amine [25]

2.3.3 Adsorption

The definition of the adsorption process is the adhesion of molecules from a fluid phase to a solid phase. In this case, contaminant molecules in the water samples are the adsorbate and adsorb to the surface of the adsorbent. Adsorption does not change the chemical composition of the adsorbed species. On the contrary, in the process of catalytic ozonation the full mineralization of ECs is desired. Adsorption is a main step in heterogeneous catalysis and is needed to make the target compounds accessible for the free radicals. Pure adsorption leads to loading and eventually saturation of the catalyst, but does not remove the compounds. As a result the ECs are moved to another phase instead of degradation.

Liquid-solid adsorption can be divided into two main mechanisms. Chemisorption is based on chemical bonding of the adsorbate on active centres and therefore on electronic transmission, it is the strongest type of bonding force. Surface groups, valence forces and zeta-potential lead to mono-layer adsorption. Adsorption is an exothermic and desorption an endothermic process. In the case of chemisorption, most adsorbents can be regenerated by applying energies higher than the enthalpy of adsorption.

Physisorption is based on molecular interactions. Van-der-Waals and electrostatic forces, as well

as polarity and surface area influence the adsorption process. Hydrogen bonding may occur between adsorbents and adsorbate and multi-layer adsorption is possible. Unipolar adsorbents, such as AC, are hydrophobic and adsorb carbohydrates. The regeneration process for physisorption is relatively simple, as the weak interaction forces can be easily revoked. Due to single use of the adsorbent, regeneration is not investigated in this study [30].
In general adsorption is determined by the following mass transfer steps:

- Convection of the fluid flow around the adsorbent particles
- Convection and/or diffusion through the boundary layer of the particles
- Diffusion in the pore system of the particle
- Surface diffusion of the adsorbed species

To estimate adsorption equilibrium between solid and liquid phase, so called adsorption isotherms are estimated. They are a function of concentration and saturation concentration at a constant temperature. The equilibrium of adsorption can be calculated with different isotherm models. Henry's isotherm, for example, is accurate for low concentrations. Whereas the Freundlich model is used for multi compound adsorption and Langmuir assumes mono-layer adsorption. Freundlich and Langmuir are the most commonly used isotherms in pollutant adsorption [31].

In the adsorption process of micropollutants, other substances which can occupy active adsorbent sites must be taken into consideration. In wastewater treatment, full removal of ECs is desired. Therefore, due to the high DOC in wastewater, adsorbent is required in excess. To quantify minimum adsorbent concentrations, dependent on the micropollutant specifications and the wastewater matrix, experimental studies must be carried out with real wastewater samples.

In a study of Contreras et al. [32], cerium oxide (CeO_2) also finds application as adsorbent for fluoride deposition. Nano-particles of CeO_2 are used for heavy metal ion adsorption from wastewater. To understand how weather CeO_2 is minimising the adsorption process efficiency due to pore blocking or accelerating it due to its positive adsorbent properties, comparative experiments should be carried out.

2.3.4 Catalyst Material

The catalytic material used in this study was selected based on a catalytic ozonation study by Goncalves et al. [33]. The study could prove the positive influence of CeO_2 doped AC material on the removal process of ERY compared to pure AC. Several studies were carried out on the mineralization of model compounds via catalytic ozonation and the application of CeO_2 dispersed AC material [34], [35], [36].

The carrier material AC is used in full scale adsorption processes for micropollutant adsorption in wastewater treatment and as post-treatment step of ozonation. The material is mostly used in powdered or granular form. AC is produced from carbon source material, such as biomass or charcoal. The material can be activated physically by carbonization at 600 - 900 °C under inert atmosphere and oxidation of the pyrolyzed material in oxygen or steam atmosphere from 600 - 1200 °C. Chemical impregnation activation can be carried out at lower temperatures and activation time. During this activation process, low-molecular substances are removed from the material and micro-pores are formed, which leads to the typical structure of AC [37]. The micro-structure of AC consists of graphite like layers with traces of aluminium, silicates and alkaline earth oxide ashes. The surface characteristics of the particles originate from the high variety of surface functional groups, like carboxyl, carbonyl and phenyl groups [38]. These surface characteristics include polarity, acidity, hydrophilicity and the zeta potential. The latter establishes on solid material, when in contact with water and depends on the other characteristics as well as on the pH of the solution. The electron-rich graphene layer regions bind to the π-electrons of aromatic groups. Oxidation leads to the increase of oxygen groups on the surface which leads to electron withdrawal from the graphene layer and decreases the interaction between the surface and organic pollutants [39]. The surface characteristics of AC can be manipulated by thermal treatment in oxygen or inert atmosphere.

Metals have shown positive properties in homogeneous catalysis in the form of metal ions as well as in heterogeneous catalysis in their solid form. Cerium species like cerium(IV) have highly oxidizing abilities. CeO_2 dispersed on AC has the capacity to store and release oxygen via the redox shift reactions of Ce^{3+}/Ce^{4+}, this aids the mineralization processes of organic pollutants [40]. A strong synergistic effect of the materials AC and CeO_2 regarding the mineralization of model compounds like oxalic acid was shown by Faria et al. [41].

Pore volume and micro-pore volume of AC decrease with the percentage of metal loading. High metal loadings of AC support can lead to metal sintering or aggregation of metal species and therefore to a decrease of catalytic activity [42]. To prepare an efficient catalytic material, a balance between AC surface and dispersion of fine particles of oxidizing cerium species must be achieved during impregnation and calcination process. The preparation procedure can be seen in Chapter 3.

During the impregnation process of AC with cerium salt ($Ce(NO_3)_3 \cdot 6\,H_2O$) in basic milieu, dehydration, dissolution and recrystallisation form the main steps. Long aging time and high pH are the essential parameters for the process. Initially cerium(III)-hydroxide precipitates and is then transformed via Ce^{3+}/Ce^{4+} oxidation to CeO_2 nano-particles. The summarizing reaction equation by Benmouhoub et al. [43] of the impregnation process can be seen in Equation 15. SEM characterisation, further explained in Chapter 4.4.2, of the unwashed and uncalcinated catalyst powder could prove the presence of both reaction products. $Ce(NO_3)_3 \cdot 6\,H_2O$ could not be detected and therefore full precipitation of cerium CeO_2 was assumed.

$$4\,Ce(NO_3)_3 \cdot 6\,H_2O + 12\,NaOH + O_2 \longleftrightarrow 12\,NaNO_3 + 30\,H_2O + 4\,CeO_2 \tag{15}$$

Calcination influences the CeO_2 particles mainly in two ways, the crystallinity and the presence of Ce^{3+} species. It therefore increases the oxygen vacancies of the catalyst surface and leads to more catalytic activity. With higher temperatures between 400 and 600 °C, the crystalline structure and density of the CeO_2 nano-particle increase [44]. It also leads to crystal growth, which negatively affects the specific surface area. Regarding AC, impregnation can lead to pore blockage. Simultaneously the surface area of AC rises with calcination due to evolution of pore volume and porosity. Metal oxides are partially redistributed within the AC pore system, as the solubility of the metals into the pores rises with calcination [42]. To achieve a balance between the negative and positive effects of calcination in terms of active surface sites and specific surface area, a calcination temperature of 450 °C was chosen.

2.3.5 Catalytic Ozonation

Catalytic ozonation was proposed as a promising AOP to improve the basic ozonation process, which is already running in full scale application with good results but lacks in removal efficiency of certain compounds and their secondary products [33]. Catalytic ozonation includes homogeneous and heterogeneous catalysis. The heterogeneous process is advantageous due to the relatively simple separation of the catalyst material from the treated water. In full scale applications the catalyst could be implemented as catalyst bed, otherwise separation can be carried out via filtration, sedimentation, centrifugation or others. In this study, fine catalyst particles were kept in suspension during the treatment process and were separated afterwards by filtration.

Heterogeneous catalysis consists of mass transfer between two or three phases. In the case of heterogeneous catalytic ozonation three phases are present, the liquid water phase, the solid catalyst phase and the gaseous ozone/oxygen phase. The seven main steps to describe heterogeneous catalysis are listed below [45].

- Mass transfer to the catalyst by convection or diffusion
- Pore diffusion to internal catalytic surface
- Adsorption on the catalytic surface
- Catalyzed reaction
- Desorption of the product from the catalyst
- Pore diffusion of the product to pore mouth
- Removal from the catalyst by convection or diffusion

Regarding the seven steps of heterogeneous catalysis, each step can be the rate determining step for the reaction and therefore different rate laws have to be applied for reaction kinetics determination. The first step is the approach of the catalyst by convection. This can be an important step in catalytic ozonation, as the catalyst concentration as well as the micropollutant concentrations are low. Ozone and catalyst powder have to be well distributed and quickly reach a homogeneous phase distribution, to increase the probability of interaction between all three phases. The mechanism can be improved by optimizing the gas flow, the stirrer design and the fluid velocities in the ozonation reactor. Pore diffusion can become the rate determining step if maximum convection is reached and the reaction mainly happens on the inner walls of the particle pores. Then, diffusion into the pores, reaction and diffusion out of the pores, considering fluid velocity inside the pore have to be taken into consideration. This can be summed up with the diffusion coefficient. Pore diffusion depends on the characteristics of catalyst pore systems and the chemical and physical properties of the target molecules.

The reaction can be the rate determining step, depending on the type of reaction mechanism. Heterogeneous catalysis can accelerate the micropollutant removal in ozonation mainly in two ways. Firstly radicals and other oxidizing species can form when ozone decomposes on the catalyst surface. Secondly the organic compounds can adsorb to the surface and directly react on the surface of the catalyst or with ozone and less selective oxidizing species. The pollutant can directly be converted at the active spot. A conversion can require two or more active spots for reaction initiation. If the second mechanism is a relevant reaction process in micropollutant removal, it is most likely that the organic compound adsorbs and reacts with the oxidizing species in the adsorbed state.

In the present study the active catalyst sites, as described in Chapter 2.3.4, are provided by AC or CeO_2. If AC acts as reaction initiator, the reaction of ozone with active groups present on the activated carbon surface indicates that AC acts rather as a radical promoter than a catalyst. This has the negative effect of material consumption and the necessity of regular renewing of AC to maintain efficient radical generation [46]. The scheme of reaction mechanism during catalytic ozonation in Figure 5 shows the different ways of catalytic activity. Adsorption and catalytic reactions occur simultaneously. The catalytic activity is described in two ways as mentioned above. The formation of radicals from ozone due to the AC surface and the active Ce^{3+} species formed from CeO_2 is shown as well as the adsorption and reaction of organic compound and ozone on the catalyst surface. Furthermore the radical reaction is pointed out as pollutant degradation and reaction with radical scavengers [33].

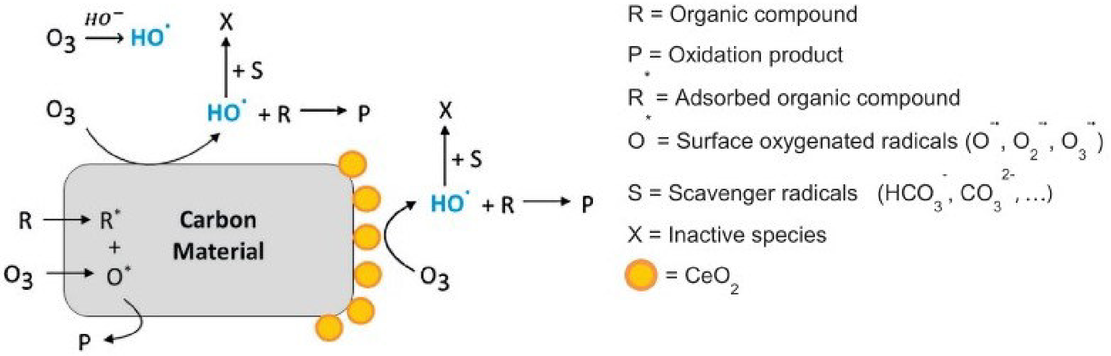


Figure 5: Reaction mechanism of catalytic ozonation on cerium doped AC surface [33]

2.3.6 Advanced Oxidation Processes

AOPs are known for their high efficiency in the degradation of ECs, which are not biodegradable and exit WWTPs unaffected.

Generally AOPs consist of two steps, the in-situ formation of highly reactive oxidizing species and the reaction of these oxidants with target contaminants. Reactive species are usually hydroxyl radicals (OH·), like in the process of ozonation. Different types of radicals and oxidising species include for example chlorine or sulfate radicals. The oxidants immediately react with pollutants and form shorter chained compounds which are then biodegradable. In the ideal case, full mineralization of target contaminants can be achieved. AOPs substantially differ in the mechanism of radical production. Depending on the process, different radical scavengers can be formed. Mass transfer of the oxidising species within the water matrix can be the limiting factor [47].

The most promising AOPs are direct ultra violet (UV) photolysis, UV/H_2O_2, ozonation based processed, Fenton, photo-Fenton, photocatalysis, ultrasound processes and their combinations [27]. Ozone and UV based processes are well-established and operating in full scale, whereas new processes are constantly developed. Process parameters like energy consumption and operation costs are important economic limitations to proposed technologies. Further critical points that must be assessed when comparing AOPs are feasibility on high volume flows of urban WWTP under constantly changing wastewater compositions. Real sustainability of the process needs to be assessed and process safety is an important topic. Safety concerns can include, for example, the risk of ozone gas release to the atmosphere, which can be toxic if inhaled in high quantities (see Chapter 2.3.1). Another topic of concern is the formation of the above mentioned potentially toxic byproducts. Generally AOPs have a high potential of improving current WWT systems and broaden their feasibility on compounds which show low reactivity with the known oxidising methods.

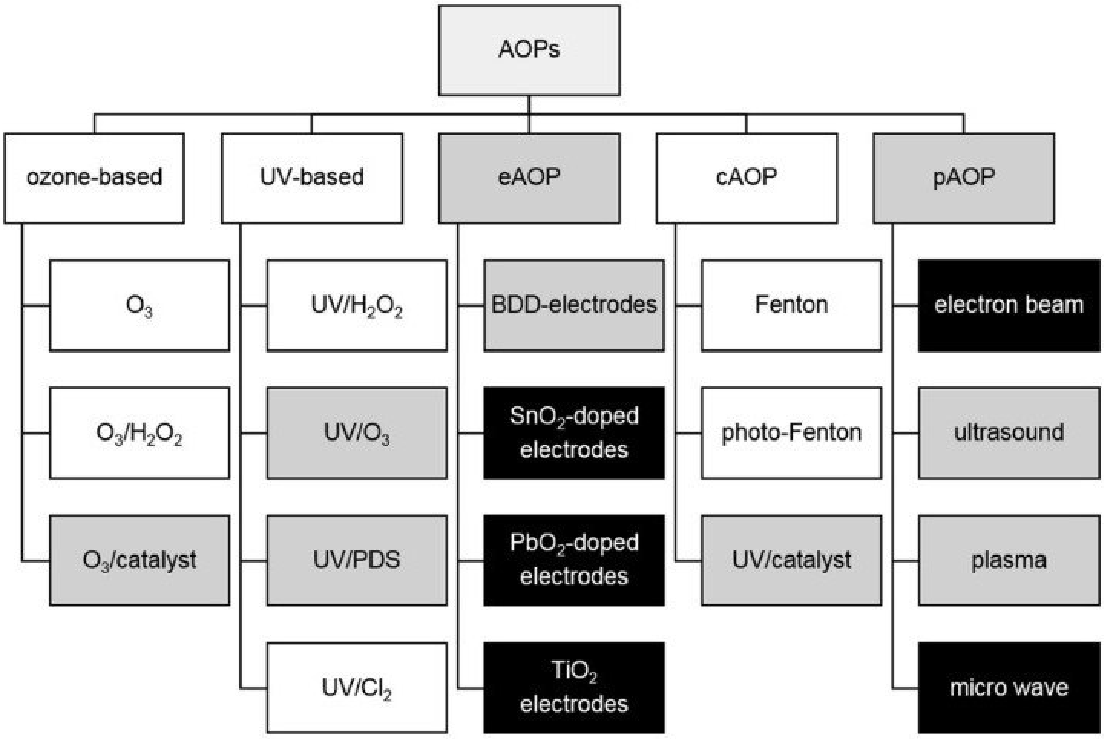


Figure 6: Overview and classification of different AOPs and marked regarding to there establishment status (white = full scale; grey = pilot scale; black = lab scale) [47]

In Figure 6, an overview on the currently existing technologies is given. The processes are organized in five categories based on their source for the production of the oxidising species. The colour code in the figure explains the status of each technology, where white indicates full scale application, grey indicates that pilot scale research has been done and black means that the process has been tested on the laboratory scale. Subsequently, each process category will be shortly explained and the advantages and disadvantages will be pointed out.

Regarding ozonation, the reaction basics of the processes are further explained in Chapter 2.3.2. The initiation of radical formation under normal conditions can be relatively slow. This is why the ozonation process can be improved by different methods.

Increasing the pH of the treated water matrix to pH > 8 results in an abundance of hydroxyl ions (OH^-) which react with ozone and initiate $OH\cdot$ formation. The addition of H_2O_2 to the water matrix forms the peroxide anion HO_2^- which directly reacts with ozone to $OH\cdot$. The process is fully established in drinking water applications. For wastewater treatment, the improvement of basic ozonation with H_2O_2 is limited, due to the high competition reactions and sufficient radical formation by ozone alone. Additionally, excess H_2O_2 has to be removed before discharging the treated water into the environment.

Heterogeneous catalysis, like investigated in this study, using different catalytic materials, is a process investigated on pilot scale. Different catalyst materials, mostly metal oxides like titanium oxide, aluminium oxide or manganese oxide, have been tested in past studies [47]. The reaction path of heterogeneous catalysis and the radical formation mechanism is further explained in Chapter 2.3.5. A chemical kinetic model based study for homogeneous catalysis with the metal ions of titanium, cobalt, nickel, copper and others has been carried out by Guo et al. [48].

UV-irradiation based AOPs are combined with different radical promoters, such as H_2O_2, sulfate, ozone or chlorine. The UV-irradiation source can consist of low pressure or medium pressure mercury lamps and LEDs. UV dose applied in AOPs exceeds the minimum dose required for pathogen disinfection which is beneficial for the final water quality. Full scale applications can be found in potable water reuse and surface water treatment. The application on wastewater is difficult due to low light transmission in wastewater and scavenger formation.

The combination of ozonation and photolysis leads to high removal of a wide contaminant range. The drawback is the low energy efficiency, as both sources require electrical energy. Sulfate radicals are produces from peroxymonosulfate and UV radiation and show advantages compared to H_2O_2, due to their higher $OH\cdot$ yield. The drawback is a higher selectivity, which results in sensibility regarding the water matrix. Chlorine is a promising initiator and is favorable in applications on waters with $pH > 7$, adverse is the fact that chlorine species can act as $OH\cdot$ scavengers themselves [47].

Electrochemical AOPs using different electrode materials are promoted as an efficient and promising eco-friendly method as no further chemicals are needed. The radical formation takes place on the surface of the electrode. Boron doped diamond electrodes (BDD) are the most studied electrodes for AOPs. Nevertheless, the short reactivity range of 1 µm might lead to high electrical costs as water pumping will be necessary to assure a homogeneous removal process. The process is limited to the electro-active surface area [49].

The Fenton process is the combination of ferrous and H_2O_2 in acidic conditions. It is one of the most studied AOPs and is operating in some industrial full scale applications. Its main advantage is the possibility of low cost operation and the non-toxic ferrous material which can be regenerated [50]. The separation of the catalytic material is relatively simple and can be achieved magnetically. The Fenton process is limited to acidic conditions due to the fact, that at higher pH values the iron precipitate as ferric oxyhydroxide. Further drawbacks are the high amount of chemicals needed and the unintended consumption of $OH\cdot$ [47].

The photo-Fenton process is an upgrade to the classical Fenton process and it can be run as solar photo-catalytic process [51]. In this process, the UV-VIS light accelerates the ferrous regeneration. The ferrioxalate complex absorbs radiation up to wavelengths of 550 nm, which makes it suitable for solar driven AOP [47]. The photo-Fenton process is more efficient in $OH\cdot$ production and shows higher removal rates of ECs compared to the classic Fenton process [52].

Ultrasound leads to the collapse of micro-bubbles which violently implode. This leads to the formation of high temperatures, pressures and the formation of highly reactive radicals. With sonochemical processes, various ECs can be removed. Due to the high energy consumption of ultrasound AOPs, combinations of the process with UV, photo-catalysts or UV/H_2O_2 are in the focus of research [47].

In summary, all processes show high EC removal potential. Some methods like UV/H_2O_2 are preferably used in disinfection applications, whereas ozonation convinces with high removal efficiency, moderate energy demand and good disinfection results. From an energetic point of view, photo-Fenton and photo-catalytic processes can be feasible for solar radiation. General drawbacks are the high energy or chemical consumption, the formation of secondary products, the potential increase of toxicity and the possible need of a subsequent biological treatment step.

2.4 Contaminants

Most AOP studies done on the removal of ECs are carried out on elevated concentrations of model compounds, such as oxalic acid and salicyclic acid [53], [36]. DCL is one of the most studied compounds and also one of the most detected substances in water bodies across the globe [54]. Antibiotics in the environment are of very high concern due to the increasingly fast development of residencies. Erythromycin (ERY) and TTC are often detected macrolide antibiotics in water bodies [55]. The concern of the negative impact of natural and artificial hormones on aquatic organisms is rising since they were first detected in wastewater almost 60 years ago [6].

The chemical composition of pharmaceuticals is the reason for their resistance in water bodies. They are designed to remain in the human body in an unchanged state long enough to be adsorbed by the body. Pharmaceuticals occupy a middle path in terms of polarity, hydrophilicity, solubility an biodegradability. This results in risk of persistence of the compound itself and their metabolites, which are due to their high variety, more complicated to assess [56].

Next to the solubility of these compounds in water, sorption on solids and sediments is an important mechanism of persistence in the environment. This process decreases the concentration in waters, which misrepresents actual measured values and enhances accumulation. The main natural attenuation processes for non-biodegradable substances are volatilisation, dispersion, dilution, sorption, photolysis and biotransformation. These processes highly depend on presence of solids suspended in water and solar radiation [57].

2.4.1 Diclofenac

Diclofenac (DCL) is one of the most commonly used pain killers worldwide, its chemical structure can be seen in Figure 7. It is used as anti-inflammatory to relieve pain in disease situations and in acute injuries. It is taken orally and applied to skin and is distributed under a variety of names, such as Diclofenac-Asteria (USA, Korea), Diclo-Denk (Germany) and Voltaren in most parts of the world. Zhang et al. [58] estimated a global consumption of 940 t of DCL per year. Nevertheless, this quantity is difficult to calculate due to the different distribution names and uncertainties in purchased and consumed quantities.

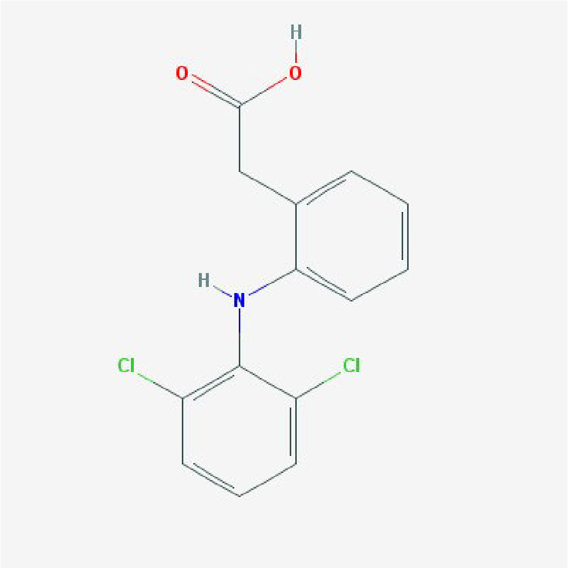


Figure 7: Chemical structure of DCL [59]

Production sites are the biggest releases of any pharmaceuticals to natural water bodies. DCL caused the first famous case of ecological damage due to pharmaceutical residues in the environment worldwide. In India it has been proved that DCL is extremely toxic to vultures, who consume it through the excrement of cattle. In this case DCL led to the extinction of the animal. DCL has been prohibited for veterinary application in many countries due to its toxicity for animals. Consequently the drug has been banned in veterinary medicine in Nepal, Pakistan and Bangladesh [15].

The drug has been selected for the first European watch list of the EU Water Framework Directive. It has been taken off the second watch list in 2018, because enough data was available by then. This includes research data according the status of DCL in the environment, consumption, occurrence, toxicity, resistance, persistence and metabolites, the interaction with other emerging contaminants and the transport in the environment.

DCL degrades into its transformation products, which are mostly hydroxyl derivatives, in the human and animal body. The main process of DCL in the environment is via the natural process of photolysis via OH· in the atmosphere. Direct photolysis is the predominant removal process in freshwater with a half-life time of 8 days. In freshwater, DCL mainly exists in its dissociated form, therefore volatilisation is not expected, and it is not biodegradable in water. The mobility of DCL in soil is moderate and it is expected to adsorb to suspended solids and sediment [59].

Residues remain as potentially toxic traces of the drug itself and its metabolites. It is worldwide found in ground-, surface-, and drinking water. It is one of the most investigated drug according residuals in the environment.

2.4.2 Erythromycin

Erythromycin (ERY) is an antibiotic used for the treatment of bacterial infections, including respiratory tract and skin infections. The chemical structure of ERY can be seen in Figure 8. It is on the WHO list for essential medications as it is effective and safe. Along with other antibiotics, such as clarithromycin, azithromycin, ERY is widely used in human and veterinarian medicine and in aquaculture. Antibiotics in the environment have particularly raised awareness in many studies over the last decade due to their potential to develop resistant mechanisms by bacteria [60]. ERY was chosen as the antibiotic to be removed in this project, due to its wide spread occurrence in water bodies and treatment plant effluents. The biodegradation on ERY in soil depends on temperature and source of organic carbon. In general, biodegradation in water is not an important fate process. The bioconcentration in aquatic organisms is classified as moderate.

Due to its pK_a of 8.9, ERY almost entirely exist in its protonated form and therefore adsorbs more strongly to carbon rich soils and clay. In water, ERY adsorbs to suspended solids and sediment, the substance only hydrolyses under basic conditions. The antibiotic shows instability and conversion under acidic conditions, which due to an intramolecular dehydration leads to limited bioavailability [61]. Due to this reason, ERY was later replaced by the antibiotic TTC, as water samples showed an initial pH of 4 in some cases and it was not possible to state whether ERY was removed by the process itself or due to acidic milieu [62].

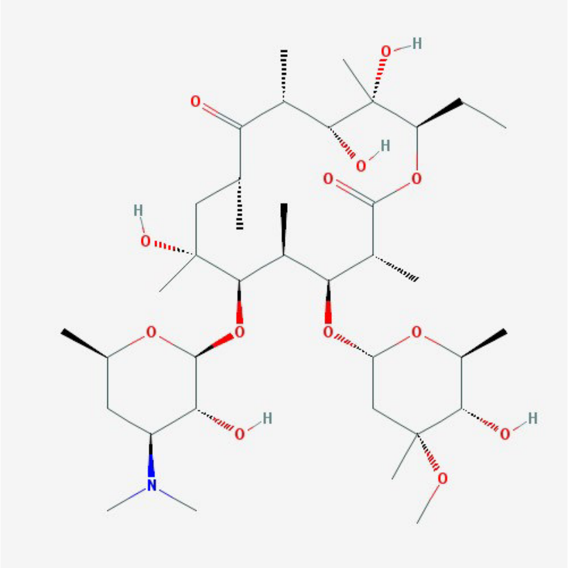


Figure 8: Chemical structure of ERY [62]

2.4.3 Tetracyclin

Tetracycline (TTC) is a broad-spectrum antibiotic for the treatment of cholera, typhus fever, malaria, syphilis and several other infections and is distributed under the name Sumycin among others. Its chemical structure can be seen in Figure 9. The antibiotic is globally consumed in human and veterinarian medicine. A particularly high amount of TTC was produced and distributed in China [63]. Biodegradation is not an important fate process, in activated sludge adsorption is the principal removal mechanism of TTC [64].

2.4.4 Estradiol

17-beta-estradiol (E2) is a natural female sex hormone that regulates menstrual and reproductive cycles. E2 is produced by all mammals and some insects, fish and other animal species. E2 is also used as a medication in hormone therapy. E2 can have health effects on the human organism such as gallstone, impairment of fertility, it is carcinogen and it affects female and male body

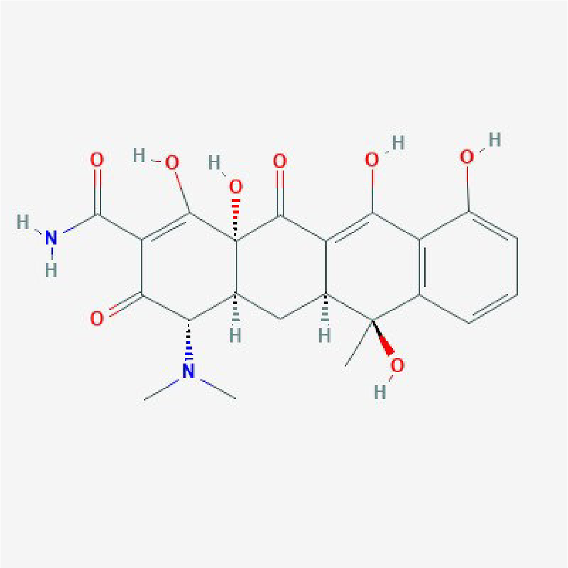


Figure 9: Chemical structure of TTC [64]

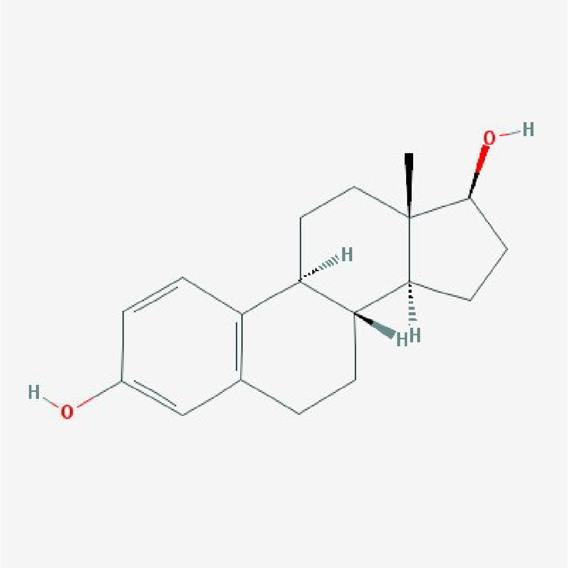


Figure 10: Chemical structure of E2 [65]

negatively. The chemical structure of E2 can be seen in Figure 10.

E2 and its metabolites are produced and released to water bodies via mammal urine, which can be as high as 5 mg/day in human organism, 0.8 - 11 mg/day for cows and 6 mg/day for swines. The main degradation process of the hormone in natural water bodies is via photo-degradation and direct photolysis by sunlight. Volatilisation from moist soil and water surfaces, biodegradation in agricultural soil, hydrolysis and adsorption to sediment or suspended solids are not expected to be important fate processes under environmental conditions. The bioconcentration shows high potential in aquatic organisms, if not metabolized by the organism [65].

2.4.5 Ethinylestradiol

17-alpha-ethinylestradiol (EE2) is a synthetic steroid and the nearly exclusive estrogen medication commonly used in birth control pills. It is also used in menopausal hormone therapy, against osteoporosis and as palliative care for breast and prostate cancer. The chemical structure of EE2 can be seen in Figure 11.

Health risk from EE2 include carcinogenicity, feminisation of male and infertility. The main process of the hormone in natural water bodies is via direct photolysis by sunlight. When released to soil it shows low mobility. Volatilisation from moist soil, biodegradation in sewage and hydrolysis are not expected to be important fate processes under environmental conditions. Whereas adsorption to sediment or suspended solids is likely. The compound has a high potential for bioconcentration in aquatic organisms, if not metabolized by the organism [66].

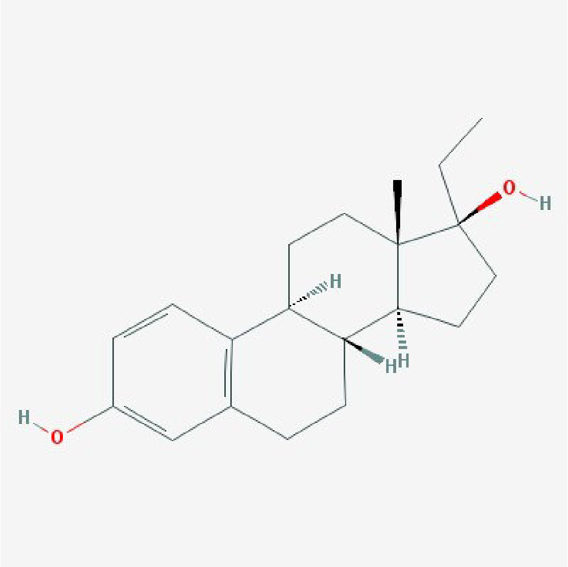


Figure 11: Chemical structure of EE2 [66]

3 Objective and Outline

Adsorption and ozonation of ECs are processes today operating in full scale in selected WWTPs in Switzerland, Germany and France. The objective of this project was to test the feasibility of catalytic ozonation as EC removal step in wastewater treatment. The removal efficiency of ECs, such as pharmaceuticals and hormones from water samples, was compared for the three mentioned processes. Finally, it was investigated, if the application of the selected catalytic material could improve the ozonation process.

The project is divided into three phases. The objective of the first phase of the project consists of the characterisation of local water streams. The characterisation is focused on pharmaceuticals, such as antibiotics, pain killers natural and synthetic hormones as well as illegal drugs and their metabolites. These findings give an insight on the status of the local water streams. The study can give a baseline for further studies to investigate the eventual necessity of micropollutant treatment in the region. The characterisation of different water streams such as entering and exiting streams from WWTPs as well as a hospital effluent could show concentration fluctuations in different streams and their influence on each other. Finally, based on the results of the first phase, the pharmaceutical concentrations of the water samples for the experimental part of the second and the third project phase, were determined.

The second and third project phase consist of experimental campaigns for the EC removal of synthetic water and real wastewater. The waters were spiked with comparably low EC concentrations of diclofenac (DCL), tetracycline (TTC), 17-beta-estradiol (E2) and 17-alpha-ethinylestradiol (EE2). Additionally, the investigation of the mixture of four compounds instead of a single model compounds distinguishes the project from former studies.

Three stages of experiments are necessary to gain know-how about the different processes. The minimum applicable dose of ozone and catalytic material has to be evaluated on the behaviour of compounds in low concentrations. Firstly, adsorption experiments are carried out to select an appropriate concentration of catalyst in the batch reactor and to compare adsorption capacities of different catalyst powders. Secondly, basic ozonation experiments are carried out under comparable conditions to gain data for ozone dose and treatment times for meaningful removal results.

Finally, basic ozonation and catalytic ozonation are carried out under similar process parameters on synthetic water and real wastewater samples. The comparison of the two processes is is evaluated to investigate if catalytic ozonation shows an improvement of the removal capacity. Moreover the evaluation shows if an increase of process efficiency can be achieved over basic ozonation.

4 Materials and Methods

The practical part of the study was divided into three phases. Phase two and three contain all experiments on EC removal and process testing, whereas in phase one an investigation of the composition of five different local wastewater streams, described in Chapter 4.1, was carried out. Phase one includes sampling and internal as well as external analysis of the samples. The outcomes of phase one are a reference for further EC concentrations used within the experimental campaign. In phase two and three adsorption, basic ozonation and catalytic ozonation were carried out with synthetic water and spiked real wastewater, with the aim to compare EC removal of catalytic ozonation over basic ozonation and adsorption.

Moreover in this section the materials applied in the experimental part of the study to meet the objectives are specified. The methods of production and characterisation of materials are described if applicable. Analytical methods utilized within the three project phases are described in detail.

4.1 Selection of Wastewater Sampling Points

For project phase one, five representative wastewater streams in the province of Gipuzkoa, Spain were analysed. The entry and exit streams of two WWTPs and the direct effluent of a hospital were selected accordingly.

San Sebastian is the capital and biggest city of Gipuzkoa. The main WWTP of San Sebastian, called WWTP Loiola, receives the wastewater of 628.000 inhabitant equivalents and leads its effluent to a subsea outflow. As the city is next to the Atlantic ocean with high tides, therfore marine water is influencing the wastewater. Most importantly the WWTP receives the wastewater from the main hospital of San Sebastian. The WWTP Loiola consists of an high load activated sludge line and a physical chemical (iron chloride solution) treatment line in case of accidental industrial dumping, to preserve the biology.

As a comparison, a WWTP without the influence of hospital effluent was selected. The WWTP of Legorreta, a village with 1500 inhabitants, is called WWTP Gaikao. It receives rural wastewater and the leachate of a closed landfill, but does not receive industry discharge. The process contains a biological carbon treatment step, nitrification and a chemical phosphorous removal step. The nitrogen removal step is carried out in an IFAS (Integrated Fixed Film Activated Sludge) process, consisting of an anoxic and an aerobic process step [67]. In the aerobic nitrification step the entering ammonium nitrogen is biologically oxidized to nitrite and further oxidized to nitrate. In the anoxic respiration step nitrate is partly reduced to nitrogen gas and part of the nitrogen leaves the WWTP in form of nitrate.

The effluent of the main hospital of San Sebastian (Donostia Unibertsitate Ospitalea) was sampled to investigate the correlations of the direct effluent of the hospital and the receiving waters of the WWTP of San Sebastian. Moreover it was examined if the receiving of the effluent of a hospital influences the general composition significantly compared to a WWTP not receiving water from a hospital.

4.2 Sampling of Wastewater

Representative wastewater samples were taken after a three-day period without precipitation, to minimize environmental influences on the wastewater composition, such as dilution and decrease of micropollutant concentrations, due to rainfall. A Wednesday was chosen as sampling day to lower the variation that can happen due to citizen migration during the weekend and to ensure that the sample represents an ordinary wastewater composition. From all five sampling points similar volumes during the same 24 h period were collected during a weekday, by different personnel with slightly different automatic sampling equipment.

The inflow and effluent samples from Loiola were taken every 30 min for 24 h, and provided by the WWTP personnel in 5 l containers. The sampling at Gaikao was performed every 15 min for 24 h. These samples were stored in three 2 l containers for each of the two sampling points. The Gaikao WWTP reported increased foam building in the biological treatment and decreased entry loading due to high precipitation rate during the previous months.

Figure 12: Set up of the sampling device Tomamuestra SIGMA 900 at the hospital (Donostiako Uniberstitate Ospitalea)

The samples at the hospital were taken at a regular sewer access point with the automatic sampling device Tomamuestra SIGMA 900. The automatic sampling instrument was set up for 24 h at the closest access point to the building. The installation can be seen in Figure 12, with time and volume specifications listed in Table 2. The water surface lies five meters below ground level and the water height was estimated to 20 cm. Two additional streams with altering volume flows are entering the main channel at the sampling spot. To ensure representative sampling the inlet of the sampling-tube is protected by a rigid cage and was submerged a few centimeters below the water surface. The sampling tool was calibrated to collect 125 ml every 20 min at a tube length of 7 m. One sampling cycle consists of pre-purging, flushing the tube once, purging, sample collection and post-purging. All the samples are collected in a single bucket. A higher amount of paper in the hospital wastewater was visibly detected, which can be explained by the small distance of the sampling point from the building and can lead to a higher DOC. Visible paper content at the inlet of the WWTPs is lower, as degradation might already occur in the pipelines.

All samples were collected and filled into three analysis container for each sample on the spot. All samples were sent to IPROMA immediately. The intern analysis of all samples with triplication were carried out on the same and the following day.

Nr. of samples	time [h]	interval [min]	total V [l]	sample V [l]
72	24	20	9	0.125

Table 2: Parameters of wastewater sampling at the hospital (Donostiako Uniberstitate Ospitalea)

4.3 Ozone

Ozone gas is the oxidising compound in the process of ozonation. It has a short lifetime, a varying stability in different media and cannot be stored in a technically meaningful way (see Chapter 2.3.1). For the on site production a ”Triogen®O_3 LAB2B” corona discharge type ozone generator from SUEZ is used. The generator can produce ozone from dry air or pure oxygen and the maximum outputs for the different inflow gases are 4 g/h and 10 g/h respectively. Pure oxygen is used as initial gas for all experiments. The generator is controlled by a control knob, which ranges from 1 to 7 and allows the adjusting of the intensity. A flow meter with a range from 2 to 10 Nl/min shows the volume flow through the generator.

The oxygen pressure is set at the oxygen gas bottle with a pressure valve and should not exceed a relative pressure of 0.275 bar for pure oxygen according to the device specifications. The gas flow and the calculated ozone dose are adjusted via a mass flow controller (MFC), which is installed at the outlet of the ozone generator.

Figure 13: SUEZ - Triogen®O_3 LAB2B ozone generator with corona discharge

4.3.1 Ozone Flow

The real flow rate of ozone depends on many parameters like intensity of the generator, oxygen flow rate, ambient temperature and gas pressure and has to be measured before and during each experiment. For the determination of the ozone concentration in the inlet and outlet gas stream, a standard method, further explained in Chapter 4.9.12 was used.

The MFC is set to a normal volume flow (normal conditions: T = 293.15 K and p = 1.013 bar), which means that the real volume flow, based on ambient conditions, must be calculated with Equation 16. The ozone dose can be calculated with Equation 17, considering the real volume flow of the gas and the ozone concentration.

$$Q_{real} = \frac{Q_N * T_N * p_N}{p_{abs} * T_{real}} \tag{16}$$

$$\dot{m}_{O_3} = wt_{O_3} * Q_{real} \tag{17}$$

Q_{real} ... $volume\ flow\ at\ ambient\ conditions\ [l/min]$
Q_N ... $volume\ flow\ at\ normal\ conditions\ [l/min]$
T_{real} ... $ambient\ temperature\ [K]$
T_N ... $normal\ temperature\ 293.15\ [K]$
p_N ... $normal\ pressure\ 1.013\ [bar]$
p_{abs} ... $absolute\ pressure\ p_N + p_{oxygen}\ [bar]$
wt_{O_3} ... $mass\ concentration\ of\ ozone\ [mg/l]$
m_{O_3} ... $ozone\ mass\ flow\ [mg/min]$

4.4 Catalyst

The catalytic material for the experiments was prepared and characterized in the laboratories of the Materials and Advanced Manufacturing Division, CEIT. The material and method of preparation were selected based on the literature study, see Chapter 2.3.4. The solid catalyst powder was produced with a wet impregnation method of AC and CeO_2, which was first published by Imamura et al. [68] and modified by Orge et al. [36].

For comparison and selection of the produced catalyst with the most promising properties, AC was impregnated with three different mass loadings of CeO_2, see Table 3. All three catalysts as well as pure AC were calcinated afterwards and characterized with scanning electron microscope (SEM) and X-ray diffraction.

Name	CeO_2 loading	Calcination Temp.
AC	0	450 °C
CAT1	5 wt%	450 °C
CAT2	10 wt%	450 °C
CAT3	20 wt%	450 °C

Table 3: Specifications of produced catalysts

4.4.1 Preparation of Catalyst

The granular AC (Norit® GAC 1240) has an original particle size range of 0.4 - 1.7 mm. Orge et al. [36] proposes a particle size of 200 - 300 µm as catalyst for catalytic ozonation experiments. To guarantee, that the catalyst powder stays in suspension during the experiments, a smaller particle size was chosen. For the generation of CeO_2 as catalytic material, cerium salt (Cerium(**III**) nitrate hexahydrate ROTI® REMETIC 99.9 %) with a molar mass of 434.2 g/mol was used. Furthermore, sodium hydroxide (NaOH) solution (3 M) and deionized water were needed for the impregnation method. Both substances AC and cerium salt were obtained from ACROS ORGANICS.

For the preparation of different catalyst powders the AC granulate was grinded and sieved to a particle size of 50 - 71 µm. To calculate the mass loading of CeO_2 on the catalyst, a full transformation of initial cerium salt to CeO_2 was assumed. Equations 18 to 21 explain the calculation of the mass ratio of cerium salt to AC to achieve the desired mass loading of CeO_2 (w_{CeO_2}).

$$m_{cat} = m_{CeO_2} + m_{AC} \tag{18}$$

$$m_{CeO_2} = m_{cat} * w_{CeO_2} \tag{19}$$

$$n_{Ce(NO_3)_3*6H_2O} = n_{CeO_2} = m_{CeO_2}/MM_{CeO_2} \tag{20}$$

$$m_{Ce(NO_3)_3*6H_2O} = n_{Ce(NO_3)_3*6H_2O} * MM_{Ce(NO_3)_3*6H_2O} \tag{21}$$

m_{cat} ... $total\ mass\ of\ solid\ catalyst\ [g]$
m_{CeO_2} ... $mass\ of\ cerium\ oxide\ [g]$
m_{AC} ... $mass\ of\ AC\ [g]$
w_{CeO_2} ... $mass\ loading\ cerium\ oxide\ [-]$
n_{CeO_2} ... $mol\ of\ cerium\ oxide\ [mol]$
$n_{Ce(NO_3)_3*6H_2O}$ ... $mol\ of\ cerium\ salt\ [mol]$
MM_{CeO_2} ... $molmass\ of\ cerium\ oxide\ 172\ [g/mol]$
$MM_{Ce(NO_3)_3*6H_2O}$ ... $molmass\ of\ cerium\ salt\ 434.2\ [g/mol]$

The impregnation method was carried out with suspensions of 15 g solid compounds suspended in 100 ml deionized water each. The 15 g consists of the desired AC to CeO_2 ratio. 200 ml NaOH solution (3 M) was added drop-wise to the homogeneous suspension under constant stirring. Afterwards the suspension was stirred for 15 h at room temperature.

The mixture was washed with deionized water and centrifuged several times. This procedure was repeated to remove the nitrate and the alkalinity from the suspension, until the pH became neutral. Particles smaller than 2.5 µm were washed out during centrifugation, which was proved by filtering the wash water. This showed that with sieving, the desired particle size distribution could not be achieved, possibly due to electrostatic forces. The formation of cerium crystals without AC support during impregnation is neglected, as the AC particles act as crystallisation initiation. With every wash circle the washing water contains a higher content of fine catalyst powder, therefore the number of wash cycles was kept at a minimum of seven.

The impregnated and washed water was evaporated and afterwards the powder was dried at 105 °C for 36 h. The dry powder was weighted and a sample for SEM analysis was taken. While evaporation during the drying process, it was noticed, that the powder of CAT3 settled down, while the powder of CAT1 and CAT2 remained in suspension.

To modify the surface of the AC, strengthen the binding forces between AC and CeO_2 and to obtain a more crystalline structure of the CeO_2 particles, a heat treatment was performed. The catalyst powder as well as the AC powder were thermally treated under argon atmosphere and an argon flow rate of 0.05 Nl/min. The heating of the oven was set to a temperature ramp of 5 °C/min and kept at 450 °C for 4 h.

4.4.2 Catalyst Characterisation

An X-ray analysis was carried out in a Philips X'pert MRD X-ray diffractometer to characterize the crystallinity of the CeO_2 particles distributed on AC powder and to compare calcinated to not calcinate powder. For this purpose the catalyst with the highest CeO_2 loading (CAT3) was characterized.

The two powders showed similar results and the peaks agreed with the wavelentgh of the CeO_2 database. A peak width of 10 theta respectively indicates an amorphous structure of the CeO_2. As for precipitation over AC, many germs for nucleation initiation are present and no specific crystalline structure can develop. Another reason can be the small particle size of only a few nm, a range where detection with X-ray is problematic. Arising carbon peaks were neglected. X-ray analysis diagrams of the calcinated sample do not significantly differ from not calcinated samples. This leads to the conclusion that at this calcination temperature, the crystalline structure is not significantly influenced.

All produced catalysts were analysed in a Philips XL 30CP SEM to obtain a visual images of the catalyst powder and the qualitative powder composition. The average particle size of the catalyst and the distribution of the CeO_2 were observed qualitatively. Furthermore, impurities were identified and the structure of especially CeO_2 particles was investigated. After calcination, impurities such as titanium, aluminium, chrome, iron and nickel were detected in the carbon powder. These impurities most probably originate from residual dust in the oven and can be neglected due to their very low concentration.

The characterisation of the pure AC powder before calcination with the secondary electron (SE) detector showed fine particles mostly ranging from 5 - 50 µm. This confirmed, that during the sieving process an agglomeration of small AC particles due to electrostatic forces took place. A removal of particles smaller than 45 µm could not be achieved with sieving. A further sieving after impregnation was not considered as it could have lead to a loss of CeO_2, which mostly nucleate on small particles. The SEM analysis of pure AC without heat treatment could identify impurities containing aluminium, silicon and sulfur in concentrations of < 1 wt%.

CAT1 mostly contains its fine structure. Some agglomerates up to 100 µm could be detected, which contain double the amount of CeO_2 than the small particles. A certain crystalline structure could not be observed, as CeO_2 particles are to small for the resolution of the SEM detector. The qualitative composition analysis showed a CeO_2 content of approximately 5 wt%. Small particles of pure CeO_2 could not be detected or identified.

CAT2 showed a more homogeneous distribution of CeO_2 particles within the powder. Bigger agglomerates with a higher cerium content were berly detected. A detailed analysis of small particles which appear bright in the images of the back scattered electron (BSE) detector showed a slightly higher cerium concentration than the overall analysis. The reason might be the small particle size of < 5 µm where the electrons also penetrate the surrounding carbon particles. Even at the highest resolution of the SE detector, the smallest particles could not be distinguished.

CAT3 showed a homogeneous distribution of cerium crystals. Big agglomerates could not be observed. It is assumed that CeO_2 formations bind fine carbon particles, which explains why the washing water of the CAT3 powder centrifugation did not contain any fine fractions.

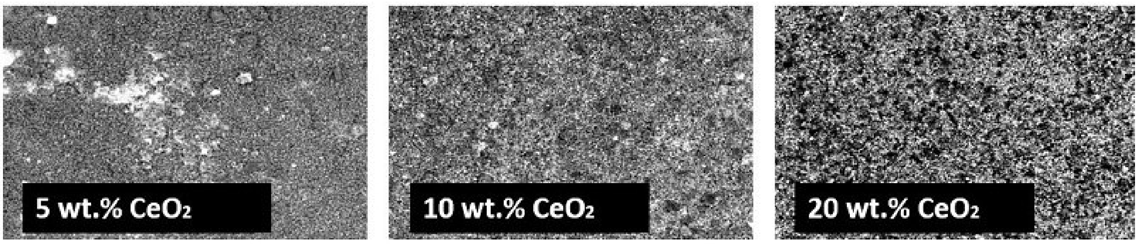


Figure 14: SEM images of three different catalysts (from left to right: CAT1, CAT2, CAT3); BSE detector, magnitude 100x

As a conclusion, the qualitative analysis with SEM shows similar composition to the initial calculated ratio of AC to CeO_2 in all powders. The distribution of CeO_2 crystals on the AC surface was homogeneous for CAT2 and CAT3 and rather inhomogeneous for CAT1. Figure 14 shows SEM analysis images of all three catalyst samples. The white spots are the regions with higher CeO_2 concentration. One of the most important characteristics of a solid catalyst is the high specific surface area. If the CeO_2 loading is too high, this can lead to pore blockage or agglomeration of CeO_2, which means that catalytic activity will not increase with CeO_2 loading. Further experiments to compare the different catalysts and their activity are needed for a more detailed understanding. Finally, CAT2 was selected as the catalyst applied in all adsorption and catalytic ozonation experiments. The decision was made as a compromise between satisfying homogeneous CeO_2 distribution, obtained from the SEM analysis, and low enough CeO_2 loading to minimize pore blockage and reduce costs in future applications.

4.5 Synthetic Water

Wastewater as well as treated wastewater contains a highly complex matrix of unknown substances in different concentrations. Therefore it is suitable to previously carry out all experiments on a solution of model compounds, so called synthetic water, to avoid interferences with other compounds, reduce errors and uncertainties. Other organic compounds present in wastewater might act as scavengers. Scavengers consume a high amount of ozone, lead to a less efficient process and to a lower removal of the tackled micropollutants. The results of the synthetic water experiments will provide a benchmark for further comparison with real wastewater experiments.

Synthetic water consists of deionized water spiked with defined concentrations of four different ECs DCL, TTC, E2 and EE2, see Chapter 2.4. The analysis of wastewater and treated wastewater samples of Gipuzkoa resulted to contain low concentrations of these ECs or concentrations below the LOD. To produce meaningful results, elevated concentrations leaned on data from a study from Comber et al. [56], were selected.
After the first experiments with concentrations of 50 µg/l and 5 µg/l respectively, the concentrations were increased by a ten-fold as the removal process was too fast for meaningful interpretation. The final concentrations for the preparation of synthetic water were 500 µg/l for DCL and TTC, and 500 µg/l for the hormones E2 and EE2.

The pharmaceuticals used in the preparation were purchased from different pharmaceutical companies. DCL was purchased from ALFA AESAR and E2, EE2, ERY and TTC were obtained from TCI-Chemicals.

4.5.1 Preparation of Synthetic Water

For project phase two synthetic water was newly prepared for each day of experiments. Mother solutions of each compound were prepared previously and than filled up to the required volume. DCL and ERY powder is soluble in water at room temperature and can directly be dissolved in deionized water. For the preparation of the mother solution 50 mg of each compound were dissolved. To dissolve 50 mg of TTC 2 ml of sulfuric acid must be added to achieve full solubility of the powder in water. Due to low solubility of the hormone powders in water, E2 and EE2 must primarily be dissolved in an organic solvent. Acetonitrile was chosen, as it does not notably react with ozone and OH·, which was shown by Lin et al. [69] and Coleman et al. [70]. Therefore 25 mg of E2 was dissolves in 50 ml and 25 mg of EE2 was dissolved in 75 ml of acetonitrile
The required volume of each mother solution was added to a stirred tank and then filled up to the volume with distilled water or wastewater, to achieve the final EC concentrations. Experiments were started immediately after preparation.

4.6 Real Wastewater

The wastewater, used in project phase three was punctually obtained from the WWTP Gaikao on the day before experimentation. On the same day, standard water analysis methods, as described in Chapter 4.9, were carried out in the intern laboratory and the water was kept refrigerated overnight. The spiking of wastewater might lead to slightly higher concentrations of ECs in the initial solution, as wastewater already contains certain substances.

4.6.1 Preparation of Spiked Real Wastewater

The preparation of real wastewater was carried out similarly to the preparation of synthetic water described in Chapter 4.5.1. Instead of deionized water, the water obtained from the Gaikao WWTP effluent was used.

4.7 Experiments for Removal of Emerging Compounds

Adsorption experiments are necessary prior to catalytic ozonation experiments to evaluate the optimal catalyst concentration. This means a balance between a reasonable probability for a catalyst particle to contemporaneously meet micropollutants and ozone and an avoidance of full adsorption of ECs on the catalyst surface. Furthermore the share of adsorption in the removal process needs to be quantified to evaluate if catalytic ozonation would lead to a more efficient process than for example a series circuit of an adsorption and an ozonation step.

Basic ozonation experiments were carried out to define an ozone dose that allows a steady decrease of concentrations without a full removal of compounds over reaction time. With the flow settings a visually well distributed bubble formation in the bubble column could be achieved. When carrying out catalytic ozonation the same settings were applied and the comparison of the results allowed a statement over improvement of the process as well as a different reaction behaviour of the compounds.

To reproduce the results from each experiment two different methods of triplication were used. For adsorption experiments, as for each treatment time step a separate experiment was carried out, for each time step enough sample was taken to divide it into three analysis bottles. The triplication of the analysis of the same sample provides the standard deviation (SD) of the analytical method. For ozonation treatment in the bubble column, one sample was taken at each time step, to keep the reduction of the water volume as low as possible. To reproduce the results, each ozonation experiment was carried out three times with the same initial water solution. The SD of the results is based on two parameters, the deviation in analysis and the reproducibility of the ozonation experiments.

4.7.1 Overview of Experiments

The flow sheet in Figure 15 shows the order in which all experiments within this study were performed. The experiments are organized in blocs indicated by roman numbers, where each bloc contains a series of three experiments. In case of I and II, adsorption experiments were carried out with three different catalysts or catalyst concentrations. For all blocs indicating ozonation experiments, the same experiment was repeated three times. Bloc VII and XI are exceptions as they were only performed once.

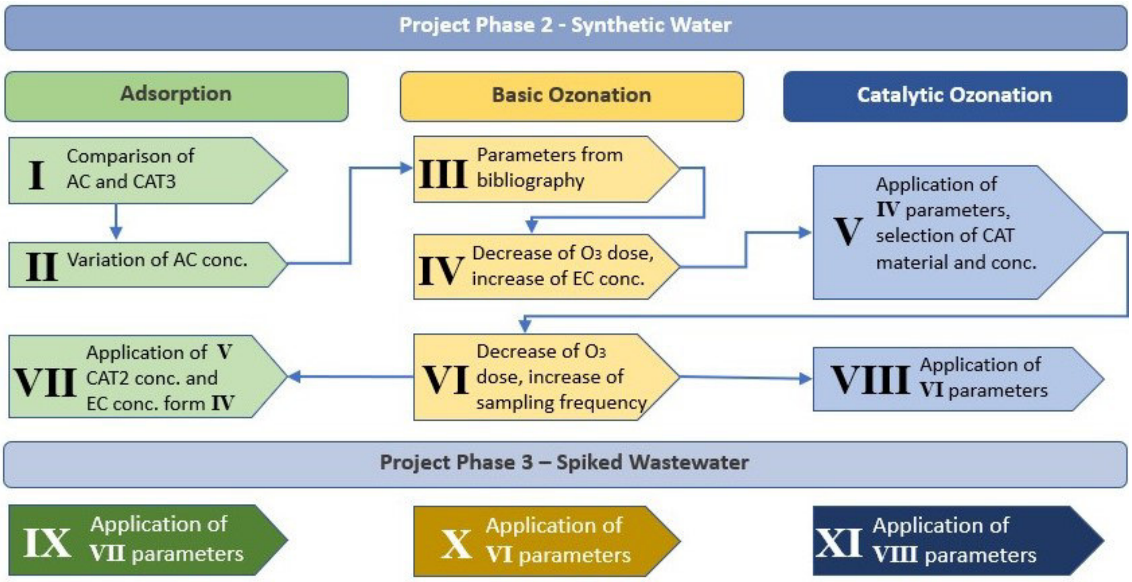


Figure 15: Flow sheet for the implementation sequence of EC removal experiments

Blocs I to VIII include all experiments conducted with synthetic water. The primary output of phase two is the development of the parameters and settings for the operation of the EC removal process. Moreover, the results obtained from the synthetic water experiments served for comparison purposes with wastewater experiments and a deeper understanding of the influence of a complex water matrix and an approximately ten-fold higher initial DOC on the process performance.

As described in Figure 15 the first experiments carried out were the adsorption experiments I and II, followed by basic ozonation III. At this point the initial concentration of ECs was increased by a ten-fold, due to the initial concentrations being too close to the LOD. Moreover, the ozone dose was decreased and ERY was substituted by TTC. Subsequently ozonation experiment IV and the first catalytic ozonation experiment V were performed. The catalyst CAT2 and its concentration were chosen resulting from the experiment II, SEM and X-ray analysis, see Chapter 4.4.2. In the following ozonation experiment VI the dose of ozone was decreased once more, the sampling frequency was increased for the first min and the total experimentation time was lowered to 20 min. The final adsorption and catalytic ozonation experiments with synthetic water were conducted with the parameters achieved from VI and V.

The final parameters were applied to the adsorption experiment IX, the ozonation experiment X and the catalytic ozonation experiment XI with wastewater within project phase three. All conclusions regarding the process evaluation were drawn from the last six experiments.

4.7.2 Set up of Adsorption Experiments

As no gas stream is needed for adsorption, the experiments were carried out in stirred beakers with a reduced volume of 2 l, instead of the 10 l bubble column reactor. Adsorption is expected to be a slower process than ozonation, hence samples were taken from the initial water and twice during the experiment. For each adsorption experiment two beakers, one for each sampling time step, were prepared. This setup allowed to stop each experiment at the required time and the result of the following time step was not influenced by the effects of reduced volume after the first sampling.

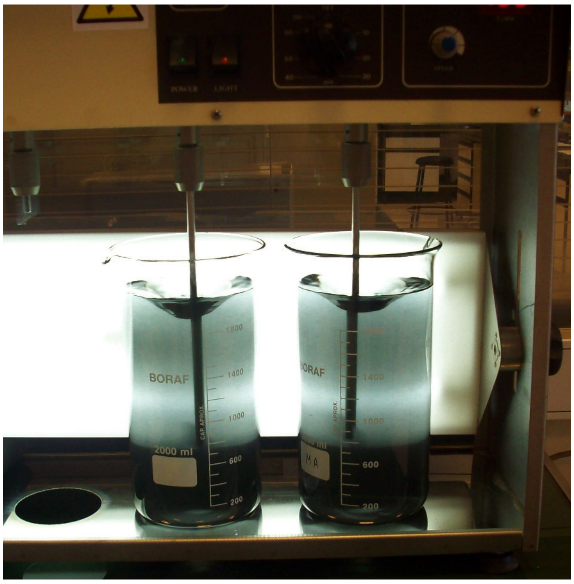


Figure 16: Set up of the adsorption experiments in stirred 2 l beakers

4.7.3 Procedure of Adsorption Experiments

Prior to the experiment, the beakers were filled with exactly 2 l of synthetic water or spiked real wastewater. The catalyst was weighed and placed next to the stirred beakers. The stirrer was set to maximum rotation speed to ensure a homogeneous distribution of the catalyst particles in the reactor. Adsorption time started when the catalyst powder was added, the remaining particles were spilled from the vessel with a few ml of sample water, removed from the beaker beforehand. The treated water samples were collected after the required adsorption time and filtered immediately with Whatman 8 µm and 1.6 µm filters. The filtration time was recorded. From each beaker three samples were bottled for triplication of analysis, labeled and sent to IPROMA on the same day.

In total six adsorption experiments were carried out on synthetic water and one on spiked real wastewater. The first experiments were needed to compare catalyst powders and to find the ideal catalyst dose for the further implementation of catalytic ozonation experiments. The first adsorption experiments were carried out based on a study conducted by Goncalves et al. [71] with a catalyst to water ratio of 143 mg/l and a typical adsorption time of 20 and 40 min. The goal of the first experiment was to compare two different catalyst powders, pure calcinated AC and CAT3, AC impregnated with 20 wt% CeO_2. The catalyst with the highest CeO_2 impregnation was chosen to investigate whether CeO_2 is affecting adsorption considerably or not, due to for example pore or not. The filtration of the AC suspension took about twice as long as the filtration of the CAT3 suspension. This can be explained by the bonding or removal of very small particles within the impregnation process. Furthermore, the AC suspension contains small particles in the lower µm range, which can cause clogging of the filtration paper pores. If particles are small enough to pass through the filter paper, adsorption goes on in the bottle and an exact result cannot be obtained. Visually a contamination of the bottled sample water could not be observed.

The analysis of the first adsorption samples showed total removal after the first sampling point at 20 min, which led to an adaption of the catalyst dose for a second adsorption experiment. The second adsorption experiment was carried out with AC and three different doses of 50 %, 10 % and 1 % of the original catalyst dose of 143 mg/l. The results showed total removal with 50 % after 20 min and close to full removal with 10 % of the original dose of AC. Further removal from 20 to 40 min was not significantly detectable. The third test with 1 % AC showed a close to linear decrease in hormone concentrations after 20 and 40 min and a decrease of 10 % of DCL after 40 min. The results of the ERY concentrations were not reliable as the concentrations showed an increase of the substance.

Leaned on the result from the previous experiments, the last adsorption experiment with synthetic water was carried out with 3 % of the original 143 mg/l catalyst in water. CAT2, the catalyst powder with 10 wt% cerium-oxide loading was used. Its selection resulted from the characterisation of catalyst powders, see Chapter 4.4.2. Additionally, the concentration of ECs in the synthetic water was increased significantly by a factor of ten. Subsequently, hormones were added with an initial concentration of 50 µg/l and DCL and TTC with a concentration of 500 µg/l. The sampling time was changed from 20 and 40 min to 3 and 20 min.

The adsorption experiment of project phase three with spiked real wastewater was carried out with the same parameters as the last adsorption experiment with synthetic water, which allowed the direct comparison and the investigation of the effect of a real water matrix on the adsorption process. The last two adsorption experiments with synthetic water and spiked real wastewater, represent the EC adsorption in the final result evaluation. The applied parameters were a CAT2 concentration of 4.29 mg/l and a sampling time of 0, 3 and 20 min.

Figure 17: Ozonation reactor set up in the CEIT laboratory

4.7.4 Set Up of Ozonation experiments

The ozonation experiments were carried out in a bubble column reactor, see Figure 17 located in the laboratory of the Division for Water and Health. The reactor itself consists of a PVC tube with an inner diameter of 105 mm and a height of 1400 mm. The stirred batch reactor can hold a volume of approximately 12 l and was operated with 10 l initial volume. The stirrer is driven by a motor, mounted on the head of the column and has three rotor blades. The reactor has four 3/8” valves for liquid in- and outlet on the side, one gas inlet at the bottom and two gas outlets at the head of the column. The gas inlet at the bottom is separated from the column with a standard aeration diffuser, used in WWTPs. The diffuser is not ozone resistant and consequently has to be replaced after an ozonation time of approximately 15 h. The inlet gas is produced in the ozone generator described in Chapter 4.3 and the flow is adjusted with an MFC, which is calibrated for an oxygen/ozone mix of maximum 4 wt% ozone and a volume flow from 0 to 2 l/min. A three-way valve at the gas inlet allows switching between compressed air and the ozone containing stream. Another three-way valve allows switching between the gas washing bottle for ozone gas determination and ozone neutralization of the inlet gas stream. The gas outflows at the head lead to determination and to the neutralization bucket and can be controlled separately. For the solution of the gas neutralization 125 g sodium thiosulfate were dissolved in 5 l of tap water, three spoons of potassium iodide and a shot of starch solution were added to indicate saturation of the neutralization unit with deep purple colour. The gas outlet tube was submerged in the solution and the neutralized gas exit was open to atmosphere. The liquid outlet at the bottom just above the diffuser is the only outflow regularly used in experiments, as all the water samples are taken from this point. For the sampling procedure a 500 ml measuring cylinder is set aside the outlet. A scheme of the reactor set-up can be seen in Figure 18.

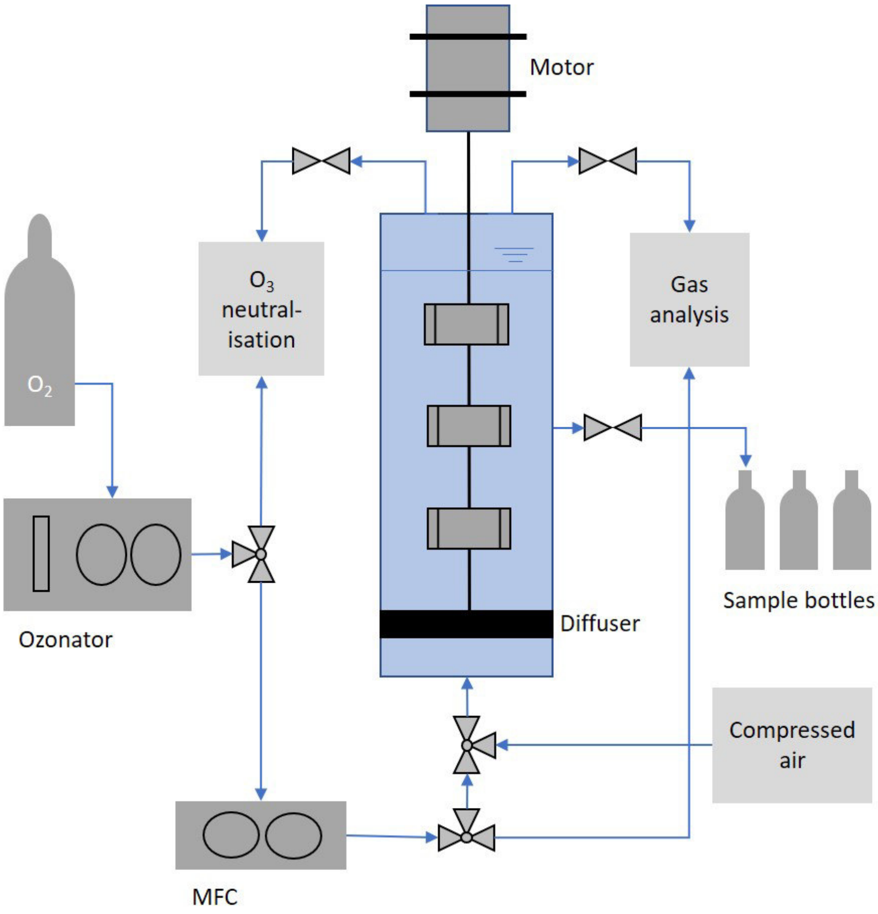


Figure 18: Scheme of the ozonation reactor

4.7.5 Procedure of Basic Ozonation Experiments

Prior to all ozonation experiments leak tests of the reactor system were performed and the neutralization solution for the not consumed ozone was prepared. Sequences of ozone stream measurements were carried out to achieve the settings for the desired ozone dose in the inlet stream. With the settings of the ozone generator and the MFC the ozone concentrations in the inlet stream can be calculated, see Chapter 4.3.1.

The ozone generator was turned on 10 min before the start of the experiment to secure a steady ozone production. The entry gas determination was repeated three times prior to all experiments with the ozone determination method explained in Chapter 4.9.12. The ozone concentration of the gas outflow was measured several times during the experiment. The mean value of the three entry determinations was used to calculate the ozone entry concentration and the difference between entry and exit was used to calculate the total ozone consumption to evaluate the EC removal based on consumed ozone.

The reactor was filled with 10 l of initial water. The tank containing the initial solution was placed on a scale, which allowed the filling of the reactor by weight. While filling, compressed air was bubbled through the reactor to prevent water from running down into the gas chamber. The stirrer was set to a rotation speed high enough to ensure a homogeneous suspension, without the formation of a swirl.

At min 0 the gas inlet was switched from air to ozone gas at the three-way valve. During experimentation, several ozone determinations at the outlet were performed. Water samples of 0.4 l each were taken from the bottom valve of the reactor, this way the batch volume of the reactor content decreased by 1.6 l during the experiment. All ozonation experiments were repeated three times for triplication. Due to the limited batch reactor volume, triplication by taking three times as much sample volume per time step was not possible. The ozone dose cannot be minimized simultaneously to sampling, as the intensity is not sensibly adjustable and a further lowering of the volume flow would lead to inconsistent bubble building. The temperature and pH of each sample were measured, and they were immediately filled into the containers, provided by the analysis institute IPROMA. By the end of the experiment the reactor was emptied, purged with compressed air, thoroughly cleaned and set up for the following experiment.

In the first experimental set the ozone generator was set to an intensity of seven and a calculated dose of 40 mg/min was applied to approximately 10 l of synthetic water for a total of 40 min. This investigation showed a quick saturation of the water and most of the applied ozone was found in the outflow. The results of the first ozonation experiment showed total removal of all substances within the first 3 min of ozonation and an ozone consumption of 120 mg after 3 min.

In the next ozonation experiments ozone dose, intensity of the ozone generator, gas flow and the initial EC concentrations were adjusted to achieve a steady degradation of ECs over time of ozone application. This led to a DCL and hormone removal to below 50 % within the first 3 min of ozonation, whereas TTC was almost fully removed. After 6 min all compounds were fully removed. The total ozone consumption at min 6 was around 30 mg. The measurement of the ozone outflow showed full solubility of ozone in the first 10 min with a dose of approximately 6 mg/min. After this time saturation was reached and ozone could be detected in the gas outflow. After 40 min, more than half of the entering ozone was still taken up by the water in the reactor.

For the final basic ozonation experiments with synthetic water the following settings were found to lead to the expected removal results. The relative pressure of the oxygen gas bottle was set to 0.275 bar and the MFC was set to a normal flow of 0.35 Nl/min, which was found to be the minimum flow to still achieve a visibly consistent bubble formation and a small range of bubble size distribution. The intensity of the ozone generator was set to two and the sampling frequency in the beginning was increased to 1, 2, 3, 6 and the total experimentation time was lowered to 20 min. Moreover, the ozone gas stream was turned off in min 3.5 to further decrease the total ozone dose. For sampling, the gas outlet was reopened to avoid vacuum formation. In this experiments no ozone outflow determination was carried out, as it was proved that at this dose all ozone dissolves in water or reacts with components and no rest can be detected in the outflow gas. All settings are summarized in Table 4

The same experimental set was carried out with spiked real wastewater with the difference, that due to the higher DOC in wastewater the ozone gas flow was turned off in min 6.5 instead of min 3.5. This results in a higher total ozone consumption.

process parameters for ozonation experiments	
temperature	ambient
pH	neutral
relative gas pressure	0.275 bar
rampling time steps	0, 1, 2, 3, 6, 20 min
total treatment time	20 min
gas flow	0.35 Nl/min
applied catalyst	CAT2
catalyst concentration	4.29 mg/l
total ozonation time - synthetic water	3.5 min
total ozonation time - wastewater	6.5 min
initial EC concentration E2/ EE2	50 µg/l
initial EC concentration DCL/ TTC	500 µg/l

Table 4: Process parameters used for experiments with the numbers VI to XI (from Figure 15)

4.7.6 Procedure of Catalytic Ozonation Experiments

Catalytic ozonation experiments were performed similarly to the basic ozonation experiments, see Chapter 4.7.5, with the difference of the addition of catalyst to the reactor content at min 0 of experimentation. An amount of 42.9 mg of CAT2 was prepared and applied for each experiment containing 10 l of water. The catalyst powder was suspended in a stirred beaker of sampling water and pumped into the reactor during the filling process with the last 2 l of initial solution. The time between addition of catalyst and the start of ozonation took up to 5 min. The same procedure was repeated for each experiment to assure a minimum adsorption time without ozone gas flow.
The samples taken during experimentation were immediately filtered with Whatman paper filter 1.6 µm before filled into the bottles for analysis.
The first catalytic experiment carried out, resulted in full removal of all compounds after 6 min. The concentrations in min 3 were slightly lower than with basic ozonation. For the final experiments with synthetic water and wastewater the same above mentioned settings were used.

4.8 Toxicity Evaluation

It is known that the product of ozonation can be transformation-products or other undesired potentially toxic by-products instead of full mineralization [29]. For example, during the ozonation of bromide rich wastewater bromate can form, which can be a human carcinogen [26]. Another undesired carcinogenic byproduct is N-Nitrosodimethylamine (NDMA) which is formed from nitrites, which are present in wastewaters in concentrations below 2 mg/l [72].

It is necessary to investigate, if toxicity increases during the treatment process of synthetic water and spiked real wastewater samples. Toxicity tests were carried out before during and after the ozone treatment with one of the triplicated experiments. The method applied is the germination method by Zucchoni et al. [73]. Three different plants, radish (raphanus raphanistrum, subsp. sativus), cat grass (dactylis glomerata) and cress (lepidium sativum) were utilized.

Primarily to all experiments petri dishes with Whatman paper filter as support, three for each water sample, were disinfected under UV light for 20 min. Ten seeds were placed in every dish and impregnated with 4 ml of water, the dishes were closed with parafilm and set to germination at room temperature in dark conditions. Each petri dish was prepared twice with the same seeds and the same water sample, for duplication. As a control four petri dishes of the same species with ten seeds each were prepared with 4 ml of deionized water. After a defined time of six days the sprouts were removed and their length as well as their dry and wet weight was measured. For wet weight, the sprouts were dabed on a paper towel and for dry weight they were dried at 50 °C over night. The germination index was calculated, see Equation 22 and the total biomass was compared to the weights of the control samples. During all experiments no significant trend in toxicity could be observed. To draw a conclusion for this study a more sensitive method for very low concentrations and a higher amount of replicas should be applied.

$$GI[wt\%] = \frac{mean\ root\ length\ sample}{mean\ root\ length\ control} * 100 \tag{22}$$

4.9 Analytical Methods

Standard analysis of the chemical water composition, the ozone content in the process gas and characterisation of the prepared catalysts were carried out in the intern laboratories of the CEIT. Micropollutant concentrations as well as the DOC of all water samples were measured in the external analysis laboratory IPROMA.

To compare and characterize the local wastewater streams, eleven different standard analytical methods were carried out. Organic components contained in the water streams consume ozone or act as ozone scavengers. Ions might influence the reaction with ozone or OH·, therefore it is important to analyse the wastewater samples with a variety of methods, keeping in mind that the composition strongly varies seasonally, weekly, hourly and regarding to the weather conditions. Analysis of all samples were carried out on the same and the following day after sampling, meanwhile all samples were refrigerated. The triplication of the samples from five different sampling points gives a total number of 15 samples per analysis. All analysis were carried out referring to the original or modified standard methods of the “21st edition of STANDARD METHODS for the examination of water and wastewater” [74].

For all photometric methods an UV-VIS spectrophotometer ”Helios alpha” was employed. All samples prepared for photometry were prior filtered with a Wathman 45 µm filter. For the EC removal experiments of phase two with synthetic waters, standard analysis methods were not carried out, except for pH measurement of all samples and ozone determination in ozonation experiments. The initial wastewater for spiked real wastewater treatment experiments of phase three was analysed with all below mentioned standard analysis methods.

For the analysis of EC mass concentrations and DOC, water samples were bottled and sent to the external analysis laboratory IPROMA. For phase one of the project, the characterisation of local wastewater streams, three samples for each sampling point, 15 in total were analysed for 40 substances and DOC. For phase two and three, which include all EC removal experiments, the initial water (synthetic water or spiked real wastewater), and samples at different time steps as well as the final samples were bottled and sent to IPROMA on the same day. Each sample includes two different bottles, one for high performance liquid chromatography and mass spetrometry (HPLC /

MS) analysis and one for DOC analysis.

4.9.1 pH

The pH is a routine measurement, as practically every phase in wastewater treatment is pH dependent. It indicates the intensity of the acidic or basic character of the solution and pH values should lie in a range from 6.5 to 8.4, values outside of this range are a strong warning indicator for abnormal water quality. Adjusting of the pH can lead to precipitation of heavy metals for example or to the breaking down of living cells, such as bacteria. Prior to biological treatment the pH of any wastewater must be neutralized to obtain a bacteria friendly milieu. Therefore, neutral pH are expected in all wastewater samples. The pH of the unfiltered samples was manually measured with a CRISON pH-meter GLP 21+, referring to the standard method 4500-H^+ B [74].

4.9.2 Conductivity

Electrical conductivity is a measure of the ability of a water sample to carry an electric current. It depends on the sum of ions dissolved in a water sample and is closely related to the salt concentration. While organic compounds which do not dissociate in water lead to a poor conductivity, most inorganic compounds are relatively good conductors. Conductivity results are expected to be higher in wastewater steams close to marine environment due to the high influence of salt water on the measured value. High conductivity can be a sign for high sulfate concentrations, which are problematic in anaerobic treatment processes and due to the possible generation of toxic sulfides. Furthermore, corrosion increases significantly with high ion concentrations which effects pipelines as well as any other installations in WWTP. The analytical method is fast and reasonably precise, the values are referred to standard temperature of 25 °C which is automatically considered by the temperature element in the conductivity cell, the results are expressed in µS/cm. The conductivity of the unfiltered samples was manually measured with a CRISON EC-Meter CLP 31+, referring to the standard method 2510 [74].

4.9.3 Total Suspended Solids and Volatile Suspended Solids

Dissolved and suspended solids may lead to unfavourable physiological reactions and play an aesthetic role for bathing and drinking waters. High values of mineralization can be problematic for most industrial processes. The limit for solids in drinking water is 0.5 g/l and its measurement is a standard procedure in effluent control of WWTPs. The right handling of samples with suspended solids play a key role in analysis to reduce errors. The total suspended solids (TSS) and volatile suspended solids (VSS) were determined by the standard method 2540 D and 2540E, respectively. The results for the concentrations were calculated with Equation 23 and 24 [74]. Furthermore, the ratio of VSS/TSS was expressed, values close to one are expected which indicate high organic proportion of the solid load.

$$TSS = \frac{m_{filter+solids} - m_{filter}}{V_s} \tag{23}$$

$$VSS = \frac{m_{filter+solids} - m_{filter+solids,cremated}}{V_s} \tag{24}$$

$TSS \ldots total\ suspended\ solids\ [g/l]$
$VSS \ldots volatile\ suspended\ solids\ [g/l]$

$m_{filter+solids} \ldots mass\ of\ filter\ and\ solids\ dried\ at\ 150°C\ [g]$

$m_{filter} \ldots mass\ of\ filter\ dried\ at\ 150°C\ [g]$

$mfilter + solids, cremated \ldots mass\ of\ filter\ and\ solids\ cremated\ at\ 550°C\ [g]$

$V_s \ldots volume\ of\ sample\ [l]$

4.9.4 Alkalinity

Alkalinity is the acid neutralising capacity of water and is an aggregate property for the sum of all titratable bases. The measurement depends on the end-point pH used for titration. In wastewater alkalinity is primarily a function of carbonate, bicarbonate and hydroxide. For the measurement of the alkalinity standard method 2320 B is used. The results were obtained by Equation 25 [74].

$$Alkalinity = \frac{V_{s-titration} * N_{titrant} * 50.000}{V_s} \tag{25}$$

$Alkalinity \ldots [g\ CaCO_3/l]$

$V_{s-titration} \ldots volume\ of\ titrant\ for\ the\ sample\ [l]$

$N_{titrant} \ldots normality\ of\ titrant\ [g\ CaCO_3/l]$

$V_s \ldots volume\ of\ sample\ [l]$

4.9.5 Chemical Oxygen Demand

The chemical oxygen demand (COD), filtered and unfiltered is the amount of a specific oxidant consumed in the full oxidation of organic and inorganic components of a sample under controlled conditions. The COD is often used as a measurement of pollutants in a water sample. Methods related to this measurement are the biochemical oxygen demand (BOD), the DOC and the total oxygen demand (TOD). A modified version of the standard method 5220 B was implemented in this analysis of COD. The modifications regarding temperature and digestion time are 220 °C instead of the original 150 °C and 10 min instead of the original 2 h. The results of the analysis are obtained Equation 26 [74].

$$COD = \frac{(V_{blank} - V_{s-titration}) * N_{titrant} * 8}{V_s} \tag{26}$$

$COD \ldots chemical\ oxygen\ demand\ [g\ O_2/l]$

$V_{blank} \ldots volume\ of\ titrant\ for\ the\ blank\ [l]$

$V_{s-titration} \ldots volume\ of\ titrant\ for\ the\ sample\ [l]$

$N_{titrant} \ldots normality\ of\ titrant\ [g\ O_2/l]$

$V_s \ldots volume\ of\ sample\ [l]$

4.9.6 Total Kjeldahl Nitrogen

The determination of nitrogen in wastewater is a routine procedure as it is a parameter for water quality and its pollution. Forms of nitrogen are biochemically inter convertible and form components of the nitrogen cycle. The Kjeldahl Nitrogen (TKN) is the sum of organic and ammonia nitrogen. Organic nitrogen includes proteins and peptides, nucleic acids and urea as well as numerous synthetic organic materials and typical concentrations vary from a few mg in surface waters to 0.2 g/l in sewage. The method 4500-Norg B was used to determine the TKN of unfiltered wastewater samples. The distillation step was carried out in a BÜCHI BL-323 distiller. Final results were obtained by Equation 27 [74].

$$TKN = \frac{(V_{s-titration} - V_{blank}) * c * z * f * M_N}{V_s} \tag{27}$$

$TKN \ldots Total\ Kjeldahl\ Nitrogen\ [g/l]$
$V_{s-titration} \ldots volume\ of\ titrant\ for\ the\ sample\ [l]$
$V_{blank} \ldots volume\ of\ titrant\ for\ the\ blank\ [l]$
$c \ldots concentration\ titrant\ [mol/l]$
$z \ldots molar\ valence\ factor\ (2\ for\ H_2SO_4)\ [-]$
$f \ldots titrant\ factor\ (1)\ [-]$
$M_N \ldots molecular\ weight\ of\ nitrogen\ 14.007\ [g/mol]$
$V_s \ldots volume\ of\ sample\ [l]$

4.9.7 Ammonia

Ammonia is present naturally in surface waters. Groundwater concentrations are typically low, as ammonia adsorbs to soil. It is mainly produced by deamination of organic nitrogen compounds and in hydrolysis of urea. In some wastewater treatment processes, it is added to the wastewater to form chlorine residual. The concentrations in WWTP effluents depend on the process. WWTP with nitrification, like in Gaikao contain 5 % of the effluent of WWTP without nitrification like Loiola. The standard spectrophotometric method of Nesslerisation with commercial Nessler reactive was employed to determine the ammonia amount in the samples. A modification of the original method NH3 B and C was applied, the wave length of the photometer was changed to 385 nm instead of 425 nm [74].

4.9.8 Nitrates

Nitrates are contained in groundwater and in trace quantities in surface waters. It is an essential nutrient for photosynthetic autotrophs. High amounts of nitrates contribute to the illness methemoglobinemia in infants. It is limited to 10 mg/l in domestic water, in the effluent of nitrifying WWTP it might be found in quantities up to 30 mg/l. The analysis of the nitrate ion concentration was carried out by the sodium salicylate standard method [74].

4.9.9 Nitrites

Nitrite is an intermediate product of nitrification. Regular WWTP effluent concentrations should not exceed 0.1 mg/l. It can reduce the oxygen transportability of blood and is toxic to aquatic organisms. The spectrophotometric method of the analysis of nitrite ions is based on the standard method including the coloured complex formation [74].

4.9.10 Total Phosphorus

Phosphorus occurs in waters as orthophosphates, condensed phosphates and organically bounded phosphates in solutions, in particles or organisms. They are used in different cleaning and washing applications, are applied as fertilizers in agriculture and reach the wastewater via run offs and are formed by biologically processes. The total phosphorus (TP) was determined by the method 4500-P E [74].

4.9.11 Orthophosphates

Phosphates are important in metabolic processes and can be the limiting nutrient to an environment. The phosphate removal from wastewater is important to avoid eutrophication. Orthophosphates (PO_4-P) were determined by the colorimetric standard method 4500-P B [74].

4.9.12 Ozone Gas Determination

The determination of the ozone gas flow is carried out with the standard method 2350 E for ozone demand. For this method a gas washing bottle is filled with 200 ml of 2 wt% potassium iodide as absorbent solution. The gas is bubbled through the solution within a measured time period. The concentrations of ozone measured in a second bottle, as proposed in the method, were found to be neglectable. The colour of the solution turns dark orange within a few seconds. Immediately after gas washing, 10 ml of sulfuric acid are added to the bottle. The sample is titrated with sodium thiosulfate solution until the sample colour turns light yellow. In this moment 2 ml of starch solution indicator are added, which gives a black to purple colour to the solution, the titration is slowly finished until complete clearing of the solution. For testing of the determination method, the gas flow should not exceed 1 Nl/min. The final concentration is calculated with Equation 28 [75], [74].

$$wt_{O_3} = \frac{V_{s-titration} * N_{titrant} * 2.4}{t_{titration} * Q_{real}} \tag{28}$$

wt_{O_3} ... $mass\ concentration\ of\ ozone\ [g/l]$
$V_{s-titration} \ldots volume\ of\ titrant\ for\ the\ sample\ [l]$
$N_{titrant} \ldots\ Normality\ of\ titrant\ [mol/l]$
$t_{titration} \ldots\ determination\ time\ [min]$
$2.4 \ldots ozone\ equivalency\ with\ 0.1\ N\ Na_2S_2O_3\ solution\ [g]$
$Q_{real} \ldots volume\ flow\ at\ ambient\ conditions\ [l/min]$

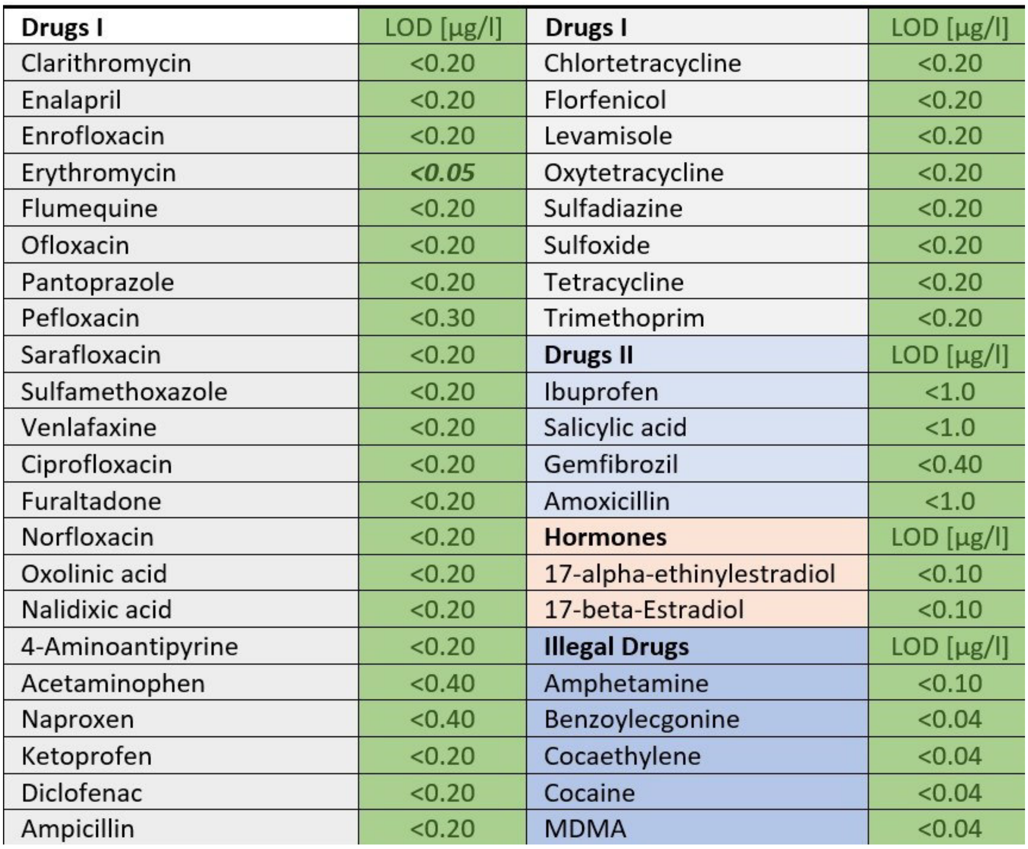
4.9.13 Emerging Compound Concentrations

The concentrations of ECs were measured externally with HPLC / MS. The analytical equipment implied was an Agilent Technologies Liquid Chromatograph, Series 1200. For the quantification of the hormones E2 and EE2 a slightly different method was applied than for DCL, ERY and TTC.

To obtain the desired low limits of quantification for hormones, a concentration and purification was carried out with the Oasis-HLB solid phase extraction technique with SPE-cartridges. The internal standard E2-d4 (17-b-estradiol deuterado), eluted with MeOH and evaporated and reconstructed in 0.5 ml leads to a factor of concentration of 2000. A XTerra C_{18} column with the measurements 1.2 x 100 mm and a Phenomex pre-column (4 x 2.0 mm) were applied. A HiP ALS SL oven heats the column and the injection volume of the sample (1 - 100 µm). The mobile phases are Milli-Q water with 0.01 % NH_3 and MeOH with 0.01 % NH_3. The API3200 mass spectrometry (MS) detection from Applied Biosystems contains an ESI (Electro Spray Ionisation) source and an APCI (Atmospheric Pressure Chemical Ionisation). The detection is realized with specific transitions for each compound. The ion precursor (Ion Precursor-Q1) is insulated and consists of a charged molecule or a fragment of the compound. With the rupture of the precursor in the Q2 fragments of a lower mass and charge are obtained (Ion Son-Q3). This fragments show OH groups in their structures and therefore deliver a negative signal, while applying the ESI sonde.

For the compounds DCL, ERY and TTC a ZORBAX Eclipse XDB-C_{18} column with the measures 4.6 x 50 mm and a particle size of 1.8 µm and a pre-column Gemini C_{18} with the measures 4 x 2.0 mm (Phenomex) were used. The mobile phase were Milli-Q water with 0.1 % formic acid and MeOH with 0.1 % formic acid. The solid phase extraction was carried out with a SPE-“on line” system, which consists of a Strata-X column with a particle size of 25 µm and measures of 2.0 x 20 mm. The Autosampler PAL System from CTC Analytics can handle injection volumes from 10 to 5000 µl. The difference in the MS is that positive and negative working mode of the electron spray can be applied. In this case the positive mode produced a good signal for each compound.

The complex matrix of wastewater causes an increase of the LOD compared to synthetic water samples due to high measurement noise. The LODs for project phase of all investigated substances are listed in Table 5. For the measurement of the experimental samples, depending on the amount of substance in the matrix, the LODs could be lowered by further purification and concentration.



Drugs I	LOD [µg/l]	**Drugs I**	LOD [µg/l]
Clarithromycin	<0.20	Chlortetracycline	<0.20
Enalapril	<0.20	Florfenicol	<0.20
Enrofloxacin	<0.20	Levamisole	<0.20
Erythromycin	***<0.05***	Oxytetracycline	<0.20
Flumequine	<0.20	Sulfadiazine	<0.20
Ofloxacin	<0.20	Sulfoxide	<0.20
Pantoprazole	<0.20	Tetracycline	<0.20
Pefloxacin	<0.30	Trimethoprim	<0.20
Sarafloxacin	<0.20	**Drugs II**	LOD [µg/l]
Sulfamethoxazole	<0.20	Ibuprofen	<1.0
Venlafaxine	<0.20	Salicylic acid	<1.0
Ciprofloxacin	<0.20	Gemfibrozil	<0.40
Furaltadone	<0.20	Amoxicillin	<1.0
Norfloxacin	<0.20	**Hormones**	LOD [µg/l]
Oxolinic acid	<0.20	17-alpha-ethinylestradiol	<0.10
Nalidixic acid	<0.20	17-beta-Estradiol	<0.10
4-Aminoantipyrine	<0.20	**Illegal Drugs**	LOD [µg/l]
Acetaminophen	<0.40	Amphetamine	<0.10
Naproxen	<0.40	Benzoylecgonine	<0.04
Ketoprofen	<0.20	Cocaethylene	<0.04
Diclofenac	<0.20	Cocaine	<0.04
Ampicillin	<0.20	MDMA	<0.04

Table 5: LOD for each compound analysed in project phase one

4.9.14 Dissolved Organic Carbon

The dissolved organic carbon (DOC) of all experimental samples was measured externally at IPROMA. The method used measures the total organic carbon (TOC), which in this case corresponds with the DOC, as all samples were filtered prior to analysis. The method functions via catalytic combustion of the sample and the measurement of the generated CO_2. The implied detector is a nondispersive infrared sensor.

Therefore the sample were previously homogenized and diluted if needed. A micro-portion of the sample is acidified to a pH below 2 and CO_2 gas is bubbled through the sample to remove carbonates and bicarbonates. The remaining solution is injected in a hot catalytic reaction zone where the carbon matter is transformed to CO_2. The resulting CO_2 concentration in the gas stream is measured and evaluated based on a previous calibration with a TOC-standard.

5 Results

The results of the present study include answers to the main objectives carried out within the three phases of experimental investigation.

To interpret results from ozonation processes for micropollutant removal, the evaluation of the present water matrix is essential. Wastewater that contains a high load of organic matter can result in a considerably high ozone consumption which stands in direct competition to the degradation of target micropollutants. In most studies on AOPs DOC content is considered the most influential parameter compared to others like pH, temperature or other inorganic radical scavengers [76]. To relate ozone consumption to DOC of the treated water the so-called specific ozone dose g O_3/g DOC was applied. The consumed ozone over DOC was calculated with the mean ozone entry value validated prior to experimental start and the mean DOC of the initial sample.

In the case of EC removal, apart from organic matter, nitrites play a mayor role as ozone scavengers, because they directly consume ozone and quickly react in a stoichiometric ratio of 1:1 and a consumption of 3.43 g O_3/g NO_2 [77]. Nitrite concentrations were analysed in project phase one, which included wastewater from the same source as used in project phase three. The results of the nitrite evaluation were below the LOD of the analytical method and therefore, compared to the DOC value, they play a minor role within this study. Consequently the influence of nitrites was neglected in the result evaluation.

5.1 Wastewater Analysis in five Sampling Points

As described in Chapter 4.1 and 4.2 samples from five different wastewater streams in Gipuzkoa were internally analysed for standard water parameters like ph, alkalinity, nitrogen, phosphorus and organic and solid content. The analytical results represent the expected values for the two types of WWTPs and can be seen in Figure 19. All parameters are presented in mg/l on a logarithmic scale for each sampling point. It can be seen that the exiting streams of the two WWTPs have distinctly lower concentrations of most compounds than the entering streams. The hospital wastewater shows an especially high DOC which can be related to the low dilution compared to the other sampling points. Visually a high paper content could be detected in the hospital effluent. Suspended solids are removed by both WWTPs to a tenth, COD to a fifth and the DOC is reduced by more than half. Ammonia is hardly removed in Loiola and fully removed in Gaikao, due to the IFAS nitrification process. The ammonia removal of the IFAS process, as described in Chapter 4.1, results in elevated nitrate concentrations in the effluent, which can be clearly seen in Figure 19. Nitrates in Loiola effluent are lowered by a third. Total phosphorus and orthophosphates are decreased in both WWTPs and show better removal in Loiola.

Within this study a quantitative investigation of micropollutant concentrations was carried out. 21 out of 41 measured compounds were detected at least in one sample, which confirms their presence. The 20 other not detected compounds can either occur in concentrations below LOD or they are not present in the investigated streams. A list of the not detected substances is included in the appendix of the thesis. To confirm their presence in lower concentrations, a qualitative study could be conducted. The correlation between sampling points and detected substances is discussed subsequently.
Since in- and outflow of the two WWTPs has been sampled contemporaneously, the composition

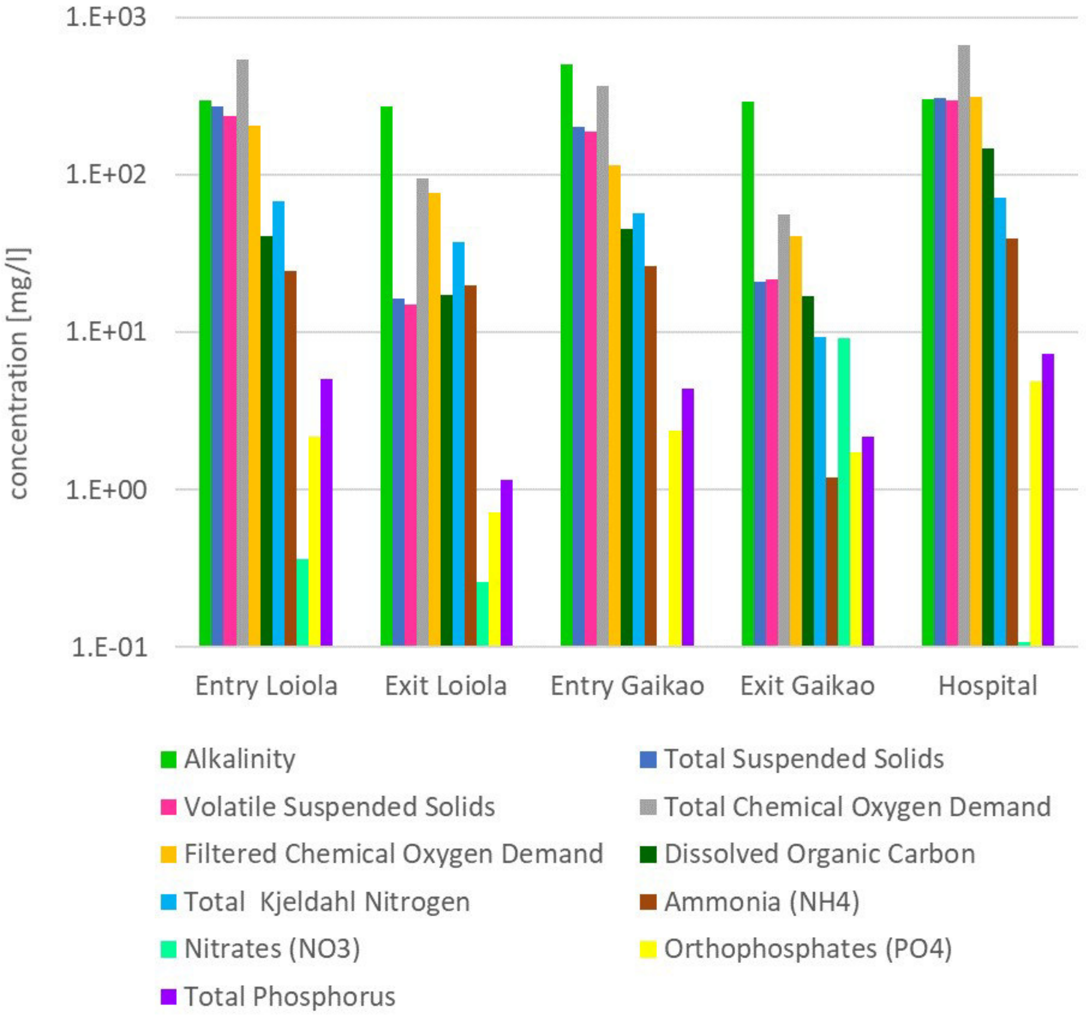


Figure 19: Standard water analysis of five wastewater streams of Gipuzkoa (Loiola = WWTP San Sebastian; Gaikao = WWTP Legorreta; Hospital = Hospital of San Sebastian)

of the wastewater does not correspond during the first and last few hours of the 24 h sampling period. As pharmaceutical concentrations are not expected to show continuous concentrations over time, this can have a high influence on the measured results. Generally, inflow concentrations of WWTPs are not constant and fluctuations of parameters like weather, wastewater flow, dilution and human behaviour can have a significant influence. To minimize fluctuations, a sampling procedure, see Chapter 4.2, was conducted.

The difference of in- and outflow concentrations of ECs can be considered as an approximation for direct removal of ECs in the WWTP. When interpreting the results, possible errors of the sampling method, analytic errors and the fact that samples were taken once and simultaneously must be considered. All samples were sent to analyses three times for triplication. A more detailed and precise study on the local wastewater composition should include measurements over a certain time period with specific intervals. The EC concentration results of the analysis of project phase one are shown in Figure 20. Entry and Exit Loiola in the graph indicate the samples from the WWTP of San Sebastian. Gaikao is the name of the WWTP of Legorreta and Hospital indicates the samples taken from the Hospital Universitario Donostia (Hospital of San Sebastian).

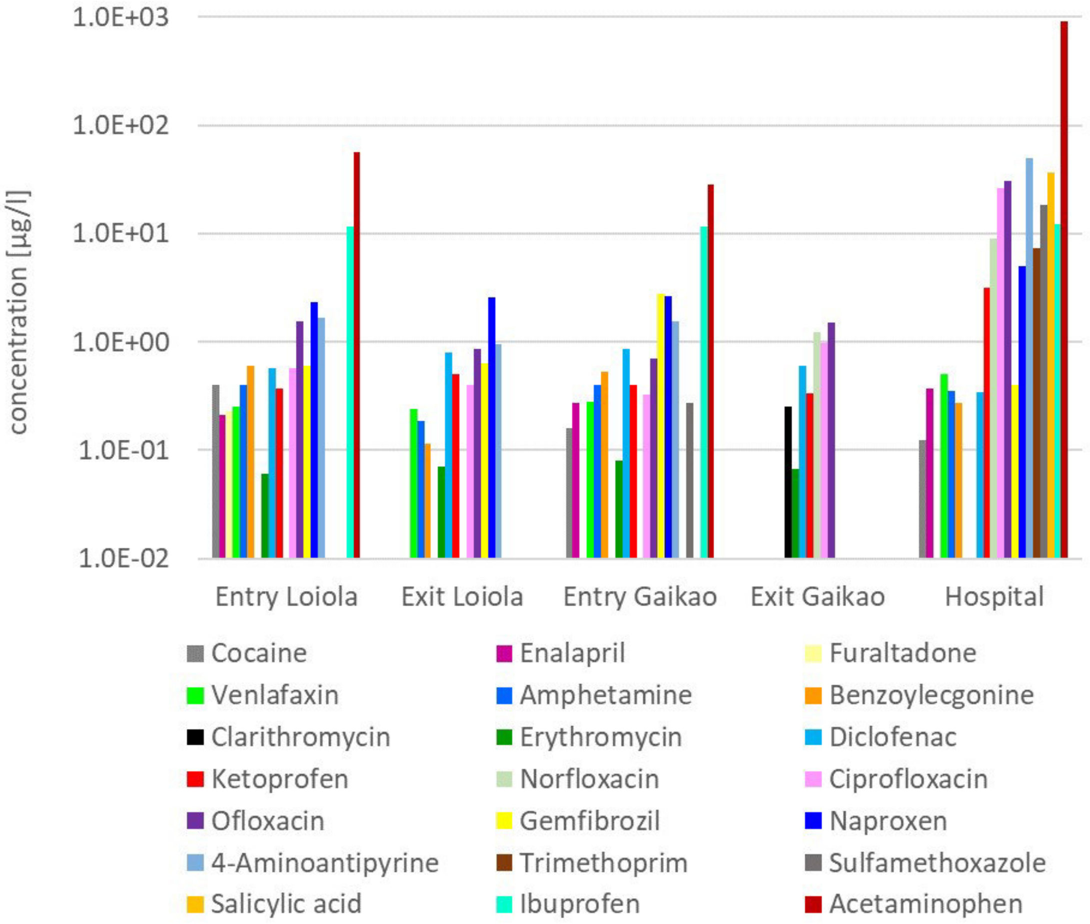


Figure 20: Occurring concentrations of investigated ECs in five wastewater streams of Gipuzkoa (Loiola = WWTP San Sebastian; Gaikao = WWTP Legorreta; Hospital = Hospital of San Sebastian)

15 out of 21 compounds were detected with triplication, which means that these substances could be detected in at least one sampling point in all three analysis repetitions. Ofloxacin, ketoprofen and DCL are the most frequently detected substances, they were detected in all sampling points with triplication. DCL shows no decrease in either of the two WWTPs. The third sample repetition of the Loiola exit stream was fauly, as it showed only two compounds in total. The substances cocaine, ibuprofen and acetaminophen were present in both WWTP entering streams as well as the hospital effluent with triplication and did not occur in the WWTP exiting streams. This leads to the conclusion that these three compounds are degradable below the LOD in both WWTP types.

Regarding this study, it can be generally stated that the WWTP of Gaikao with the IFAS nitrification process and chemical phosphorous removal shows better results in terms of the removal of certain substances. The substances sulfamethoxazole, venlafaxin, 4-aminoantipyrine, naproxen, gemfibrozil, acetaminophen, benzoylecgonine and amphetamine were detected at least in one of the inlet samples of Gaikao. Contemporaneously non of these substances were detected in the outlet sample. 4-aminoantipyrine, naproxen, amphetamine and benzoylecgonine are detected with triplication in the inflow of Gaikao and are not detected in the outflow, which is a strong indicator of degradation in the Gaikao type WWTP. The four substances occur in both streams of Loiola, where naproxen shows no decrease and 4-aminoantipyrine, amphetamine and benzoylecgonine show a slightly lower concentration in the exit compared to the entry stream. As it has been previously confirmed, advanced biological systems could improve removal efficiencies for ECs.

Acetaminophen shows the highest concentrations in all streams. It showed the highest concentration in the hospital effluent with 915 µg/l, which is more than 30 times higher than in the Gaikao entering stream. The analgesic, with the more common name Paracetamol was not detected in any exit stream and is considered fully biodegradable. Another substance with high occurrence in the hospital stream is salicyclic acid, which is the active ingredient of the pharmaceutical aspirin and trimethoprim. Despite their high occurrence in the hospital stream, the substances could not be detected in the entering stream of Loiola. The absence of the compounds in the inlet of Loiola and any other streams could be an indication of their biodegradability within the wastewater stream before entering the WWTP. Another explanation can be their dilution below the LOD, to prove this explanation a mass balance of all streams is necessary. Norfloxacin was detected in the hospital effluent and in the Gaikao exit stream. Higher concentrations of one substance in the exit stream can be explained by the above mentioned simultaneous sampling. A peak load of the substance has entered the WWTP before sampling start and left the plant when sampling has started.

Furaltadone and clarithromycin appear in one single sample with concentrations close to the LOD, therefore no conclusion can be drawn for the biodegradability in WWTPs of the two compounds. Enalapril and venlafaxin are detected irregularly in concentrations close to their LOD, . Ciprofloxacin occurs in significantly higher concentration in the hospital effluent than in the other wastewater streams. The WWTP results of the substance show no significant decrease, therefore biodegradation is not expected.

14 out of 18 measured substances in the outlet stream of the hospital occur in at least one sample of the Loiola entry stream. The sometimes very high concentrations in the hospital effluent are highly diluted when reaching the general WWTP. The detected substances in the hospital effluent hardly influence the concentrations of Loiola, when comparing the composition to Gaikao, which does not receive any hospital water. This is an important recognition of the study, as the influence of hospital water on the WWTP entry composition was one of the main objectives of project phase one.

The one metabolite included in the study is cocaethylene, the metabolite of cocaine, this substance was not detected in any of the samples. Other metabolites with possible harmful properties could originate from any of the examined substances. Not all metabolites of the investigated substances are known and the attempt to detect all of them goes beyond the scope of this study.

The LODs for the analysis of a complex matrix like wastewater, see Table 5, are higher than for synthetic water. For ERY the LOD could be lowered by the analysis institute on request to 0.05 without warranty on quantified data. The concentrations measured in all streams were very close to the lower LOD. The presence of ERY could be proved. The substance was not detected in the hospital effluent. The comparably high LODs re problematic for substances like hormones as they typically occur in ng/l range and with the present analytical method, no **??**ormones could be detected in the waters of Gipuzkoa. The substances DCL, ERY, TTC, E2 and EE2, used for experimentation of the removal processes can be justified to the effect, as DCL occurs constantly in all sampling points except for one which is assumed to be faulty. ERY was detected at a lower LOD in 8 out of 15 samples. ERY was later substituted by TTC due to its instability at low pH of initial synthetic water samples. TTC was not detected with the present LOD of 0.2 µg/l. All four compounds are or were on the EU watch list and are reported not to be biodegradable in regular WWTPs [60].

5.2 Adsorption Results

As described in Figure 15, previously to catalytic ozonation experiments, adsorption experiments were carried out to define the ideal catalyst concentration. The experiments were carried out with adsorption on AC and four different concentrations. The water matrix consisted of deionized water spiked with 50 µg/l DCL and ERY and 5 µg/l E2 and EE2. The initial catalyst concentration, leaned on the study of Goncalves et al. [78] resulted in full removal of all compounds after 20 min. The following experiments, including 50 %, 10 % and 1 % of the highest AC concentration of 143 mg/l resulted in different final EC concentrations. The removal results of ECs from synthetic water are shown in Figure 21. Full adsorption on AC of all investigated ECs could be achieved after 20 and 40 min respectively. The adsorption with the lowest AC concentration of 1.43 mg/l resulted in a final removal of 17 % after 40 min. The SD of the experimental results is significantly higher if full removal is not achieved. The removal value of the lowest AC concentration at 20 min shows the highest SD. Based on these results a final catalyst concentration of 3 % of the initial 143 mg/l was chosen for the following adsorption and catalytic ozonation experiments.

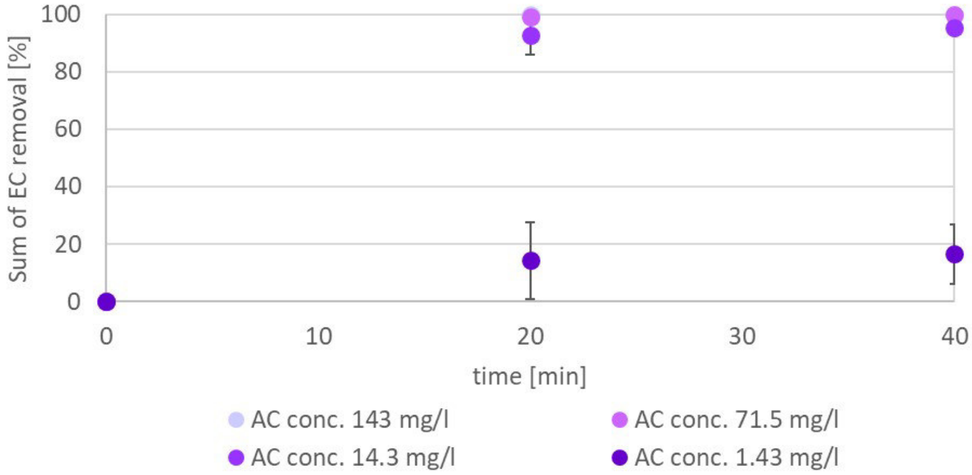


Figure 21: Adsorption experiments with different concentrations of AC for the EC from synthetic water. Sum of ECs includes DCL, ERY, E2 and EE2

A direct comparison of Figure 21 and Figure 22 was not carried out due to the difference in initial EC concentrations by a ten-fold and the application of different adsorption material.

Adsorption experiments with CAT 2 and a catalyst concentration of 4.29 mg/l were carried out on synthetic water and spiked real wastewater. It should be noted that in all the following result graphs ERY was no longer investigated and replaced by TTC. Moreover, the initial EC concentrations were increased by a ten-fold. The results of the adsorption on CeO_2 impregnated AC can be seen in Figure 22, 23 and 24. In Figure 22 the removal of the sum of all compounds is shown. Figure 23 and 24 show the removal of the individual compounds DCL and TTC as well as E2 and

E2. The graphs directly compare the removal results achieved from synthetic water and spiked real wastewater.

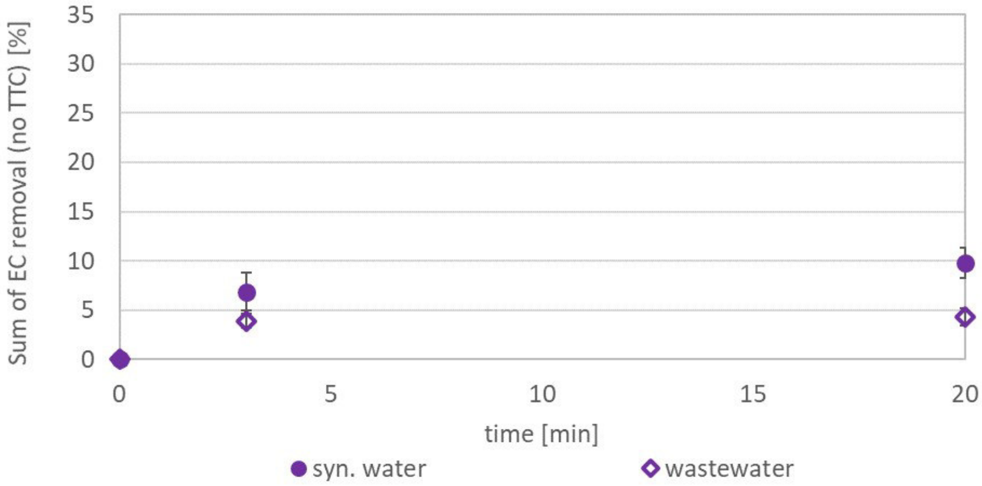


Figure 22: Adsorption results of the sum of ECs (including DCL, E2, EE2) on CAT2, with a concentration of 4.29 mg/l. Removal shown at three time steps from synthetic water and spiked real wastewater

The results for initial TTC concentrations of about 210 µg/l were well bellow the initially added 500 µg/l, after 3 and 20 min the concentration increased in both experiments, which can be seen in Figure 23. TTC showed good stability and steady degradation during ozonation experiments. However, due to the high deviation of the initial TTC value in adsorption experiments, TTC results were not considered in the graph showing the removal of the sum of ECs.

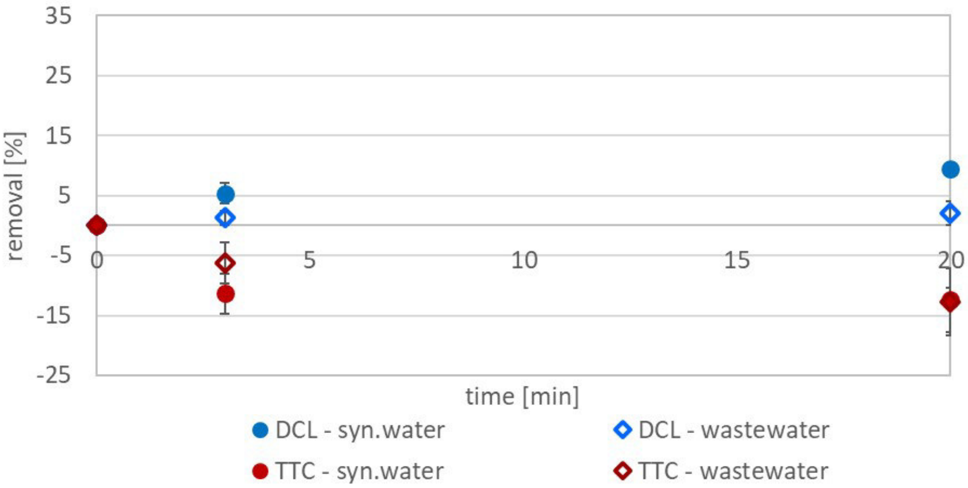


Figure 23: Adsorption results of the ECs DCL and TTC on CAT2, with a concentration of 4.29 mg/l. Removal shown at three time steps from synthetic water and spiked real wastewater

The samples for adsorption analysis were taken in min 0, 3 and 20. It results from the graphs in Figure 22, 23 and 24, that all compounds show a faster removal between min 0 and 3 than from min 3 to 20. Regarding the sum of ECs, the removal from synthetic water still increases from min 3 to 20. The removal increase from wastewater from min 3 to 20 is not significant as it lies with in

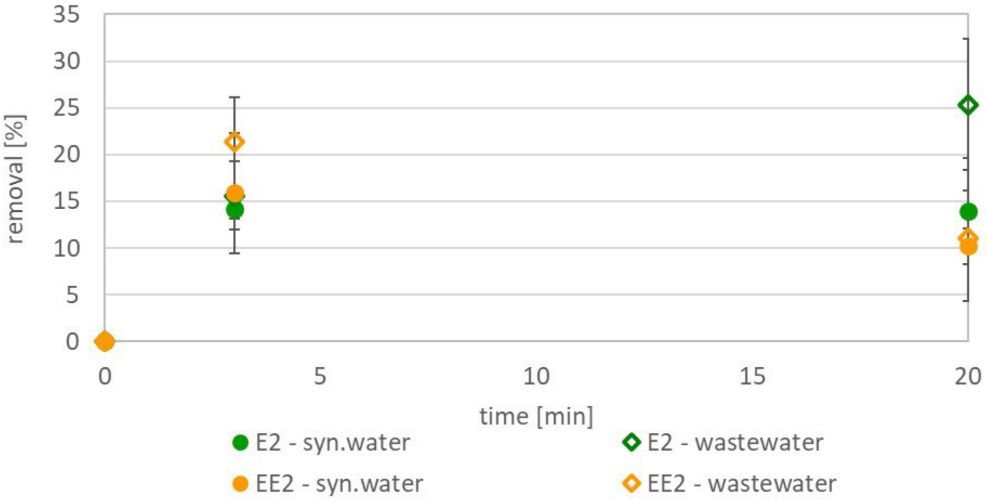


Figure 24: Adsorption results of the ECs E2 and EE2 on CAT2, with a concentration of 4.29 mg/l. Removal shown at three time steps from synthetic water and spiked real wastewater

the SD of the two values. Regarding the sum of all compounds, excluding TTC, the total removal from synthetic water stops at a value of 10 %, whereas from wastewater a final removal of 5 % could be reached.

Figure 23 shows that DCL was removed from synthetic water by 5 % within the first 3 min and finally reached a removal of 10 %. From wastewater the removal was lower and reached a final removal value of 2 %. As mentioned above, TTC removal values decrease, which means higher concentrations were measured after adsorption than from the initial sample.

Figure 24 shows that E2 removal from synthetic water stagnates from min 3 to 20 with a total decrease of 14 %. From wastewater, E2 could be removed by 16 % after 3 min and by 25 % after 20 min. EE2 could be removed from synthetic water by 16 % after 3 min, the final removal after 20 min was lower and showed 10.5 %. Wile from wastewater EE2 adsorbed with 21 % of the initial concentration after 3 min and stopped at a final removal of 11 %. In general the removal of hormones from wastewater showed higher percentages as from synthetic water.

5.3 Basic Ozonation Results

The results of basic ozonation experiments, analysed by the external analysis institute IPROMA are presented in the Figures 25, 26 and 27. The results from the analysis institute were obtained in concentration over time. The removal in % was calculated from those values. Each value in the graphs represents the mean value obtained from three experiments carried out with the same parameters and initial water. The following illustration represents the measured values converted into removal over time plots.

The graphs in Figure 25, 26 and 27 compare the basic ozonation of synthetic water to the basic ozonation of spiked real wastewater.

The values in Figure 25 represent the sum of all ECs, where hormones, due to their ten times lower initial concentration have a smaller influence on the depiction of the sum. Therefore, in the Figures 26 and 27 all ECs are considered individually.

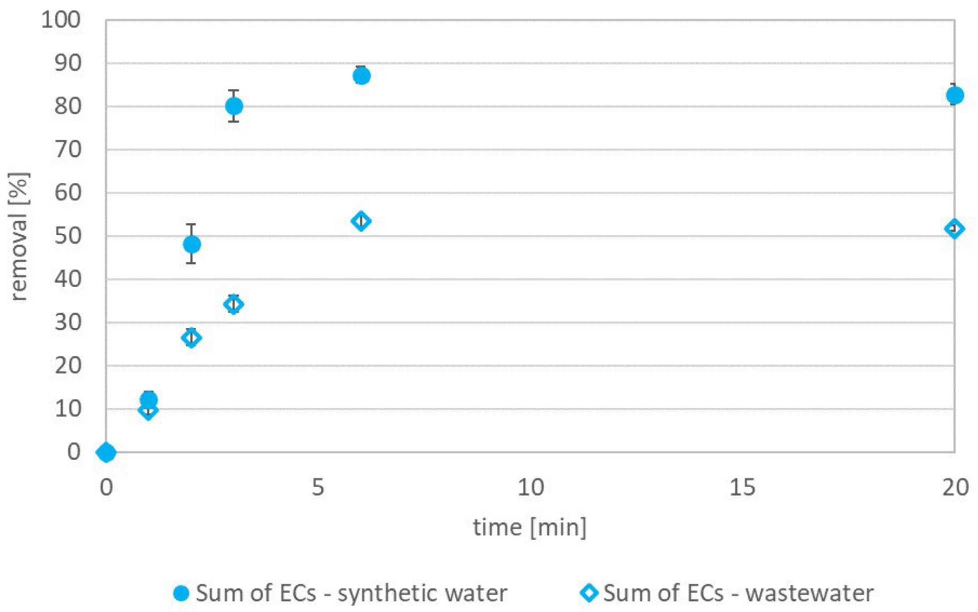


Figure 25: Basic ozonation results for the removal of the sum of ECs (including DCL, TTC, E2, EE2) over time from synthetic water and spiked real wastewater

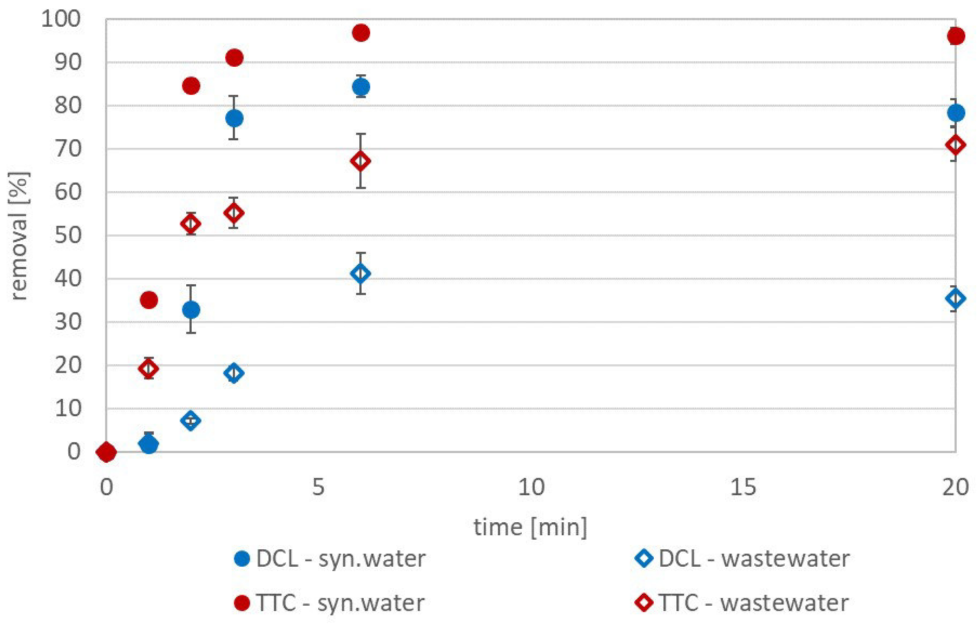


Figure 26: Basic ozonation results for the removal of individual ECs DCL and TTC over time from synthetic water and spiked real wastewater

The removal of the sum of ECs in both initial waters increases fast from min 0 to 3. The ozone gas stream was turned off after 3.5 min for synthetic water and 6.5 min for wastewater. This can be seen, as the removal values for synthetic water start to flatten out after 3 min and for wastewater after 6 min. The removal of the sum of all compounds after 20 min is slightly lower than in min 6 for synthetic water and wastewater, whereas the last two values of wastewater diverge less in wastewater. The removal results of both water types in the first time step are close to each other, while after the second time step the values start to diverge. After 2 min close to double the removal was achieved in synthetic water compared to wastewater. The SDs reach a maximum of 4.5 % for the synthetic water value in min 2 and show an average of 1 - 2 %. Consequently the SDs are not apparent in some data points in the graph. The removal of individual ECs are plotted in the Figures 26 and 27.

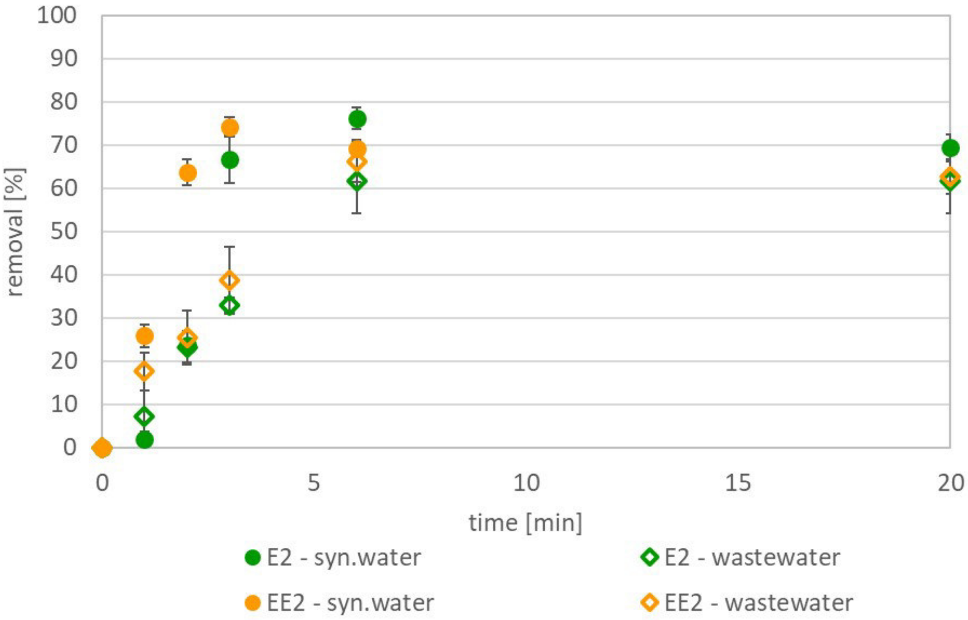


Figure 27: Basic ozonation results for the removal of individual ECs E2 and EE2 over time from synthetic water and spiked real wastewater

In Figure 26 it can be seen that the removal from wastewater shows more deviation between the compound DCL and TTC than in synthetic water. It is evident from this graph that the maximum removal from synthetic water is reached within the first 3 min whereas the maximum removal in wastewater ozonation is reached after 6 min. As above mentioned this rises from the different time points for turning off the gas stream. The final removal values from DCL in both waters are below the the value at 6 min. TTC shows stagnating final values in synthetic water and a slightly increasing value in wastewater.

Figure 27 shows the removal of the compounds E2 and EE2 in both water types. The two compounds show less deviation between the two water typs as well s between each other. The hormone removal from wastewater almost shows a linear trend. E2 in synthetic water and EE2 in wastewater show a significant decrease in removal of the final sampling time step. Whereas E2 in wastewater and EE2 in synthetic water show similar results for the last two time steps.

The highest removal values could be reached for TTC in synthetic water of 96 % and 71 % in wastewater. The lowest values were achieved in the DCL removal in wastewater with a maximum value of 42 % after 6 min. Summing up DCL shows the slowest removal in wastewater, while TTC show a quick initial degradation in both waters. The hormones show more steady results. For hormones a significant diference between two water types can be seen within the first three time steps, whereas the values in min 6 are closer to each other and the final values in min 20 almost all lie within the SD of the values for both hormones.

5.4 Catalytic Ozonation Results

The catalytic ozonation experiments were carried out similar to basic ozonation with the addition of CAT 2 in a dose of 4.29 mg/l. The results of the catalytic ozonation experiments are presented in Figure 28, 29 and 30. The format in the following graphs is, similar to the basic ozonation graphs, removal over time for the sum of all ECs and for each individual compound.

Regarding Figure 28, the maximum removal values from synthetic water are almost reached in min 3. The removal from wastewater increases slower and reaches a maximum at 6 min where it stagnates until the last sampling point. The SD from wastewater data points, regarding the first 3 min of experimentation are higher than from synthetic water. For synthetic water the second value shows the highest SD. All other results show minor SDs. The maximum removal value of the sum of ECs in synthetic water reaches 93 % after 6 min of ozonation. The final value after 20 min is slightely lower than after 6 min.

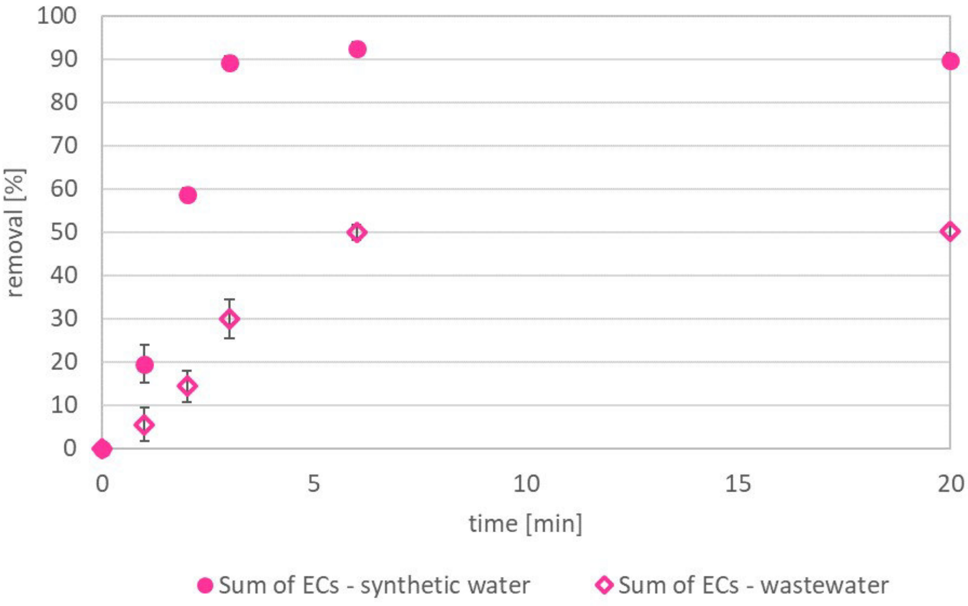


Figure 28: Catalytic ozonation results for the removal of the sum of ECs (including DCL, TTC, E2, EE2) over time from synthetic water and spiked real wastewater

The removal of DCL and TTC is compared in Figure 29. Both compounds are quickly removed in synthetic water, where TTC shows faster removal and higher final removal values. In min 2 TTC in synthetic water could be eliminated by more than doble as DCl, whereas the values at min 3 show a difference of approximately 10 %. wastewater shows faster removal than DCL and reaches 69 % after 6 min and slightly more after 20 min. DCL is more slowly removed in wastewater compared to the other compounds and reaches a maximum value of 34 % after 6 min. The values for both compounds in both water types show consistent fnal values fo the last two time steps with minor deviations. The TTC values show the highest SDs at ozonation initiation. The SDs of the final DCL and TTC values are too small to be visible in this graph.

In Figure 30 the removal values of the two hormones from wastewater and synthetic water show similar results for each time step. For each sample the values of the two hormones correspond exactly. The SDs for the first three time steps in wastewater are high compared to synthetic water.

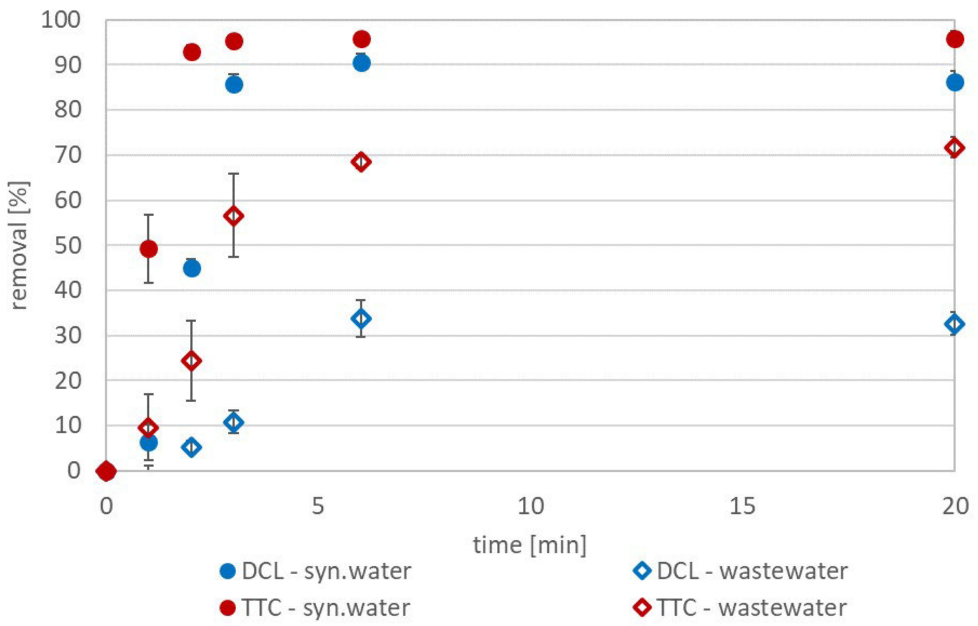


Figure 29: Catalytic ozonation results for the removal of individual ECs DCL and TTC over time from synthetic water and spiked real wastewater

For synthetic water only the results in min 1 show a higher SD, whereas all other values show neglectable SDs. The values for the last two time steps for both hormones in both waters are consistent and decrease slightly more in synthetic water.

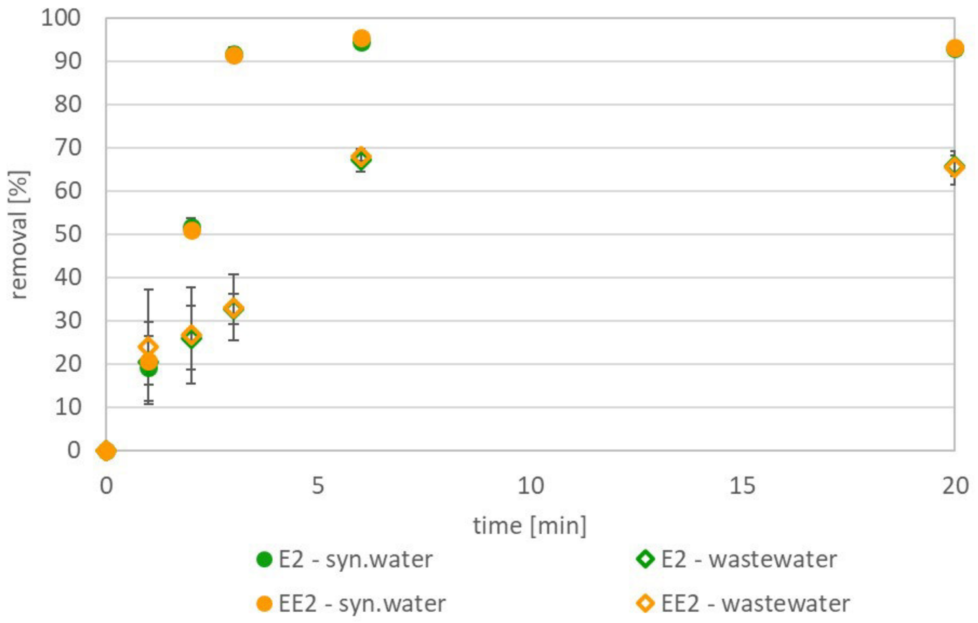


Figure 30: Catalytic ozonation results for the removal of individual ECs E2 and EE2 over time from synthetic water and spiked real wastewater

5.5 Comparison of Basic Ozonation and Catalytic Ozonation Results

To compare basic ozonation and catalytic ozonation experiments carried out with synthetic and real wastewater, the results are plotted in one graph. The mean removal results of all ECs by basic and catalytic ozonation are shown in Figure **??**. Each individual compound is plotted for both processes with both waters in Figures 32, 33, 34 and 35. For meaningful interpretation of the results, the removal values are plotted over the specific ozone dose g O_3/g DOC consumed at each time step. The SD values are plotted, representing the triplication data for the experimental repetitions. On the y-axis the SD values represent deviations regarding concentration measurements. On the x-axis the SD values represent deviations regarding ozone consumption related to the DOC content of each initial water.

For interpretation of the removal values, a nonlinear regressions with exponential rise to maximum was fitted to each data set. The Equation 29 was used to fit data from ozonation experiments on DCL and two other model compounds by Rizzo et al. [76] and was therefore chosen for trend line illustration for the following graphs.

$$F = a * (EXP(-b * x)) \tag{29}$$

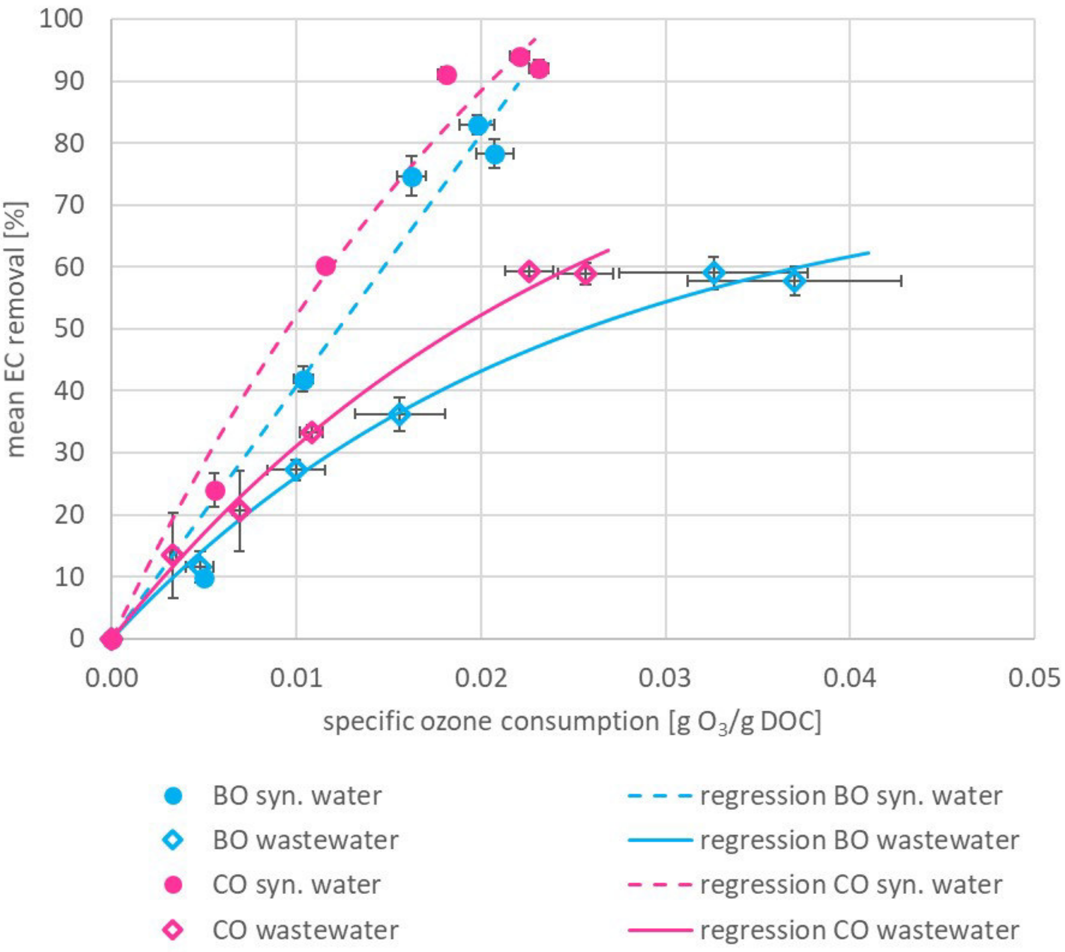


Figure 31: Removal of ECs (mean value over all compounds) over specific ozone consumption during the process of basic ozonation (BO) and catalytic ozonation (CO), carried out on synthetic water and wastewater spiked with DCL, TTC, E2 and EE2

In Figure 31 the mean values of all EC removal results are plotted. In this way all compounds influence the trend lines in the same way. The blue results represent basic ozonation and the pink results represent catalytic ozonation. The trend lines of catalytic ozonation in both water types are above the basic ozonation results. The removal of catalytic ozonation in synthetic water reaches a maximum value of 94 %, whereas with basic ozonation a maximum removal of 83 % could be reached with a smaller ozone dose. The SDs of the mean values of all results obtained from synthetic water treatment are minor. The different trend of the wastewater regression curves origins from the higher amount of ozone applied during basic ozonation, measured prior to the experiment. Therefore catalytic ozonation resulted in the same maximum elimination value with 0.02 g O_3/g DOC less consumed. The results at the end of the trend line are nearby, as the ozone gas stream was turned off as mentioned above.

The removal results of the compound DCL are presented in Figure 32. It can be observed that the trend lines of basic and catalytic ozonation in synthetic water are exactly corresponding. With catalytic ozonation higher final results could be achieved and the SDs are lower than for basic ozonation. Regarding wastewater, the trend line of catalytic ozonation increases faster at lower specific ozone consumption. The final values of basic ozonation are higher, considering the higher specific ozone consumption. All regressions show a linear trend. Compared to all other compounds, DCL shows the slowest increase in wastewater.

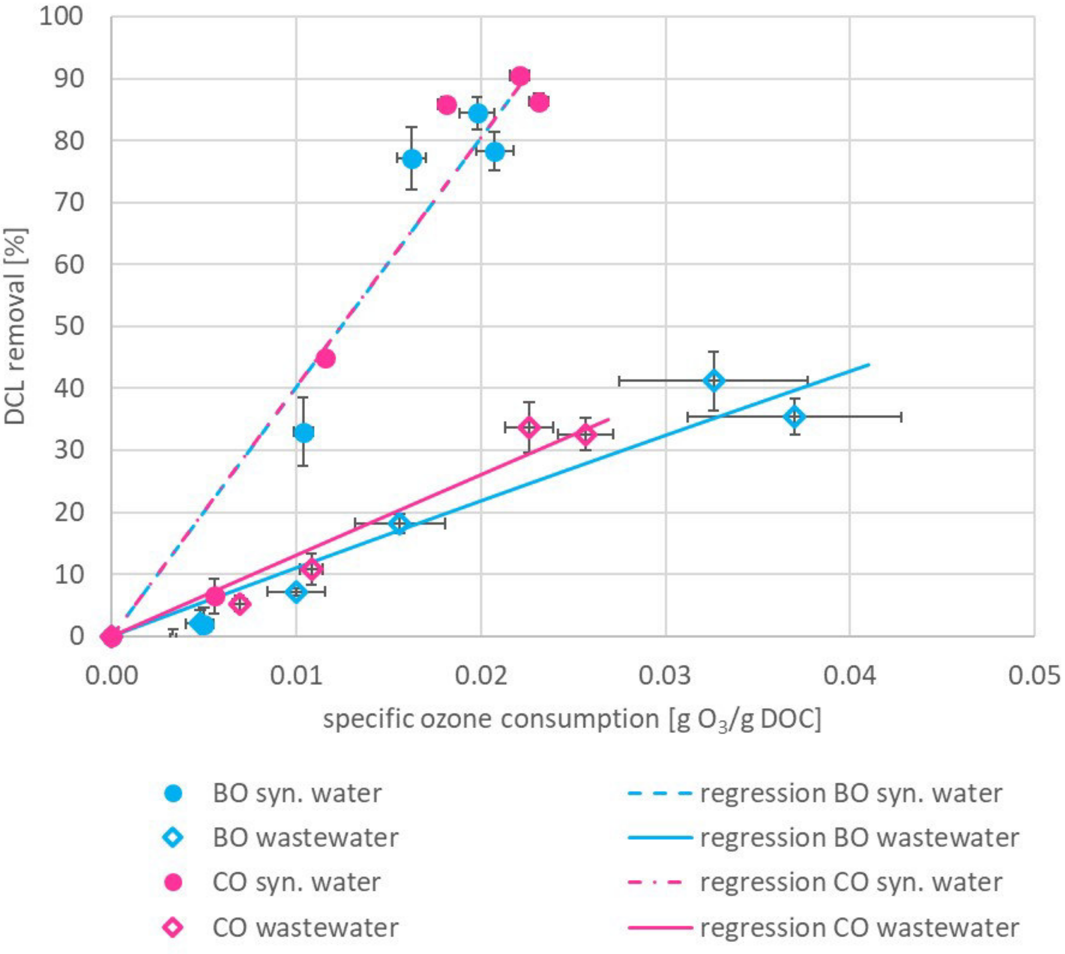


Figure 32: Removal of DCL over specific ozone consumption during the process of basic ozonation (BO) and catalytic ozonation (CO), carried out on synthetic water and wastewater spiked with DCL, TTC, E2 and EE2

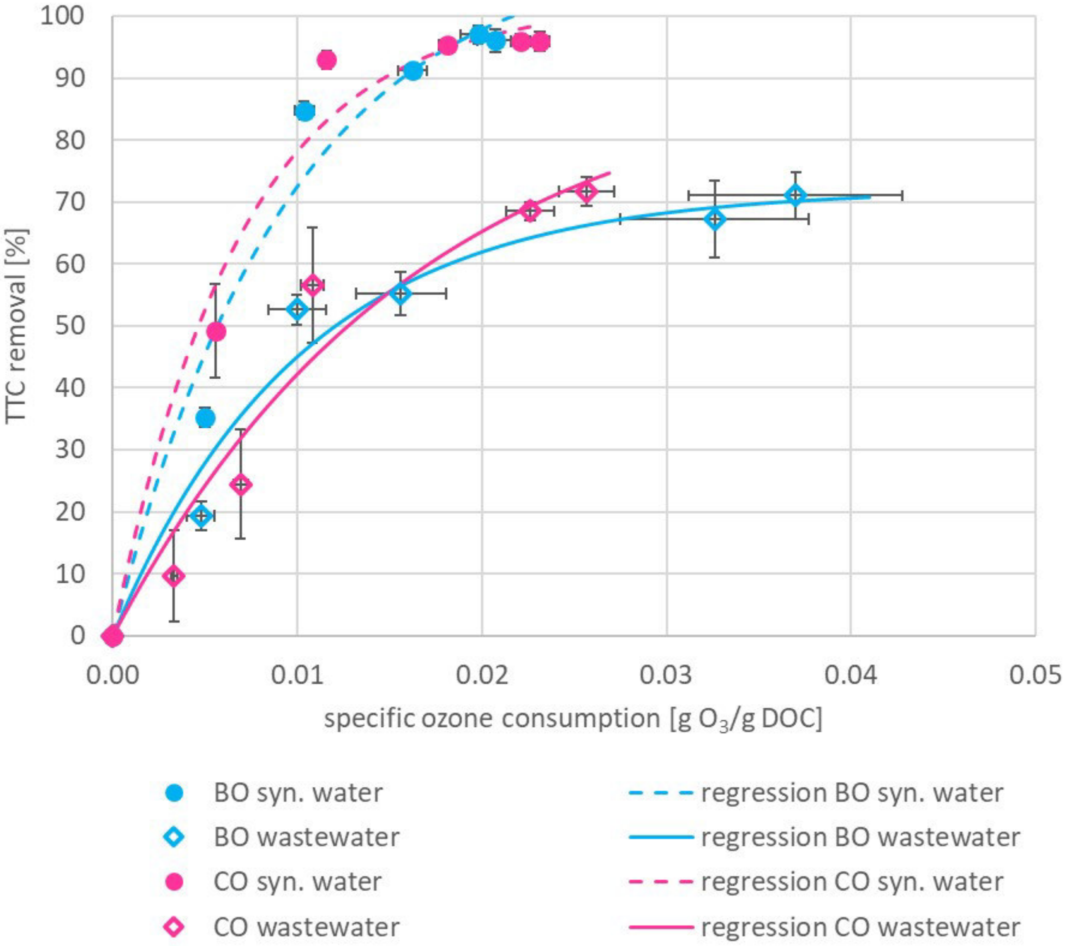


Figure 33: Removal of TTC over specific ozone consumption during the process of basic ozonation (BO) and catalytic ozonation (CO), carried out on synthetic water and wastewater spiked with DCL, TTC, E2 and EE2

The regressions of TTC removal in Figure 33 show a different trend compared to the linear regressions of DCL. The removal in both waters and with both processes increases quickly within the first time steps and flattens out closer to the final values. The difference between catalytic ozonation and basic ozonation in the case of TTC is not significant and the SDs for TTC values are especially high, compared to other compounds. The final removal values are the highest compared to all other compounds of close to 100 % for synthetic water and around 70 % for wastewater.

The two graphs in Figure 34 and 35 are corresponding in most data points. The regressions for synthetic water are linear, whereas wastewater regressions especially for EE2 show a slightly more exponential regression. In the case of hormones the catalytic ozonation results are significantly higher in all data points than basic ozonation results. The final removal values reached in synthetic water are up to 20 % higher than with basic ozonation.Furthermore the SDs of catalytic ozonation in synthetic water are neglectable, while catalytic ozonation in wastewater shows the largest SD values. In wastewater the final results diverge less in terms of removal value for EE2, while for E2 they diverge slightly. The greater difference can again be seen in the ozone consumption, where the same or slightly higher removal was achieved with significantly lower ozone consumption with catalytic ozonation.

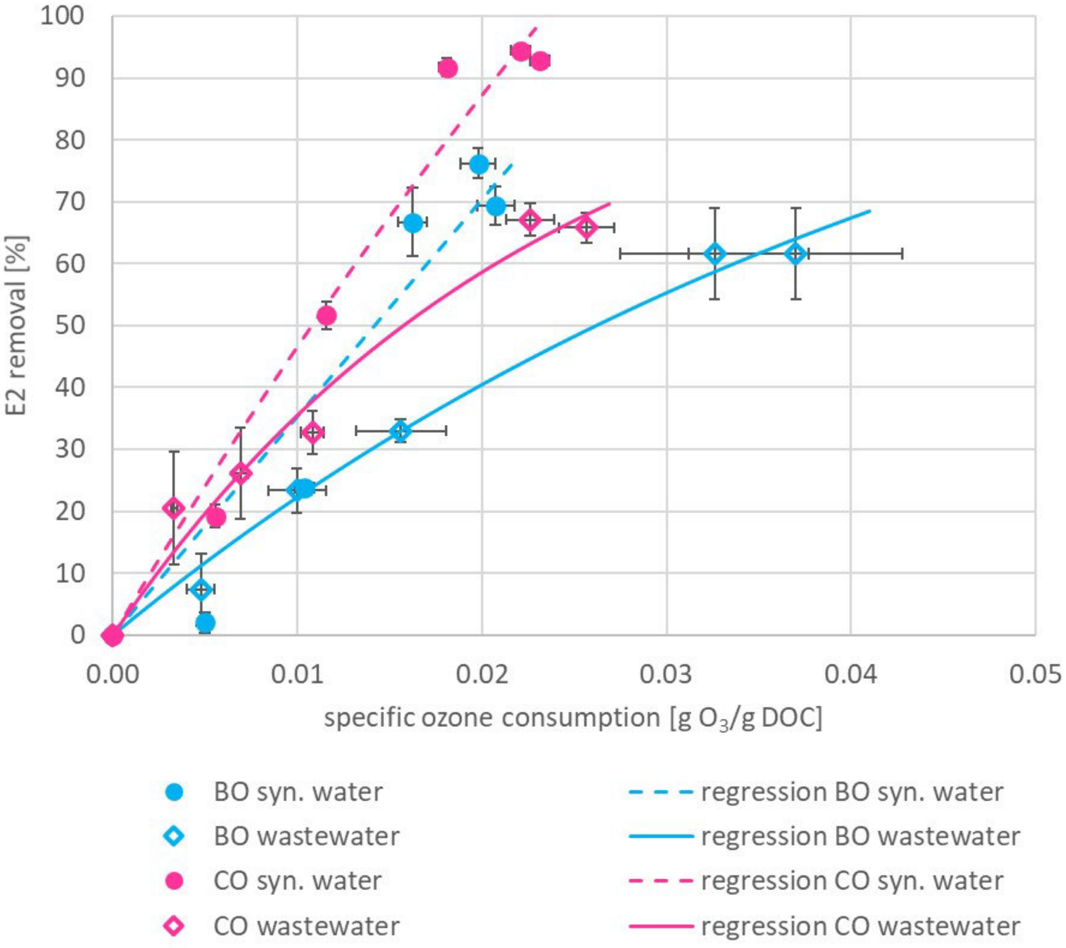


Figure 34: Removal of E2 over specific ozone consumption during the process of basic ozonation (BO) and catalytic ozonation (CO), carried out on synthetic water and wastewater spiked with DCL, TTC, E2 and EE2

The DOC concentrations of the treated water for each experiment were measured. The DOC values for synthetic water with EC concentrations of 500 and 50 µg/l respectively were up to ten times higher than the DOC values of synthetic water with lower initial EC concentrations. This increase originates from the organic solvent acetonitrile, used to initially dissolve the hormones. Acetonitrile was added in concentrations of 195 mg/l. The higher EC concentrations make a total of 1.1 mg/l of organic content.

The initial DOC concentrations vary between 54 mg/l for the synthetic water and 78 mg/l for the wastewater used in catalytic ozonation. The wastewater samples have a slightly higher DOC than the synthetic water samples and there is no trend for an influence of catalyst on the DOC concentrations. During all ozonation experiments DOC values do not show a clear decrease. A influence of the measured DOC on the EC elimination results could not be obtained.

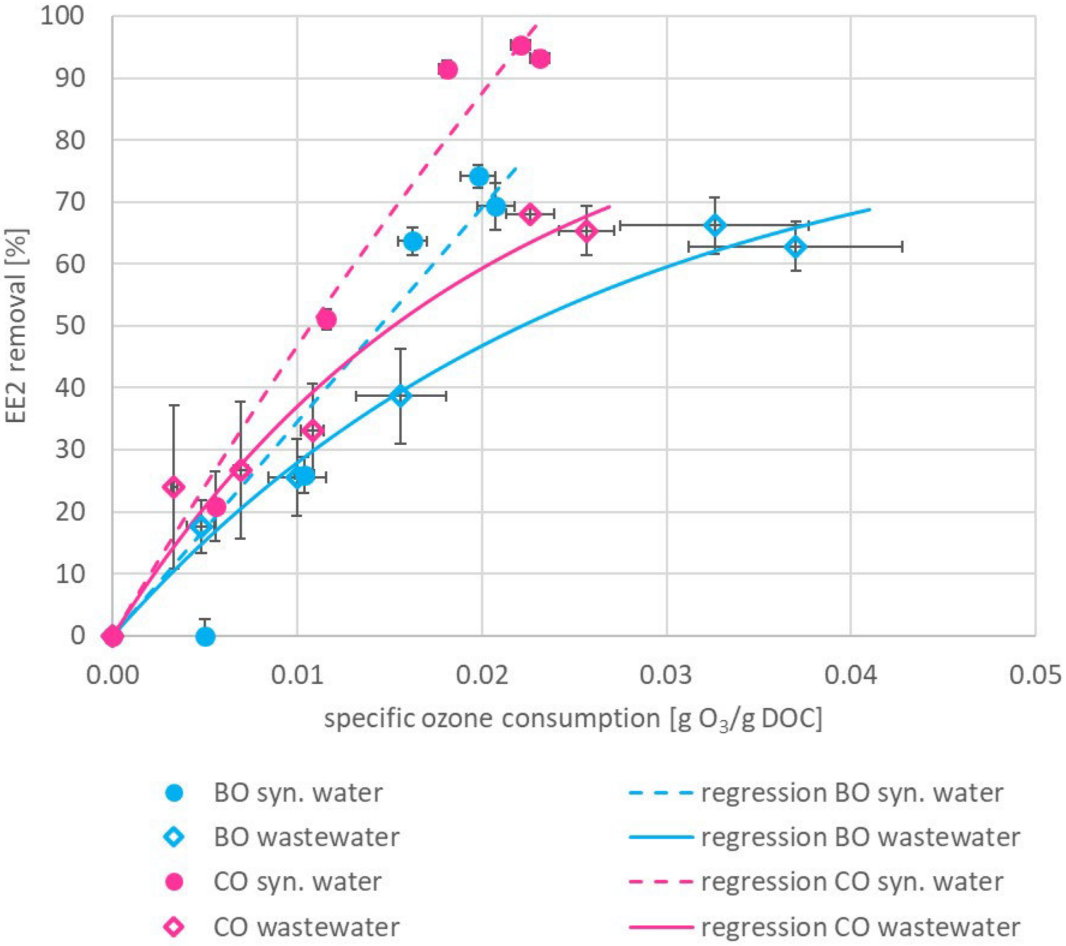


Figure 35: Removal of EE2 over specific ozone consumption during the process of basic ozonation (BO) and catalytic ozonation (CO), carried out on synthetic water and wastewater spiked with DCL, TTC, E2 and EE2

6 Discussion of Results

One of the challenges in micropollutant research is the low concentration in ranges of µg/l and ng/l and the consequential limitation in analysis. Most experimental research has been done on elevated concentration levels to achieve valuable results [56], [53], [36]. The behaviour of components in lower concentration can deviate and is not sufficiently investigated yet. Therefore an analytical campaign on five wastewater streams has been carried out. The main results of the investigation can confirm the expected wastewater composition regarding the present treatment systems. Furthermore it gives an insight to the EC mix of local water streams.

ECs adsorption on AC were the initial experiments carried out within this study with the objective to evaluate the concentration of catalyst needed for further catalytic ozonation experiments. During adsorption experiments on AC, the antibiotic ERY was found not to be stable under the current adsorption conditions. During adsorption, rising concentrations and initial concentration with very high SD were detected. It could be shown that the macrolide antibiotic is unstable at low pH values. The initial synthetic water showed a pH of around 5 and was neutralized with NaOH previous to experimentation. For TTC the same phenomena of rising concentrations could be detected during adsorption experiments, which might arise from instability of the compound at low pH values. For further ozonation experiments, the initial solution was neutralized immediately and the analytical results of TTC were satisfying.

The initial adsorption results showed almost full removal of all compounds for catalyst doses as low as 14.3 mg/l within 20 min. Compared to Goncalves et al. [78], who reports an ERY removal of 25 % after 300 min. The deviation of the two studies is especially high and further adsorption experiments on different catalyst, catalyst concentrations and water matrices should be carried out to support the reported outcomes.

The adsorption results of DCL were increasing steadily compared to other compounds. TTC did not show reliable results as mentiones above and E2 shows the highest adsorption from wastewater after 20 min, considering the especially high SDs of all final values from both hormones. The high SDs might be an indicator for interferences between the compounds. Another explanation can be that adsorption of hormones on CAT2 is not an irreversible process but a balance between adsorption and desorption. One conclusion that can be draw regardless, is that the applied catalyst material influences the removal process significantly.

With the implementation of basic ozonation experiments, the removal of ECs, by bubbling ozone rich gas through the treatment water was investigated. The marginally slower increase of removal in min 1 observed for most experiments, compared to the following time steps, might mark the time needed for the distribution of ozone in the reactor. Moreover, the transfer from the gas phase to the aqueous phase, the decomposition of ozone and the initiation of the radical chain reaction are initiated within the first seconds.

In general, the SDs for most ozonation results are low, compared to adsorption results. Each point represents the reproducibility of the experiment. As triplication was achieved by carrying out all experiments three times. Especially the endpoint results of each experiment show hardly any SD for experiments carried out on synthetic water, where catalytic ozonation experiments could be reproduced with the lowest SD. All experiments were carried out three times and mostly a good reproducibility could be achieved. Deviations in certain sampling points could be caused by spiking of the initial waters, reactor filling, treatment and sample volume, timing of catalyst addition and diverging ozone flow, caused by the generator.

One possible explanation for the marginally lower endpoint removal at 20 min for during basic ozonation might be the position of the water sampling outlet, which is placed at the bottom of the reactor and close to the diffusor of the gas inlet, see Figure 18. Influences like ozone bubbles, caught in the outlet tube or inhomogeneous concentration distribution due to the ongoing gas stream should be considered.

Different behaviour of compounds in synthetic water and in wastewater could be confirmed, especially for DCL, where the removal increase was much slower for wastewater and the final values could only reach half the elimination of synthetic water. This leads to the conclusion that different compounds react differently in a complex matrix, whereas in synthetic water the removal process is approximately the same for all investigated ECs. One possible reason might be the complex matrix interactions, the ozone scavenging compounds and the presence of radical chain carrying compounds in wastewater. Consiquently future studies on EC removal should be carried out on wastewater samples to produce valuable results.

With the use of the regressions the removal efficiency of the different processes could be compared. The trend line of the mean values of basic ozonation in synthetic water indicates that a slightly higher ozone dose would be necessary to reach the same final removal results as reached with catalytic ozonation. Regarding the compound regressions and previous experiments with higher ozone dose, it can be assumed that full removal from synthetic water can be achieved with ongoing ozone input. This assumption can be taken for all compounds, particularly for DCL, E2 and EE2 showing a linear regression. Regarding TTC total elimination was almost reached from synthetic water. With wastewater experiments with higher ozone does were carried out previously and all compounds could be removed from the complex matrix. Regarding to the regression line, full removal from wastewater with the current methods could be possibly achieved by applying double the ozone dose on average for all target compounds.

TTC, as presented in Figure 33 shows a rapid removal at the initiation of the treatment. The regression lines of all data sets flatten out after the first 2 - 3 min of ozonation. In the case of TTC higher final removal values from wastewater could be achieved than for DCL. The results from basic ozonation of wastewater stagnate at a specific ozone dose of 0.025 to 0.04, which leads to the assumption that with this dose even during a longer application time, full removal cannot be achieved. In this case, basic ozonation of wastewater shows an insignificantly faster rise in removal results.

The removal of hormones is presented in Figure 34 for E2 and Figure 35 for EE2. The similarity of the results for E2 and EE2 is evident and a good prove for reliability of the analytical data, as E2 and EE2 molecules with a similar structure. The difference of removal from synthetic water and wastewater deviates less than for the other two compounds DCL and TTC. It is outstanding that hormone removal through catalytic ozonation shows significantly better results than basic ozonation for synthetic water as well as wastewater. Catalytic ozonation of synthetic water is the experiment closest to full removal of E2 and EE2. A possible extrapolation of the regression line indicates, that full removal would be possible with an addition of 0.005 g O_3/g DOC.

The removal graphs lead to the conclusion, that catalytic ozonation is preferable over basic ozonation when it comes to the removal of hormones. Within the removal of the painkiller DCL or the macrolide antibiotic TTC an improvement of the ozonation process with the addition of an CeO_2 loaded AC catalyst could not be confirmed.

7 Conclusion

The main objective of this study was to investigate the feasibility of catalytic ozonation on the removal of ECs from wastewater streams. Punctual investigation of micropollutant concentrations of real wastewater streams gave a good insight into local wastewater compositions. 21 out of 41 measured compounds could be detected in at least one out of five streams. Certain compounds for example ibuprofen were detected in the entry but not in the exit stream, which confirms their biodegradability in regular WWTPs. DCL for example was detected in all streams, which proves that an additional stage after mechanical and biological treatment is necessary to remove specific compounds from wastewater streams. The investigated effluent from the main Hospital of San Sebastian showed EC concentrations up to two orders of magnitude higher than in other streams. A significant influence of the wastewater entering the WWTP by the effluent of a hospital could not be detected.

To draw a conclusion on the experimental results, all three investigated processes were capable of removing 100 % of the target ECs from synthetic as well as real wastewater. A catalyst dose of 4.3 mg/l and a maximum specific ozone dose of 0.04 g O_3/g DOC were found to deliver the most meaningful results in terms of process comparison. With these parameters, removal rates of 75 - 100% in synthetic water and 35 - 75% in real wastewater could be achieved during catalytic ozonation. DCL showed the lowest maximum removal of 35% from wastewater, whereas TTC showed the highest removal at ozonation initiation. Subsequently, low ozone and catalyst application can lead to development of an economically feasible removal process, due to the requirement of small amounts of chemicals and electrical energy. The difference in the removal kinetics of certain compounds leads to the outcome that a broader field of substances should be tested. To quantify the minimum amount of ozone gas necessary for total removal of each compound, further experiments with gradual increase of ozone dose are recommended.

In all experiments, the significant influence of the complex wastewater matrix on the removal process was confirmed. It can be concluded that experimental studies on real wastewater samples are essential to evaluate the feasibility of APOs.

Moreover, catalytic ozonation with CeO_2 doped AC catalyst showed higher removal rates for hormones from synthetic water compared to basic ozonation. A similar maximum removal was achieved by carrying out both processes on real wastewater, where catalytic ozonation resulted in a decrease in specific ozone consumption. For the compounds DCL and TTC, satisfying removal could be achieved with both processes. This leads to the verdict that out of the investigated processes, catalytic ozonation is the preferable AOP for the removal of hormones in wastewater. Follow-up studies focused on the optimization of process parameters should be carried out. The AOP catalytic ozonation shows promising potential to deliver a significant contribution to protect water bodies.

As the pathways for entering the ecosystem are as diverse as the variety of micropollutants, multiple approaches to solve this problem must be considered. The most meaningful step towards water protection is a clear reduction in consumption of harmful substances. This can start by the consumer and should be advanced by potential restrictions and the implementation of regulations in production sites and other micropollutant releasing industries, agriculture and aquaculture.

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Appendix

Project Phase 2 - Experiments with synthetic water

(AD = Adsorption, BO = Basic Ozonation, CO = Catalytic Ozonation)

experiment	V sample	t	O_3 consumed	O_3 consumed	DOC	DCL	TTC	E2	EE2
	[l]	[min]	[mg O_3]	[mg O_3/mg DOC]	[mg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]
BO I	10	0	0.00	0.00	62	509	276	48	54
BO II	10	0	0.00	0.00	62	499	255	50	57
BO III	10	0	0.00	0.00	56	502	302	49	51
BO I	10	1	2.98	0.00	58	489	174	48	56
BO II	10	1	2.98	0.00	59	509	164	49	56
BO III	10	1	2.98	0.01	55	484	202	47	50
BO I	9.6	2	5.96	0.01	61	352	43	36	42
BO II	9.6	2	5.96	0.01	60	362	43	38	42
BO III	9.6	2	5.96	0.01	55	298	40	38	36
BO I	9.2	3	8.94	0.02	63	119	22	16	20
BO II	9.2	3	8.94	0.02	59	143	24	20	22
BO III	9.2	3	8.94	0.02	56	82	27	13	17
BO I	8.8	6	10.43	0.02	65	78	2.9	12	14
BO II	8.8	6	10.43	0.02	60	94	9	13	16
BO III	8.8	6	10.43	0.02	54	63	13	10	12
BO I	8.4	20	10.43	0.02	62	111	4	15	18
BO II	8.4	20	10.43	0.02	58	127	13	17	19
BO III	8.4	20	10.43	0.02	55	89	16	13	13
CO I	10	0	0.00	0.00	54	472	197	42	49
CO II	10	0	0.00	0.00	55	469	214	39	45
CO III	10	0	0.00	0.00	52	483	218	39	49
CO I	10	1	2.98	0.01	49	445	98	35	35
CO II	10	1	2.98	0.01	45	415	90	31	38
CO III	10	1	2.98	0.01	44	473	132	31	40
CO I	9.6	2	5.96	0.01	45	254	14	20	25
CO II	9.6	2	5.96	0.01	45	251	11	20	22
CO III	9.6	2	5.96	0.01	46	279	19	18	23
CO I	9.2	3	8.94	0.02	48	55	9	3.2	4
CO II	9.2	3	8.94	0.02	45	65	9	2.7	3.2
CO III	9.2	3	8.94	0.02	45	82	11	4	5
CO I	8.8	6	10.43	0.02	46	35	5	2	2.6
CO II	8.8	6	10.43	0.02	44	41	10	2	1.9
CO III	8.8	6	10.43	0.02	42	59	11	2.6	2.1
CO I	8.4	20	10.43	0.02	46	55	4	2.9	3.2
CO II	8.4	20	10.43	0.02	44	58	10	2.4	2.5
CO III	8.4	20	10.43	0.02	43	82	12	3.3	4
AD I	2	0	-	-	54	472	197	42	49
AD II	2	0	-	-	55	469	214	39	45
AD III	2	0	-	-	52	483	218	39	49
AD I	2	3	-	-	49	450	228	36	42
AD II	2	3	-	-	52	452	232	33	41
AD III	2	3	-	-	49	446	239	34	37
AD I	2	20	-	-	47	423	217	33	43
AD II	2	20	-	-	48	430	240	36	44
AD III	2	20	-	-	48	437	250	34	41

Project Phase 3 - Experiments with spiked real wastewater

(AD = Adsorption, BO = Basic Ozonation, CO = Catalytic Ozonation)

experiment	V sample	t	O_3 consumed	O_3 consumed	DOC	DFC	TET	E2	EE2
	(l)	(min)	(mg O_3)	(mg O_3/mg DOC)	(mg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)
BO I	10	0	0.00	0.00	54	474	303	32	38
BO II	10	0	0.00	0.00	54	467	372	31	35
BO III	10	0	0.00	0.00	77	477	393	31	40
BO I	10	1	2.87	0.01	54	452	253	27	29
BO II	10	1	2.87	0.01	78	457	289	30	30
BO III	10	1	2.87	0.00	75	481	318	30	34
BO I	9.6	2	5.74	0.01	53	443	154	23	25
BO II	9.6	2	5.74	0.01		434	169	24	28
BO III	9.6	2	5.74	0.01	74	439	180	25	31
BO I	9.2	3	8.60	0.02	53	377	140	22	20
BO II	9.2	3	8.60	0.02	78	388	179	21	25
BO III	9.2	3	8.60	0.01	73	395	157	20	24
BO I	8.8	6	17.21	0.04	52	247	121	9	11
BO II	8.8	6	17.21	0.04	64	292	92	13	14
BO III	8.8	6	17.21	0.03	73	295	132	14	13
BO I	8.4	20	18.64	0.04	52	287	104	10	12
BO II	8.4	20	18.64	0.04	77	314	101	11	14
BO III	8.4	20	18.64	0.03	75	315	100	15	16
CO I	10	0	0.00	0.00	82	459	334	32	36
CO II	10	0	0.00	0.00	80	450	282	39	45
CO III	10	0	0.00	0.00	72	468	348	41	51
CO I	10	1	2.58	0.00	79	454	324	29	34
CO II	10	1	2.58	0.00	78	461	265	31	31
CO III	10	1	2.58	0.00	70	467	279	28	33
CO I	9.6	2	5.16	0.01	80	429	291	27	32
CO II	9.6	2	5.16	0.01	78	424	208	27	29
CO III	9.6	2	5.16	0.01	70	452	229	28	34
CO I	9.2	3	7.74	0.01	79	394	104	23	27
CO II	9.2	3	7.74	0.01	71	413	129	26	31
CO III	9.2	3	7.74	0.01	70	421	186	26	29
CO I	8.8	6	15.48	0.02	80	278	111	10	12
CO II	8.8	6	15.48	0.02	70	308	89	12	14
CO III	8.8	6	15.48	0.02	70	327	103	15	16
CO I	8.4	20	16.77	0.02	79	294	105	12	14
CO II	8.4	20	16.77	0.02	72	316	77	13	16
CO III	8.4	20	16.77	0.03	70	318	91	13	15
AD I	2	0	-	-	53	483	267	38	48
AD II	2	0	-	-	63	480	281	36	48
AD III	2	0	-	-	60	486	298	40	49
AD I	2	3	-	-	59	469	276	32	41
AD II	2	3	-	-	61	473	293	32	36
AD III	2	3	-	-	52	489	331	32	37
AD I	2	20	-	-	51	463	314	32	43
AD II	2	20	-	-	49	472	325	26	42
AD III	2	20	-	-	49	485	313	27	44

Project Phase 1 - Pharmaceutical concentrations in 5 sampling points

detected pharmaceuticals		**mean detected concentration [µg/l]**										not detected pharmaceuticals
	LOD [µg/l]	**Entry Loiola**	**SD**	**Exit Loiola**	**SD**	**Entry Gaikao**	**SD**	**Exit Gaikao**	**SD**	**Hospital**	**SD**	
Erythromycin	0.2	0.06	0.00	0.07	0.01	0.08	-	0.07	0.01	-	-	Enrofloxacin
Furaltadone	0.2	0.23	-	-	-	-	-	-	-	-	-	Flumequin
Clarithromycin	0.2	0.00	-	-	-	-	-	0.25	-	-	-	Pantoprazole
Diclofenac	0.2	0.57	0.06	0.80	0.00	0.87	0.29	0.60	0.00	0.34	0.00	Pefloxacin
Enalapril	0.2	0.21	-	-	-	0.27	-	-	-	0.37	0.01	Sarafloxacin
Gemfibrozil	0.4	0.60	0.00	0.63	0.15	2.80	-	-	-	0.40	0.00	Oxolinic acid
Venlafaxin	0.2	0.26	0.01	0.24	0.01	0.28	-	-	-	0.50	-	Nalidixic acid
Ketoprofen	0.2	0.37	0.03	0.50	0.00	0.40	0.18	0.34	0.01	3.13	0.06	Ampicillin
Naproxen	0.4	2.33	0.15	2.60	0.14	2.67	0.83		-	5.00	0.00	Chlorotetracycline
Trimethoprim	0.2	0.00	-	-	-	-	-		-	7.33	0.58	Florfenicol
Norfloxacin	0.2	0.00	-	-	-	-	-	1.23	0.61	9.00	1.00	Levamisole
Ibuprofen	1	11.67	2.08	-	-	11.67	1.15		-	12.33	1.53	Oxytetracycline
Sulfamethoxazole	0.2	0.00	-	-	-	0.27	-		-	18.33	0.58	Sulfadiazine
Ciprofloxacin	0.2	0.57	0.06	0.40	-	0.33	-	0.97	0.12	26.33	4.51	Sulfadoxine
Ofloxacin	0.2	1.57	0.40	0.85	0.21	0.70	0.10	1.50	0.17	31.00	4.58	Tetracycline
Salicylic acid	1	0.00	-	-	-	-	-	-	-	36.33	2.31	Amoxicillin
4-Aminoantipyrine	0.2	1.67	0.12	0.95	0.07	1.53	0.23	-	-	50.00	2.65	17-Alpha-Ethinylestradiol
Acetaminophen	0.4	56.00	9.54	-	-	28.67	2.52	-	-	915.67	30.14	17-Beta-Estradiol
Amphetamine	0.1	0.40	0.00	0.19	0.02	0.40	0.09		-	0.36	0.02	Cocaethylene
Benzoylecgonine	0.04	0.60	0.00	0.12	0.01	0.53	0.06		-	0.27	0.00	MDMA
Cocaine	0.04	0.40	0.00		-	0.16	0.01		-	0.12	0.01	
DOC		40.67	2.08	17.33	0.58	45.00	29.44	17.00	0.00	147.67	12.74	