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Treball Final de Grau

A preliminary design of an ozonation process in a municipal wastewater treatment plant for water reuse

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M’agradaria dedicar aquestes línies a les persones que de manera directa i indirecta han fet possible que fes aquest treball.

En primer lloc, agrair a la tutora d’aquest TFG, la Dra. Carme Sans Manzón els suggeriments, les idees i sobre tot la paciència, per fer possible el desenvolupament d’aquest treball.

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CONTENTS

SUMMARY

In the last few years, water scarcity has arisen as a major problem around the world. This scarcity has put pressure on water accessibly for human use such as drinking water, irrigation, industry, etc. Moreover, climate change, population growth and water pollution have exacerbated the situation. This project focuses on water reuse, a strategy currently under study to deal with this problem.

Wastewater needs to go through complex treatments in order to be reused. These complex processes must be designed to disinfect water and eliminate or reduce the concentration of pollutants and micropollutants (MP). Advanced oxidation processes (AOPs) are well known technologies that can effectively contribute to reducing biological and chemical pollutants. The aim of this project is to study the application of the ozonation process using a preliminary design in the Vilaseca/Salou municipal wastewater treatment plant as a tertiary treatment. A mathematical model was used for a subsequent micropollutant abatement estimation, which showed that depending on the flow of water to be treated and ozone dose applied, ozonation can be a very effective process for eliminating MP.

Keywords: Water scarcity, water reuse, micropollutants (MP), advanced oxidation processes (AOPs), ozonation, municipal wastewater treatment plant, tertiary treatment.

RESUM

En els últims anys l'escassetat d'aigua ha aparegut com una gran problemàtica a tot el món. Aquesta escassetat comporta que hi hagi poca aigua accessible per a ús humà, com aigua per beure, reg, indústries, etc. A més a més, el canvi climàtic, l'augment de població i la contaminació de l'aigua han agreujat la situació. Aquest projecte es centra en la reutilització de l'aigua, una estratègia que s'estudia actualment per fer front a aquest problema.

Per a poder reutilitzar l'aigua residual, aquesta ha de passar per tractaments complexes. Aquests processos complexes s'han de dissenyar per a desinfectar l'aigua i eliminar o reduir la concentració de contaminants i microcontaminants. Els processos d'oxidació avançada (AOPs) són una tecnologia reconeguda que contribueix eficaçment a la reducció de contaminants biològics i químics. L'objectiu d'aquest projecte és estudiar l'aplicació del procés d'ozonització en un disseny preliminar a la planta depuradora d'aigües residuals municipals de Vilaseca/Salou com a tractament terciari. Posteriorment es fa servir un model matemàtic per a realitzar l'estimació de l'eliminació o reducció dels microcontaminants, que va demostrar que en funció del cabal d'aigua a tractar i la dosi d'ozó pot ser un procés molt efectiu per a aquesta funció.

Paraules clau: Escassetat d'aigua, reutilització de l'aigua, microcontaminants, processos d'oxidació avançada (AOPs), ozonització, planta depuradora d'aigües residuals municipals, tractament terciari.

1. INTRODUCTION

The purpose of this first section is to explain the framework of the project and to set forth the most important concepts and techniques for wastewater treatments.

1.1. WATER SCARCITY AND REUSE

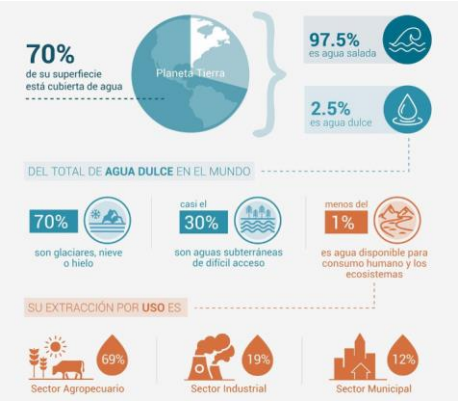

Figure 1. Water in the planet
(Centro Virtual de Información del Agua, 2017. October 2020)

Figure 1 shows schematically the distribution of the water in the world. As can be seen, less than 1% of the world's water is freshwater, water that we drink, bathe in, irrigate farm fields with, etc (1) (2).

Because of the small amount of water that is accessible for direct human use and other factors like population growth, climate change and water pollution, it can be stated that there is a problem of water scarcity.

Water scarcity can be understood as insufficient water resources to satisfy long term average requirements (3). This means that a number of people worldwide lack access to water. Water scarcity can also be defined as a lack of safe water delivery or a water deficiency (4).

Water pollution in the form of large pieces of waste materials to invisible chemicals is another factor in the crisis of freshwater. These pollutants end up in our planet's lakes, groundwater, oceans, etc (5). As a result of this water pollution and inadequate sanitation, a lot of people are exposed to water-borne illnesses that can even cause death (2).

Climate change and droughts are two other factors. Although water scarcity and droughts are different phenomena, they can aggravate the impact of each other. Even in areas where there is

abundant rainfall droughts can occur so it is necessary to put water conservation plans into place (3). Figure 2 is a summary of some issues with water scarcity.

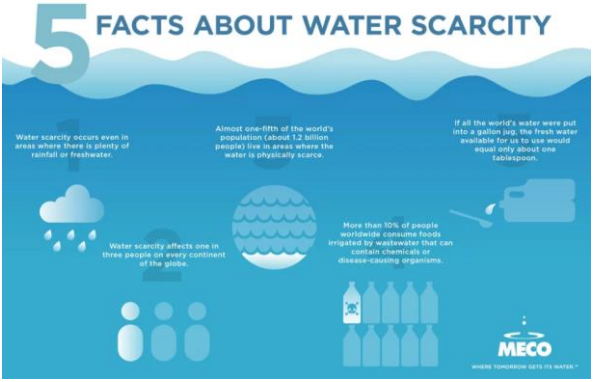

Figure 2. Facts about water scarcity
(N. Herold, MECO, 28/04/19. October 2020)

The future of sustainable water resources will depend primarily on how they are managed, how climate change plays out, the extent of water pollution, and the pressure exerted on supply due to the evolution of sectorial water uses, population, etc.

Solutions and strategies are being investigated to solve the problem of scarcity water. One of the answers is water conservation and maybe the most important component of the strategy is water reuse. Other solutions that are being studied are tapping other resources, reducing demand through pricing, etc (6).

Water reuse, according to EPA, is a way of recycling treated wastewater for beneficial aims, such as agricultural and landscape irrigation, industrial processes, toilet flushing, etc. This is a sustainable manner to provide another water resource as it involves a reduction of the environmental impact by reducing or eliminating wastewater (6).

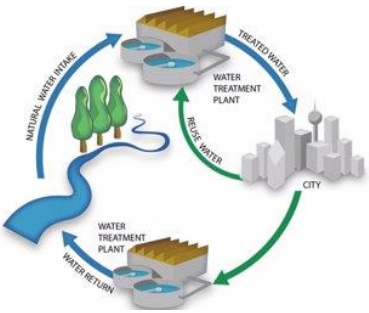

Figure 3. Water reuse
(D. Abraham, Water online, 05/06/20. October 2020)

As is shown in Figure 3, water reuse is a change in the water cycle which generates water conservation and maintains the world's freshwater supplies.

Reused water can be high quality or low-quality water, depending on the treatments it goes through. In Spain, there is legislation for regenerated water. This water can be reused for different applications. Depending on its quality it can be used for urban, agricultural, industrial, recreational and environmental uses. Table 1 shows some examples for each use (7).

Table 1. Reused water uses

USES	
Urban	Irrigation of private gardens, sanitary device discharge, irrigation of green urban areas, street cleaning, fire protection system, cleaning of vehicles industrial.
Agricultural	Irrigation of crops where direct contact between water and products are allowed, these can be fresh or subsequently treated in industry. Irrigation of crops without direct contact between water and products, these can be woody crops, nursery plants, etc.
Industrial	Process and cleaning water, except in the food industry. Process and cleaning water for food industry and refrigeration towers and evaporative condenser.
Recreational	Golf course irrigation, pond and ornamental circulating flows, where public access to water is prevented.
Environmental	Aquifers recharge, forest, green areas irrigation, wetland maintenance, etc.

Each use implies a specific water quality treatment including filtration, chlorine treatment, etc. These treatments are simple. The treatment to apply depends on the parameter of quality outlined in the royal decree 1620/2007 (7). However, to obtain high quality water more complex treatments such as adsorption, membrane and advanced oxidation processes are required. One use of high-quality water is potable reuse. For example, in the USA and Australia indirect potable reuse is already implemented (8).

Potable reuse refers to recycled or reclaimed water, also known as purified water, which has gone through a lengthy treatment. It can be used in agricultural applications, such as a municipal drinking water source, in industrial processes and for other municipal uses. The water quality

required will depend on its final use and risk of human exposure. Depending on the process that water undergoes there are two techniques, indirect and direct potable reuse (Table 2) (8).

Table 2. Potable reuses

Indirect potable reuse (IPR)	Direct potable reuse (DPR)
After the wastewater goes through an extensive treatment, it goes into an environmental buffer, like a surface reservoir or groundwater basin. It is used to provide enhanced quality. (Figure 4)	After the wastewater goes through an extensive treatment and monitoring to assure that water quality requirements have been reached, it is introduced into a municipal water supply system. (Figure 5)
 Figure 4. Schematic diagram of indirect potable reuse	 Figure 5. Schematic diagram of direct potable reuse

One of the reasons why obtaining high quality water is more complex is due to the presence of micropollutants (MP). These are pollutants which exist in very small concentrations in water. MP can be defined as anthropogenic chemicals; derived from human activities such as personal care products, pharmaceutical ingredients, endocrine disruptive compounds, etc. But they can also be derived from toxic chemicals, emerging contaminants, etc. Because of this, they can be found in agricultural, industrial and domestic wastewater (9).

Micropollutants are not eliminated with secondary treatment, and thus tertiary treatments or advanced treatments are required.

1.2. LEGISLATIVE FRAMEWORK

Most of the issues related with water are legislated, for example rights, power, reuses, documentation, etc. In Spain, the legislation pertaining to water and water reuse is based on two main laws; these are water law and royal decree 1620/2007.

1.2.1. Water Law

Royal Decree 1/2001 lays out legislation pertaining to water use. This Royal Decree became effective on the 25 of July 2001, the day after it was published in the BOE (10).

The objective of this law is the regulation of the public water resources, the uses of the water, etc. It also establishes the basic rules for the protection of continental, coastal and transition water. Lastly, mineral and thermal waters are regulated with specific legislation (10).

The water law addresses water reuse in Article 109. It establishes the owner of the water treatment plant must pay the cost to treat the water and this water must meet established demands for quality. Additionally, it establishes that the Government must develop basic conditions of reuse. It also must fix the quality of purified water depending on its future use. Lastly, it establishes the obligation to have an administrative license for the water reuse (10).

1.2.2. Royal Decree 1620/2007

The objective of this law is to establish a legal system for reclaimed water reuse, in accordance with article 109 of the water law. It was published in the BOE on the 8 of December 2007 (7).

It describes the basic conditions for reclaimed water reuse. Purified water can be reused for urban, agricultural, industrial, recreational and environmental uses. Depending on the use, the quality required is different and there can also be different requirements for the same use, and the sampling frequency (Table 4). The quality of the water can be evaluated with analysis of the samples. For example, Table 3 shows the quality required of water for industrial uses (7).

Table 3. Quality required of water for industrial uses
(BOE, 08/12/07. October 2020)

USO DEL AGUA PREVISTO	VALOR MÁXIMO ADMISIBLE (VMA)				
	NEMATODOS INTESTINALES	*ESCHERICHIA COLI*	SÓLIDOS EN SUSPENSIÓN	TURBIDEZ	OTROS CRITERIOS
3.- USOS INDUSTRIALES					
CALIDAD 3.1[1] a) Aguas de proceso y limpieza excepto en la industria alimentaria. b) Otros usos industriales.	No se fija límite	10000 UFC/100 mL	35 mg/L	15 UNT	OTROS CONTAMINANTES contenidos en la autorización de vertido aguas residuales: se deberá limitar la entrada de estos contaminantes al medio ambiente. En el caso de que se trate de sustancias peligrosas deberá asegurarse el respeto de las NCAs. Legionella spp.: 100 UFC/L
c) Aguas de proceso y limpieza para uso en la industria alimentaria	1 huevo/10 L	1000 UFC/100 mL Teniendo en cuenta un plan de muestreo a 3 clases[2] con los siguientes valores: n=10 m =1.000 UFC/100 mL M=10.000 UFC/100 mL c=3	35 mg/L	No se fija límite	OTROS CONTAMINANTES contenidos en la autorización de vertido aguas residuales: se deberá limitar la entrada de estos contaminantes al medio ambiente. En el caso de que se trate de sustancias peligrosas deberá asegurarse el respeto de las NCAs. Legionella spp.:100 UFC/L Es obligatorio llevar a cabo detección de patógenos Presencia/Ausencia (Salmonella, etc.) cuando se repita habitualmente que c=3 para M=10.000
CALIDAD 3.2 a) Torres de refrigeración y condensadores evaporativos.	1 huevo/10 L	Ausencia UFC/100 mL	5 mg/L	1 UNT	*Legionella spp:* Ausencia UFC/L *Para su autorización se requerirá:* – La aprobación, por la autoridad sanitaria, del Programa específico de control de las instalaciones contemplado en el Real Decreto 865/2003, de 4 de julio, por el que se establecen los criterios higiénico-sanitarios para la prevención y control de la legionelosis. – Uso exclusivamente industrial y en localizaciones que no estén ubicadas en zonas urbanas ni cerca de lugares con actividad pública o comercial.

Table 4. Sampling frequency
(BOE, 08/12/07. October 2020)

Uso	Calidad	Nematodos Intestinales	*Escherichia Coli*	SS	Turbidez	NT y PT	Otros contaminantes	Otros criterios
1.- USO URBANO	1.1 y 1.2	Quincenal	2 por semana	Semanal	2 por semana	–	El Organismo de cuenca valorará la frecuencia de análisis sobre la base de la autorización de vertido y del tratamiento de regeneración.	Mensual
2.- USO AGRARIO	2.1	Quincenal	Semanal	Semanal	Semanal	–		Mensual
	2.2	Quincenal	Semanal	Semanal	–	–		Quincenal
	2.3	Quincenal	Semanal	Semanal	–	–		–
3.- USO INDUSTRIAL	3.1	–	Semanal	Semanal	Semanal	–		Mensual
	3.2	Semanal	3 por semana	Diaria	Diaria	–		*Legionella spp. 3 por semana*
4.- USO RECREATIVO	4.1	Quincenal	2 por semana	Semanal	2 por semana	–		–
	4.2	–	Semanal	Semanal	–	Mensual		–
5.- USO AMBIENTAL	5.1	–	2 por semana	Semanal	–	Semanal		–
	5.2	Semanal	3 por semana	Diaria	Diaria	Semanal		Semanal
	5.3	–	–	Semanal	–	–		–
	5.4							Frecuencia igual al uso más similar

Lastly, the Royal Decree contains all the information pertaining to the administrative licenses for all the processes of water reuse (7).

1.3. ADVANCED TREATMENTS

The process to get purified water from wastewater goes through different steps, as shown in Figure 6. These are (11):

1. Preliminary treatment: removal or reduction in size of large, suspended, or floating solids with sifter, degreasing, etc.
2. Primary treatment: removal of part of the suspended solids with mechanical processes of sedimentation, flotation and coagulation-fluctuation.
3. Secondary treatment: biological process to eliminate organic substances, and in some cases eliminate nitrogen and phosphorus. Not elimination of non-sedimental solids.
4. Tertiary treatment: additional treatments to regenerate and reuse water. The most important technologies are adsorption, membrane and advanced oxidation processes.

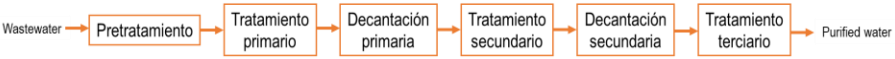

Figure 6. Diagram of wastewater treatment

These additional treatments are used to reduce the pollutant residual charge, suspension solids, turbidity, pathogens microorganisms, micropollutants, etc. to ensure water quality (12).

1.3.1. Adsorption

Adsorption is possible because of the properties of some materials which allow organic materials to attach to their surfaces from the liquid state, as is shown in Figure 7. This process is used to eliminate phenol, odour, colour, flavour, etc. The most commonly used adsorbent in water treatment is active carbon (13).

Depending on the adsorption forces, the process can be divided into two categories: physical and chemical adsorption. The former is made by intermolecular interaction, Van der Walls forces. The latter involves formation and destruction of chemical bonds. Usually both adsorptions occur together, not isolated (13).

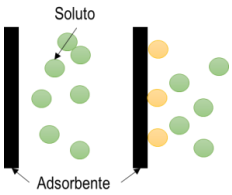

Figure 7. Adsorption process

1.3.2. Membrane

Membrane is a generic name and includes different separation processes that have membrane in common. A membrane is a physical obstacle used to separate two phases. There are two types defined by the driving force (14):

1. The driving force is an electric field. The process is called Electrodialysis and the membrane eliminates electrically charged ions dissolved in water (14).

2. The driving force is pressure. The difference between the pressure on both sides of the membrane is the thrust to separate particles from the water. There are different processes depending on the size of the particles that can be separated from the liquid, as is shown in Figure 8. Microfiltration and Ultrafiltration refer to the processes that use a membrane that allows more particles to pass through. Conversely reverse osmosis is the process that uses a thicker membrane and only lets water pass through. In between these processes there is Nanofiltration. This process uses a similar membrane as the reverse osmosis but with low pressure (14).

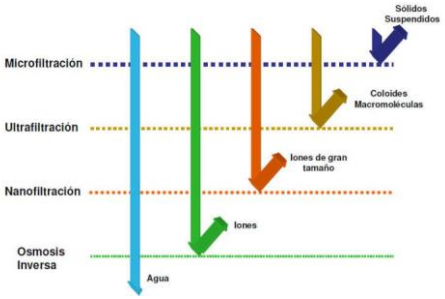

Figure 8. Different processes depending on the sizes
(S.Tuset, Condorchem Envitech, 07/01/19. October 2020)

1.3.3. Advanced oxidation processes (AOPs)

AOPs are physicochemical processes that use radical generation, mainly hydroxyl radical ($OH^{\bullet}$) to disrupt the chemical structure of the pollutants. The radicals used are highly effective in organic substance oxidation (15).

One of the objectives of these treatments is to oxidize different pollutants to the point of mineralization or intermediate oxidation where other depuration methods can be applied. Mineralization consists in transforming organic pollutants into inorganic molecules, for example, carbon to carbon dioxide (15).

These processes are quite useful due to the fact that the reactives used, for example ozone (O_3) and hydrogen peroxide (H_2O_2), decompound into innocuous products and by-products are

not generated. The reactives mentioned are expensive, and photochemical processes require a large amount of energy. Therefore, some strategies have been proposed. One strategy is to combine the advanced oxidation processes with other processes, for example with biological processes (15).

AOPs can work with or without light which means there are two groups: photochemical advanced oxidation processes and non-photochemical processes (15). Among them, the AOPs currently used to treat municipal water for micropollutant abatement at an industrial scale are ozonation and a combination of UV/hydrogen peroxide. Even though both processes are used, most water treatment plants use ozonation.

The Combination of UV/hydrogen peroxide is a photochemical process, since it requires UV-C light radiation to make hydroxyl radicals from the photolysis of H_2O_2, according to Equation 1 (15).

$$H_2O_2 \rightarrow radiation \rightarrow 2OH^{\bullet} \text{ (1)}$$

After photolysis, hydroxyl radicals can further react according to Equations 2-4, and also with the organic pollutants on the effluent. Figure 9 shows a diagram of the reactor where this process occurs (15).

$$OH^{\cdot} + H_2O_2 \rightarrow HO + H_2 + O_2 \text{ (2)}$$
$$2OH^{\cdot} \rightarrow H_2O_2 \text{ (3)}$$
$$OH^{\cdot} + HO_2 \rightarrow H_2O + O_2 \text{ (4)}$$

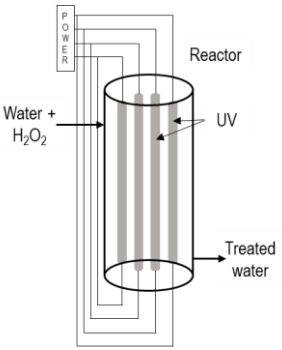

Figure 9. Diagram of UV/hydrogen peroxide reactor

1.3.4. Ozonation

Ozonation is a non-photochemical process, meaning that it does not need light radiation. It is effective for wastewater depuration, potabilization of water, disinfection, organic micropollutant oxidation, inorganic pollutants oxidation and elimination of colour and flavour. Figure 10 shows a general diagram of the ozonation process, which has 4 phases, namely feed gas preparation, ozone generation, contact between ozone and the solution to be treated and ozone destruction (15).

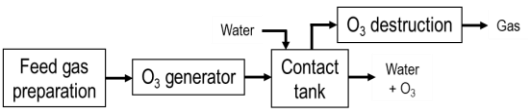

Figure 10. Diagram of Ozonation process

The feed gas is usually air or oxygen, which are introduced into the ozone generator with a set flow. As is shown in Figure 11, if the gas feed is air, this needs to undergo a treatment before it is introduced into the reactor. The air has to be very dry and free of suspended solids. When the feed gas is pure oxygen, it can be introduced into the reactor without any treatment (17).

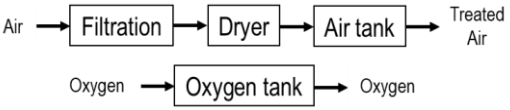

Figure 11. Schematic diagram of feed gas preparation

Ozone generation is the second phases of the process. Because of ozone's short life and the ease with which it decompounds into oxygen it has to be generated in situ (16). There are three options for the generation. These are electrochemical discharge, UV methods and corona discharge. The technique used to produce ozone on an industrial scale is corona discharge. It is also known as silence electrical discharge and is based on a high tension alternate electric discharge. Figure 12 shows the feed gas passing through an electric field. Tension creates a corona discharge between electrodes and electrons stay in-between them. These electrons give oxygen the energy to separate and create ozone, as shown in Equations 5-6. M is an intermediary which takes the extra energy from the reaction (15).

To avoid the creation of electric arcs both electrodes are separated by a dielectric, usually made of glass.

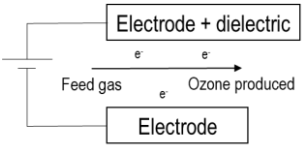

Figure 12. Schematic diagram of ozone generation by corona discharge

Ozone formation

$$O_2 + energy \rightarrow 2O^- \ (5)$$

$$O_2 + O^- + M \rightarrow O_3 + M \ (6)$$

Ozone decomposition

$$O_3 + O_2 \rightarrow 2O_2 + O \ (7)$$

$$O_3 + O \rightarrow 2O_2 \ (8)$$

Ozone generation produces a large amount of heat which can cause ozone decomposition, by Equations 7-8, consequently the process needs a good refrigeration system. Some parameters of ozone generation to keep in mind are shown in Table 5 (15).

Table 5. Parameters of ozone production

System parameters	System length and width, dielectric thickness.
Process parameters	Ozone concentration and production, efficiency, etc.
Operational parameters	Tension type, frequency, work pressure, work temperature, gas composition, etc.

Contact between ozone and the solution to be treated is the third phase of the process. There are different contactors for ozonation, these are bubble column and bubble diffuser in a contact tank, a reactor equipped with a turbine or an axial diffuser, a reactor with a U tube, a packing bed column and static mixers (18). The most commonly used in water treatment plants is the first one. This type of reactor is available in two forms: the simple bubble column and a contact tank with multiple compartments in series. Usually, on an industrial scale, the latter is used (17), because it achieves better ozone transfer than the others (24). In the contact tank ozone has to be scattered as finely as possible and this is done by way of a thin bubble diffuser. Usually, in the first compartment water goes down, as is shown in Figure 13, and in the subsequent compartment it goes up. Every tank has sampling spots to test ozone concentration (15).

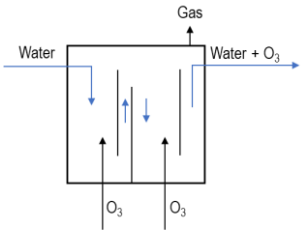

Figure 13. Schematic diagram of contact tank

The transfer between ozone and dissolved compounds is controlled by physical parameters, such as temperature, gas flow rate, ozone partial pressure, etc. Chemical factors like pH, ionic strength, composition, etc. also control this process (18).

Ozone destruction is the last phase of the process. The gas emitted into the atmosphere has to have less than 0,1 ppm of ozone. Usually, the gas that comes out of the contact tank has more ozone and this extra ozone has to be recycled or destroyed. As is shown in Figure 14, to destroy the gas firstly it has to be dried. Then it is heated and goes through a destruction unit (15).

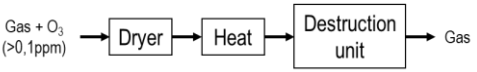

Figure 14. Schematic diagram of ozone destruction

Ozone destruction can be carried out using different methods. These are thermal, term-catalytic and adsorption and reaction with active carbon (16).

- Thermal destruction is the most widely used method in Europe. It is based on heating the gas to 300-350 ºC in a short period of time, less than 5 seconds.
- Term-catalytic destruction works with catalyst which can be metallic or metallic oxide. The former works at 29 ºC and the latter works between 50 and 70 ºC. The catalyst can be deactivated with some substances present in the gas.
- Adsorption and reaction with active carbon is not a method which is recommended because the reaction is slow and creates carbon particles which can cause an explosion.

Instead of destroying ozone from the main chamber it can be reused in another chamber, this can be reused from the main chamber to another one.

Ozone has a high redox potential and because of this it is an excellent disinfectant and can be used to degrade pollutant and micropollutant compounds (16). The reaction between ozone and organic compounds can be direct or indirect. The former is a selective mechanism and reacts with aromatics, amines, etc. The latter is less selective and reactions are with radicals created from ozone decomposition in water, like hydroxyl radical. These reactions are important in wastewater treatment thanks to their high velocity, but low efficiency of ozone generation still poses a problem (15). Something important to keep in mind when working with ozone is that pH affects stability. More pH means ozone has less stability (15) which promotes the indirect mechanism. At municipal wastewater pH (neutral or slightly alkaline), both mechanisms participate in MPs abatement.

2. OBJECTIVES

The general objective of this project is to select, develop and perform a preliminary design of an ozonation process to integrate in the wastewater treatment plant Vilaseca/Salou as tertiary treatment. The final purpose is to obtain water of high quality, which could be reused in many different ways, for example in agricultural uses, irrigation of crops where direct contact between water and product are allowed, and in industry.

Therefore, the specific objectives of this study are:

- To make a preliminary design of a tertiary treatment based on the ozonation process.
- To use ozonation modelling for a micropollutant abatement estimation.
- To estimate the operational costs of the proposed tertiary treatment.

3. DESCRIPTION OF THE WATER TREATMENT PLANT

The water treatment plant used in this study is located in Tarragona, Catalonia. Figure 15 shows an aerial view of the Vilaseca/ Salou EDAR, where the distribution of the plant can be seen.

Figure 15. Aerial view of Vilaseca/Salou EDAR
(Google Earth, 2020. November 2020)

The EDAR collects wastewater from Cap de Salou, Mare de Déu de Núria, Salou, Xalets de Salou, La Pineda, La Plana and Vila-seca. Wastewater also arrives from Port Aventura theme park. Table 6 shows some general information of the Vilaseca/Salou EDAR. Due to its location, the wastewater flow changes considerably depending on the time of the year. Moreover, it is situated in an area with a high level of water consumption, but with a meagre water supply (19). In addition to the problems associated with this lack of water, the plant reuses a third of the total wastewater it treats and the regenerated water obtained is of low quality, a fact that restricts its

applications. If legislation for water reuse prospers, this plant would be a good candidate for improved tertiary treatment.

Table 6. General information of Vilaseca/Salou EDAR

General information	
Administration	Agència Catalana de l'Aigua (ACA)
Operating company	CADAGUA
Launch year	1995
Basin	Stream between Cunit and Vandellòs and Hospitalet de l'Infant
Spilt point	Mediterranean Sea
Treatment	Biological and tertiary treatment
Design flow [m^3/day]	47.500
Design equivalent population [h-e]	197.917
Design flow of tertiary treatment [m^3/day]	16.800

This EDAR uses a simple tertiary treatment, and was designed to process 35% of the wastewater. The purified water is reused for recreational uses, mainly for irrigation of public parks. Figure 16 shows schematically the process that the wastewater goes through in the water treatment plant (19).

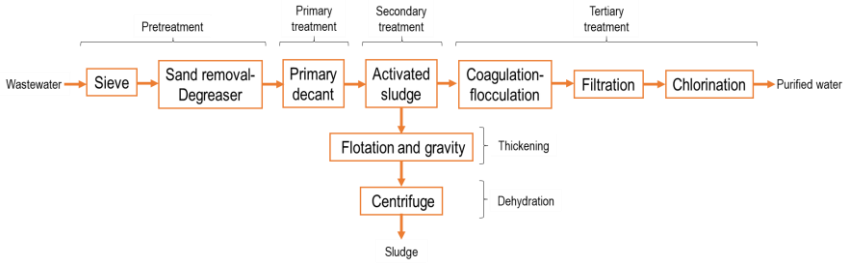

Figure 16. Schematic diagram of Vilaseca/ Salou EDAR process

The current treatment to which wastewater is subjected when it arrives at the plant starts with a pretreatment. This consists of a sieve and a sand removal equipment- degreaser. After this,

wastewater passes through primary treatment, which involves decantation. The last phase for all the water is the secondary treatment, a biological treatment with conventional active sludge. At this point water and sludge are separated by way of a secondary decanter.

Some of the water, 35%, goes through the tertiary treatment, which includes a physicochemical treatment, sand filtration and lastly chlorination. A floatation and gravity process renders the sludge thicker and then with a centrifuge process it is dehydrated. After this treatment, dehydrated sludge can be stored in silos.

In summary, the wastewater treatment plant uses a classic treatment, which produces low quality water for reuse, since only parameters like suspended solids (SS), turbidity and coliforms are improved in the current tertiary treatment. The object of this project is to achieve higher quality water and eliminate MP.

4. PRELIMINARY DESIGN OF THE OZONATION PROCESS

The quality of the water after the secondary treatment, which means the quality of the water that will go through the tertiary treatment, is collected in Table 7 (19). The design flow for the ozonation process will be 16.800 m^3/day. The main reason for this selection is to decrease capital investment, since most of the already operational tertiary operations could be integrated into the new process.

Table 7. Physicochemical characteristics

pH	7,6
BOD_5 (mg/l)	11
Suspended Solids (SS) (mg/l)	12
Turbidity (NTU)	1,2
Faecal coliforms (ufc/100ml)	$2{,}10 \cdot 10^4$
Nematode eggs (nº egg/l)	0

The new tertiary treatment consists of three treatments in series, as is shown in Figure 17.

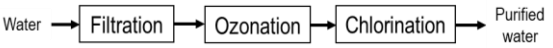

Figure 17. Schematic diagram of tertiary process

Because of the presence of a significant quantity of suspended solids on the effluent after the secondary treatment (see Table 7), a pre-filtration step is needed before initiating the ozonation process. The concentration of SS in the wastewater is high, and that is a problem, since SS consume ozone and solubilize organic matter. This means that, in order to obtain higher quality water, more ozone would be necessary, and the operational costs of the process would increase.

The wastewater flow treated in this process is the same as the current process in the plant. This allows some of the equipment of the plant to be reused and saves on investment costs. Thus,

the already existing sand filter will be used for SS removal. The eliminating percentages and information on the equipment are collected in Table 8 (19).

Table 8. Filtration information

Elimination percentage [%]		Filtration information	
BOD_5	42,9	Type	Horizontal pressure filtration
SS	0 -18,2	Filter bed thickness [m]	0,5 anthracite /0,3 siliceous sand
Nitrogen (N)	35,7	Uniformity coefficient	< 1,6
Phosphorus (P)	0 – 66,7	Cycle duration [min]	16

After the ozonation process, the purified water may have some dissolved ozone. This is not a problem, since ozone is very instable and converts back into oxygen. This means it does not leave any harmful residual by-product and also that water has no remaining disinfectant. The consequences of this are that microorganisms can grow again. For this reason, a post-chlorination treatment is also necessary in order to provide residual disinfection capacity during water distribution. Chlorination is used for disinfection, but unlike ozonation, some chlorine remains in the effluent after treatment and this residual chlorine prolongs disinfection and microorganisms cannot grow back (20). As in the previous treatment, the plant already has a chlorination treatment with hypochlorite that can be reused for the new process. Some information about the equipment is collected in Table 9 (19).

Table 9. Chlorination treatment information

Oxidant agent	Hypochlorite
Hypochlorite concentration	2 mg /l
Mixing system	No
Reaction time	6 min
Dose control	Free chlorine measurement
Dispenser	TIMSA. Model DH-1170
Chlorine sounding line	ENDRESS + HAUSER. Model P-140

Figure 18 shows a diagram of the complete ozonation process, which includes the three main units of this process: the ozone generator, the contact tank and the destruction unit. Among other

benefits, this process will eliminate or reduce most micropollutants, eliminate faecal coliforms and other microbial pollutants.

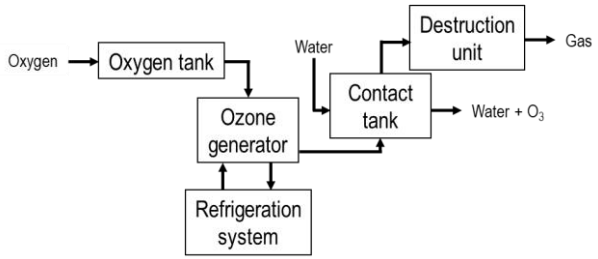

Figure 18. Schematic diagram of Ozonation process

As the diagram shows, the selected feed gas for ozone generation is oxygen, instead of air. There are different reasons for this choice, including that it can produce more ozone per area unit of generator, it needs less energy than air, the dimensions of the equipment needed are half those that would be needed if the feed gas were air and it needs less equipment because oxygen does not need pre-treatment before entering the ozone generator (21). In addition, bibliographical references show that the plants currently in operation use oxygen as feed gas (21).

The normalized ozone dose used to create the preliminary design is 0,5 mg O_3/mg DOC (dissolved organic carbon), as this is the most common rate used in operating wastewater treatment plants (28). This dose is set according to the DOC, which means there must be 0,5 mg of solubilized ozone for each mg of DOC. If a lower dose is chosen, the micropollutant abatement would decrease, which means water quality would be lower. If a higher dose is used, this problem with MP abatement would disappear, but the treatment cost would increase. Operational costs would increase, because more oxygen and more energy would be needed to be able to produce all the ozone. Moreover, the investment cost would also increase as a larger ozone generator would be needed.

To be able to design and select the equipments, apart from the parameters already presented in Table 7, other parameters, like dissolved organic carbon, nitrite content and alkalinity, are needed. When real parameters were not found for the wastewater treatment plant, bibliographic data was used to find the most representative data for a typical effluent. These data are collected in Table 10 (28).

Table 10. Parameters from bibliography

DOC [mg/l] =	5,30
NO_2^- [mg/l] =	0,03
Alkalinity [mg/l] =	400

Table 11 shows the operation information needed to be able to design and select the equipment. The values were calculated using conversion factors and knowing the design flow, as previously said, 16.800 m^3/day, the ozone dose, aforementioned, 0,5 mg O_3/mg DOC, and some of the parameters from Table 7 and Table 10, like DOC of wastewater after filtration is 5,3 mg/l. Also knowing all the efficiencies involved in the process, like ozone generator efficiency (13%) and contact tank efficiency (90%).

Table 11. Ozonation process operation information

Oxygen Flow [m^3 O_2/h]	14,737
Oxygen needed [kg O_2/day]	507,350
Ozone concentration [mg O_3/l]	2,944
Ozone flow [m^3 O_3/h]	0,963
Ozone produced [kg O_3/day]	49,467

After consulting operation information of different commercial generators, the ozone generator selected is one from *ZonoSistem, Ingeniería del Ozono S.L.* Some characteristics of it are collected in Table 12 (22). The numbers in the table are the maximum values it can achieve, but depending on the necessity they can be adjusted. The estimated efficiency of the ozone generator is 13%, slightly higher than most generators, which is between 4-12% (15). The efficiency was not supplied by the manufacturer, but with ozone formation Equations 5 and 6 and the ratio between maximum ozone production and required oxygen flow (Table 12), could be calculated.

Table 12. Ozone generator characteristics

Model	GRV4
Equipment	Electrical panel and transformer, generation ferrule, refrigeration hydraulic, meters and instrumentation and oxygen and ozone pneumatic.
Max ozone production	4 kg O_3/h
Ozone concentration	148 g O_3/m^3
Required oxygen flow	28,6 m^3/h
Energy power consumed	30 kW
Refrigeration flow	8 m^3/h
Work conditions	Humidity < 85%, temperature 5-35 ºC, work pressure 0,6-1,4 bar

Figure 19 shows the ozone generator, which is quite compact.

Figure 19. Ozone generator GRV

The contact tank has been designed based on parameters and factors found in the bibliography. According to that, the following design parameters of the contact tank for an optimal ozone transfer were selected:

- The transfer efficiency chosen is 90%, because, according to EPA, a contact tank with a diffuser depth between 4,9 and 6,1 m can achieve an efficiency of between 80-95% (24).

- The contact time selected is 10 minutes, because to achieve disinfection contact time needed is 6 to 10 minutes (24). Although micropollutants with high ozone reactivity can be eliminated in seconds, those with low ozone reactivity need several minutes (23).
- The tank high selected is 7,5 m, because the water height should be 5-6 m, adding 1,2-1,8 m on the top to have space for foam case it forms (24).
- The tank has 3 compartments, the minimum required for separate stages. To improve ozone transfer efficiency, the last compartment should not have ozone input (24).
- The ratio between ozone and contact volume, should not exceed 0,03 to obtain the best results (24).

After establishing parameters and factors to consider, calculations are made, knowing the amount of wastewater to treat and the amount of ozone needed to treat it. A summary of the results is collected in Table 13. Starting the calculations with volume, this was calculated by way of the formula volume equals design flow multiplied by residence time. Then some extra volume, 25 m^3, was added for safety, as previously said, some free space is needed in case foam forms. This extra volume was calculated based on the freeboard. Knowing the number of compartments, volume was divided to obtain the compartment volume. Depth and base were calculated using volume and height.

Table 13. Contact tank characteristics

Total volume	170 m^3	Compartment base	2,5 m
Compartment Volume	39 m^3	Depth	2,1 m
Water height	6 m	Contact time	10 min
Freeboard	1,5 m	Transfer efficiency	90%
Diffuser submergence	5 m	Deflectors number	3
Height	7,5 m	Ozone entrance	2

To make the contact tank design clearer and easy to visualize, a two-dimension schematic design is included in Figure 20.

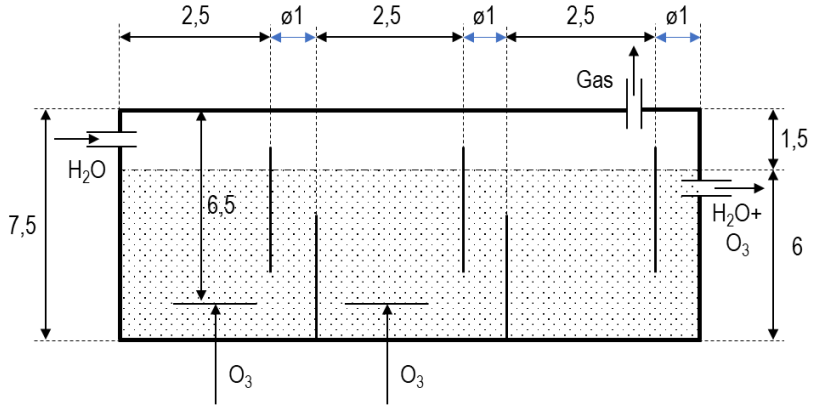

Figure 20. Schematic contact tank design

The contact tank has an efficiency of 90%, meaning that 10% of the ozone produced does not transfer into water (24). The gas that goes into the atmosphere cannot have this amount of O_3, for this reason an ozone destruction unit is needed. Among the possible destruction methods, thermal destruction of ozone was selected. It was selected by an elimination process. According to the bibliography there are three methods for ozone destruction (16). One is adsorption and reaction with active carbon which is not a recommended method because the reaction is slow and creates carbon particles which can cause an explosion. The second one is term-catalytic destruction which has an inconvenience, the catalyst can be deactivated with some substances present in the gas. For these reasons, the thermal destruction method was selected, and bibliographical references show that it was the most widely used method in Europe (16).

The commercial destruction unit selected is from *SUEZ* and its characteristics are described in Table 14. When gases leave the contact tank they are funnelled to the destructor unit where they are heated to 400ºC. At this point the ozone half-life is drastically reduced so decomposition takes seconds. When gas leaves this unit, it is below the safety limit (<0,1ppm). As is shown in Figure 21 it is a compact destruction unit. This is one of the reasons why it was chosen, together with it has high ozone destruct efficiency, it is processor controlled, it has a long service life and it has high product integrity and low maintenance (25).

Table 14. Ozone destruction unit characteristics

Model	ODT- 003 (Figure 21)
Flow	3,72 kg /h
Ozone level	Out < 0,1 ppm
Operating pressure	< 1,46 bars
Electrical rating	0,8 kW
Size (L x H x W)	66 x 32,5 x 25 cm

Figure 21. Ozone destruction unit ODT-003

5. MICROPOLLUTANT ABATEMENT ESTIMATION

When ozonation is applied to wastewater, the oxidation of a micropollutant can be complete, or it can be just a concentration reduction. The experimental monitoring of MPs is very costly since complex analytical equipment is required, like high-resolution mass spectrometry. Instead, kinetic modelling can be used for MPs removal estimation. In this work, the ozonation kinetic model proposed by Lee and von Gunten will be applied (26).

MP abatement during ozonation occurs by oxidation of both ozone (O_3) and hydroxyl radical ($OH^{\bullet}$). The kinetic of it can be formulated by Equation 9. The integration of it over the reaction time in an ideal batch or plug-flow reactor transforms it into Equation 10 (26).

$$-\frac{d[MP]}{dt} = k_{O3}[O_3] + k_{.OH}[OH^{\bullet}] \quad (9)$$

$$-ln\frac{[MP]}{[MP]_0} = k_{O3}\int[O_3]dt + k_{.OH}\int[OH^{\bullet}]dt \quad (10)$$

The percentage of the abatement of a MP can be expressed as shown in Equation 11.

$$\%abatement = 100 * \left(\frac{[MP]_0 - [MP]}{[MP]_0}\right) = \left(1 - \frac{[MP]}{[MP]_0}\right) * 100 \quad (11)$$

To calculate the percentage, first it is necessary to resolve Equation 10. To solve this equation, the two second order constants (k_{O3} and $k_{OH^{\bullet}}$) for each MP, ozone exposure $\int[O_3]dt$ and hydroxyl radical exposure $\int[OH^{\bullet}]dt$ are needed (26).

The two second order constants are physicochemical constants and reflect the reactivity of MP with ozone and hydroxyl radicals. Their values can be obtained using two methods. The former consists of a large kinetic database for reaction, where values are obtained in lab-scale experiments. The latter consist of prediction methods based on chemical calculations for accurate estimations or quantitative structure-activity relationship (26).

One way to determine ozone exposure is by integrating over time ozone degradation curves (26). The ozone decay depends on the water and some quality parameters such as dissolved organic matter, alkalinity, pH, temperature, etc. Based on different experimental studies, ozone exposure can be estimated by Equation 12 (26).

$$\int[O_3]dt\ [Ms] = (1{,}3\cdot 10^{-7})e^{\left(25*\frac{\Delta O_3}{DOC^*}\right)}\ \text{ for } 0 < \frac{\Delta O_3}{DOC^*} < 0{,}3$$
$$\int[O_3]dt\ [Ms] = (1{,}3\cdot 10^{-2})\left(\frac{\Delta O_3}{DOC^*} - 0{,}3\right)^2 + (3{,}8\cdot 10^{-3})\left(\frac{\Delta O_3}{DOC^*} - 0{,}3\right) + \quad (12)$$
$$(3{,}8\cdot 10^{-4})\ \text{for}\ \frac{\Delta O_3}{DOC^*} > 0{,}3$$

Where DOC is dissolved organic carbon, DOC* refers to the normalized and nitrite corrected ozone dose and ΔO_3 is ozone decomposition, which is the difference between ozone that is transferred into water and what is not transferred into it. The thoric applied ratio ($\Delta O_3/DOC^*$) can be estimated by Equation 13. This is done to be able to compare consistency and variability of ozone exposure across wastewater, as generally ozone consumption in wastewater is controlled by dissolved organic matter and nitrite composition (26).

$$\frac{\Delta O_3}{DOC^*} = \frac{\Delta O_3}{DOC} - \frac{48}{14} * \frac{[NO_2^-]}{DOC} \quad (13)$$

Hydroxyl radical exposition means an integration of its concentration over time. Hydroxyl radicals have a short-life and thus hydroxyl exposure can be calculated as the ratio between OH• formation ($r_{OH^\bullet}$) and consumption ($\sum k_{Si}[S_i]$) rates (Equation 14). OH• consumption can be determined by the sum of the species in the water *(Si)* that react with it, with the corresponding reaction constants (k_{Si}) (26).

$$[OH^\bullet] = \frac{r_{OH^\bullet}}{\sum k_{Si}[S_i]} \quad (14)$$

Since OH• is formed by ozone decomposition, the numerator of Equation 14, can be expressed as $r_{\cdot OH} = \eta r_{O3}$, where r_{O3} is the ozone decomposition rate and it is multiplied by the molar OH• yield from ozone decomposition ($\eta \approx 0{,}5$) (26). Ozone decomposition, as previously said, is the difference between ozone that is transferred into water and what is not transferred into it, and can be expressed as $r_{O3} = \Delta O_3$ (26).

Hydroxyl radical is an unselective and extremely reactive oxidant. The species present in wastewater that react with it are dissolved organic matter and alkalinity. The kinetic constant for the reaction between OH• and dissolved organic matter is done based on the DOC concentration ($k_{\cdot OH,DOC}$ = 1,2·10^8 – 1,4·10^9 M^{-1} s^{-1}) (26), and the kinetic constants for the reaction between OH• and alkalinity are $k_{\cdot OH,HCO_3^-}$ = 8,5·10^6 M^{-1} s^{-1} (26) and $k_{\cdot OH,CO_3^{2-}}$ = 3,9·10^8 M^{-1} s^{-1} (26). Because of this and the paragraph before, $\int[OH^\bullet]dt$ can be expressed as Equation 15 (26).

$$\int [OH^\bullet]\, dt[Ms] = \int \frac{r_{OH^\bullet}}{\sum k_{Si}[S_i]}\, dt$$
$$= \int \frac{\eta \Delta O_3}{k_{\cdot OH,DOC}[DOC] + k_{\cdot OH,HCO_3^-}[HCO_3^-] + k_{\cdot OH,CO_3^{2-}}[CO_3^{2-}]} dt \quad (15)$$

The concentration of carbonate and bicarbonate is determined by the total alkalinity value and the pH. With these parameters and pKa1 = 6,3 and pKa2 = 10,3, a modified version of the Henderson-Hasselbach equation, expressed as Equation 16 and 17, can be applied. In wastewater treatment with ozonation CO_2 does not contribute significantly to the scavenging of radicals, and so it is not considered in this calculation (27).

$$\alpha_{HCO_3^-} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \quad (16)$$

$$\alpha_{CO_3^{2-}} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \quad (17)$$

To be able to apply the model, wastewater parameters are needed, like DOC, NO_2^-, pH, etc. All the parameters are collected in Table 7 and Table 10.

The last parameter needed to make the calculations is the transferred ozone dose. As explained in the previous section, the efficiency of the ozone contactor is about 90% and for this reason in the next calculations the ozone concentration used is 2,65 mg/l, since the other 10% of the total dose applied goes into the destruction unit and does not react with the micropollutants (24).

There are hundreds of micropollutants that can be found in wastewater. The ones used in this project to calculate the abatement rate are Acesulfame, 1,4-dichlorobenzene, Aciclovir, Alachor, Amoxicilin, Atenolol, Atrazine, Benzophenone, Butachlor, Caffeine, Desethylatrazine, Diatrizoic acid, Ibuprofen, Linuron, Naproxeno, Paracetamol, Phenol, Propachlor, Simazine and Tetracycline. The values and the references of k_{O3} and $k_{OH\cdot}$ for each micropollutant can be found in Appendix 1. The reason these are the selected micropollutants is because these are found in the effluents of many wastewater treatment plants. In addition, they have varied kinetic with ozone, from very low to intermediate to very high. However, if we look at their $OH^{\cdot}$ radical kinetic constants these are all quite high, this is because as previously mentioned, hydroxyl radical is an unselective and extremely reactive oxidant (26).

Using this information and the equations from section 6, the percentages of the abatement of the different MPs abatement rate are shown in Figure 22.

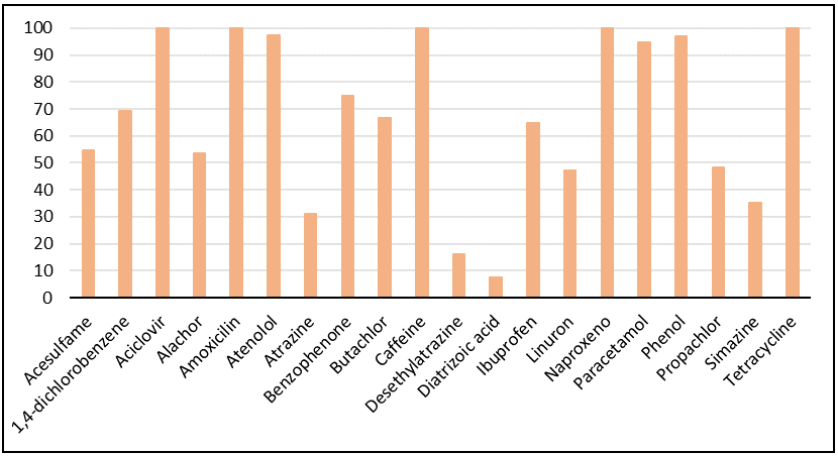

Figure 22. %abatement

Analyzing the results in Figure 22, 25% of the micropollutants studied were completely abated. Without counting this 25% of the MP, the concentration of nine MP was reduced more than 50%. Only 10% of all the MP included in this project were reduced less than 20%.

The main reason for the differences between the MP abatement rates is their kinetic constants with ozone. When a kinetic constant has a small value, this means the reactivity between MP and the oxidant is small too. This means the reaction between them is short and the oxidant is not able to oxidize a large part of the MP.

6. ECONOMIC ESTIMATION

To be able to make an operational costs estimation, costs were divided into categories, energy, chemical, etc. and treatments such as processes of ozonation, pre-filtration and post-chlorination. Then they were added together to calculate the total cost of the proposed tertiary treatment.

To be able to calculate the costs, some considerations were made:

- The plant works 330 days and 24h/day. The 35 remaining days are for maintenance and cleaning of equipment.
- For energy cost calculations, the net price for electricity for industrial use in the first semester of 2019, this is 0,092 € /kWh was considered (31). Also, a specific energy was considered, the energy needed for micropollutant abatement by ozonation, which is 0,45 kWh /m^3 of water to be treated (32). This value includes total energy consumption of the ozonation process, like ozone production, the contactor, the destructor, etc.
- For chemical cost calculations two data are needed: the supply cost of pure oxygen for ozone generation which is €1,66 /kg O_2 (29), and the cost of sodium hypochlorite (NaClO) which is €0,29 /kg (30).

The first step of the treatment is filtration which, according to the plant data, consumes 3.400 kWh/day (19). Knowing the plant works 330 days per year and the cost of electricity, the annual filtration energy cost would be €103.224.

The next step of the treatment is the ozonation process. In this work, the ozonation operational cost estimation model proposed by IOA Pan American Group will be applied (29). Within the operational cost, the main ones in this treatment are energy and oxygen consumption. To be able to do the estimation the needed values are collected in Table 15 and Table 16.

Table 15. Data to estimate the chemical cost

Chemical cost	
Oxygen needed [kg O_2/day]	507,35
Cost of pure oxygen [€/ kg O_2]	1,66

Table 16. Data to estimate the energy cost

Energy cost	
Design flow [m^3/day]	16.800
Specific energy [kWh/ m^3]	0,451
Cost of electricity [€/kWh]	0,092

To estimate chemical cost of the ozonation process, the days of the year that the plant is operational, the amount of oxygen needed and the cost of pure oxygen (29), values already presented in Table 15 will be used. The annual chemical cost is estimated at €277.926,56 and has been calculated with a conversion factor that can be expressed as Equation 18.

$$O_2\ cost = O_2\ needed * price * days\ of\ the\ year \quad (18)$$

To estimate the energy cost of the ozonation process the days of the year that the plant is operational, the design flow, the specific energy (32) and the cost of electricity, values already presented in Table 16 will be used. The annual energy cost is estimated at €229.904,14 and has been calculated with a conversion factor that can be expressed as Equation 19.

$$Energy\ cost = design\ flow * specific\ energy * price * days\ of\ the\ year \quad (19)$$

The last cost in Table 17 is other costs which includes labour, maintenance, contact services, etc. To estimate this cost, the bibliography suggested using 20% of annual energy and oxygen cost (29). According with this data its value is €101.566,14 /year.

Table 17. Ozonation process operational cost

Ozonation Cost	Total cost [€/year]	Percentage of the total cost [%]
Energy	229.904,14	37,73
Oxygen	277.926,56	45,61
Other	101.566,14	16,67
Total	609.396,84	100,00

The last step of the treatment is chlorination. According to the bibliography this process consumes 2 mg NaClO/l (19). To calculate the annual cost, the amount of NaClO required and the cost of NaClO, as previously said, is €0,29 /kg will be used. The NaClO required is 11.088 kg/

year, and was calculated with a conversion factor that can be expressed as Equation 20. Multiplying both numbers, the annual chlorination chemical cost its estimated at €3.219,12 /year.

$$NaClO\ required = [NaClO] * design\ flow * \ days\ of\ the\ year \quad (20)$$

The tertiary treatment operational cost is the sum of all the previous calculations, collected in Table 18. The chemical cost is the sum of oxygen and hypochlorite costs. The energy cost is the sum of ozone production, water to be treated, extras and the pre-filtration costs. Other only takes into account the cost of the ozonation part, since the information found about maintenance and other costs from filtration and chlorination involves all the tertiary treatment that is already in the plant, and the cost of these parts cannot be separated from the rest. Thus, in Table 18, the other cost of these two treatments is missing.

Table 18. Summary of operational cost estimation

Cost	Total cost [€/year]	Percentage of the total cost [%]
Energy	333.128,14	46,54
Chemical	281.145,68	39,27
Others	101.566,14	14,19
Total	715.839,96	100,00

Analyzing the results in Table 18, the major cost is energy but in similar proportion to the chemicals. The energy cost represents 46% of the total cost. Ozonation process and the pre-filtration are included in this cost. If we compare the values we see that 69% of the energy cost is related to the ozonation process. This is due to this includes energy consumption from the ozone generator, ozone destruction, cooling water pumps, etc.

The chemical cost represents 39% of the total cost. Hypochlorite and oxygen are included in this cost. If we compare the values we see that 99% of the chemical cost is oxygen. This is due to the difference in quantity required and the cost between the reactives. To see it clearly, the amount of oxygen necessary in a day is 507,35 kg with a unit cost of €1,66 /kg while the amount of hypochlorite necessary in a day is 33,60 kg with a unit cost of €0,29 /kg.

As previously said the other costs only include the ozonation process cost, because the rest were not found in the bibliography. Thus, this value is not a representative one and it would be bigger, and the total cost would be higher too.

The cost per m^3 of water can be calculated with the total cost and the treated flow, in this case the design flow and this cost has a value of €0,13 /m^3. It is quite a reasonable cost considering all the treatments water goes through to be able to obtain high quality water.

An analysis of Table 17 would show that the cost of energy and oxygen represent a similar percentage of the ozonation process operational cost, 38% and 46% respectively. These results are consistent with everything found in the bibliography that the most significant costs are energy and oxygen and the percentage of each are proximate (29).

7. CONCLUSIONS

Considering the main objective of this project, which was to select, develop and perform a preliminary design of an ozonation process to integrate in a wastewater treatment plant as tertiary treatment, the following conclusions were obtained:

- The wastewater treatment plant selected for the design is in Vilaseca/Salou. It was a good candidate as it is near an area with a high level of water consumption, but with a meagre water supply, and the current treatments provide low quality water for reuse.
- The final tertiary treatment includes three phases: filtration, ozonation and chlorination, with the objective of obtaining high quality water, with lower micropollutant content.
- The equipment in the plant used for the filtration and chlorination processes will be reused for the current treatment.
- The micropollutant abatement achieved with the water flow and the ozone dose is good. 25% of them are eliminated and only 10% of the total micropollutants studied are reduce less than 20%.
- The operational cost estimation of the tertiary treatment is approximately €720.000 per year. The major cost is energy, due to the consumption of energy during the ozonation process.
- The cost per m^3 of water is €0,13, quite a reasonable cost considering all the treatment water goes through and high-quality water is obtained.
- The operational cost for the ozonation process is approximately €610.000 per year, the major costs being oxygen and energy in similar proportion. Between both costs oxygen is the highest, due to the price of oxygen and the amount of oxygen needed.

In summary, although the operational costs are high, being able to generate high quality water that can be reused in many different ways can contribute to mitigating the global problem of water scarcity.

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ACRONYMS

IPR	Indirect potable reuse
DPR	Direct potable reuse
AOP	Advanced oxidation processes
UV	Ultraviolet
BOE	Boletín Oficial del Estado
EDAR	Estación Depuradora de Aguas Residuales (Water treatment plant)
ACA	Agència Catalana de l'Aigua (Catalan water Agency)
MP	Micropollutant
EPA	United States Environmental Protection Agency
SS	Suspended solids
DOC	Dissolved organic carbon

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APPENDIX 1: VALUES AND REFERENCES OF KINETIC CONSTANTS

Table 19. Kinetic constant ($k_{OH\cdot}$) and reference

MP	$k_{OH\cdot} \cdot 10^9$ [L/mol s]	$k_{OH\cdot}$ reference
Acesulfame	4,50	Kaiser, 2013
1,4-dichlorobenzene	7,95	Real, 2007
Aciclovir	5,00	Prasse, 2015
Alachor	5,20	Sanches, 2010 + De Laat, 1996
Amoxicilin	5,43	Benitez, 2009 + Andreozzi, 2005
Atenolol	7,10	Yu, 2015
Atrazine	2,30	De Laat, 1994 + Chramosta, 1993
Benzophenone	9,40	Seo, 2019
Butachlor	7,40	Acero, 2003
Caffeine	6,40	Kesavan and Powers, 1985 + Shi, 1991
Desethylatrazine	1,20	De Laat, 1994
Diatrizoic acid	0,54	Real, 2009
Ibuprofen	7,04	Huber, 2003 + Packer, 2003 + Yuan, 2009
Linuron	4,30	De Laat, 1996
Naproxeno	8,61	Benitez, 2009 + Packer, 2003 + Pereira, 2007
Paracetamol	5,85	Andreozzi, 2003 + Yang, 2009 + Bisby, 1985 + Bisby and Tabassum, 1988
Phenol	10,3	Land and Ebert, 1967 + Field, 1982
Propachlor	4,45	De Laat, 1996 + Acero, 2003
Simazine	2,90	De Laat, 1994 + Chrimosta, 1993 + Haag and David Yao, 1992
Tetracycline	7,70	Dodd, 2006

Table 20. Kinetic constant (k_{O3}) and reference

MP	kO_3 [L/mol s]	k_{O3} reference
Acesulfame	88	Kaiser, 2013
1,4-dichlorobenzene	3,00	Hoigné & Bader, 1983
Aciclovir	16000	Prasse, 2012
Alachor	2,80	Beltran, 2000
Amoxicilin	6000000	Andreozzi, 2015
Atenolol	1700	Benner, 2008
Atrazine	24	Yao & Haag, 1991
Benzophenone	1,20	Seo, 2019
Butachlor	5,32	Acero, 2003
Caffeine	25000	Rivas, 2011
Desethylatrazine	0,18	Acero, 2000
Diatrizoic acid	0,05	Real, 2009
Ibuprofen	7,20	Vel Leitner & Roshani, 2010
Linuron	2,50	de Laat, 1996 + Benitez, 2007 + Chen, 2008
Naproxeno	200000	Huber, 2005
Paracetamol	1400	Andreozzi, 2003
Phenol	1300	Hoigné & Bader, 1983
Propachlor	0,94	De Laat, 1996
Simazine	3,15	Yao & Haag, 1991 + Xiong & Graham, 1992
Tetracycline	1900000	Dodd, 2008

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