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Removal of contaminants of emerging concern from wastewater by a combination of sunlight and chlorine.

Eliminació de contaminants de preocupació emergent de l'aigua residual mitjançant llum solar i clor.

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"Sometimes I'll start a sentence, and I don't even know where it's going. I just hope I find it along the way."

Michael Scott

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REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDGs)

The Sustainable Development Goals (SDGs) are a follow-up of goals adopted by the United Nations in 2015 as part of the 2030 agenda. These goals describe an ambitious plan by which in no less than 15 years poverty, hunger, climate effect, and social inequalities would be completely eradicated.

The 17 SDGs are interconnected with each other. Any action taken in one of these areas will directly or indirectly affect the rest. All countries must make an effort to provide all possible technology, resources, and knowledge to try to achieve these objectives and thus reach social, economic, and environmental sustainability.

To try to contribute to the proper development of these objectives, it has been decided to specify which are the main SDGs that will be addressed in this work. Table 1 divides the 17 SDGs into five subgroups, known as the 5Ps: people, in which equality is promoted; prosperity for sustainable development: planet, focusing mainly on caring for the environment and combating climate change and, finally, peace and partnership between countries to fulfill the 2030 agenda [1].

People	Prosperity	Planet	Peace	Partnership
1. No poverty	7. Affordable and clean energy	11. Sustainable cities and communities	16. Peace, justice, and strong institutions	17. Partnerships for the goals
2. Zero hunger	8. Decent work and economic growth	12. Responsible consumption and production		
3. Good health and well-being	9. Industry, innovation, and infrastructure	13. Climate Action		

People	Prosperity	Planet	Peace	Partnership
4. Quality education	10. Reduced inequalities	14. Life below water		
5. Gender equality	15. Life on land			
6. Clean water and sanitation				

Table 1. The five main areas of the SDGs [1].

Considering the 5Ps philosophy and the corresponding SDGs, together with the main topic of this work, that is, the elimination of micropollutants from wastewater and the potential reuse of the treated effluent, it is quite straightforward to see how it could directly contribute to the development of SDG number 6, clean water and sanitation.

In addition, as discussed above, our research may also contribute to other SDGs such as SDG number 14 (life below water), as less polluted effluents would be released to the environment, or not released at all, and SDG number 3 (good health and well-being), since eliminating emerging pollutants from wastewater contributes to improving life in aquatic ecosystems and avoids possible effects on human health generated by them, SDG number 9 (Industry, innovation, and infrastructure), as the study of new water cleaning technologies will generate further innovation and industrial growth, and SDG number 11 (sustainable cities and communities), since the last goal of applying technologies for micropollutants removal from wastewater is water reuse and thus the preservation of aquatic resources.

CONTENTS

1. SUMMARY

Wastewater treatment plant (WWTP) are not designed to eliminate contaminants of emerging concern (CECs). This group of compounds is made up of remains of medicines, hormones, pesticides and personal hygiene products, among others, and is characterized by being organic, of anthropogenic origin, poorly biodegradable and are found in trace levels in secondary effluents. However, they can suppose a danger to the environment and people, especially if they are released into the aquatic environment or if the water from the treatment plants is used for agricultural irrigation or other applications involving human interaction.

To achieve a significant attenuation of CECs in WWTPs and reduce the risks associated with this type of pollution, it is necessary to implement advanced water treatments such as Advanced Oxidation Processes (AOPs). This family of technologies is based on the generation of highly oxidizing species that can chemically destroy a wide variety of organic pollutants.

Some of the most promising AOPs are those based on the use of ultraviolet light (UV) and weak oxidants, although the operating costs of these treatments are high due to much of the electricity requirements for the operation of the lamps. For this reason, attempts have been made to replace ultraviolet radiation with natural light from the Sun.

The aim of the project is to evaluate the feasibility, both economic and technological, of a possible new AOP that combines chlorine and the use of sunlight as a source of radiation in the removal of CECs from wastewater. The basic aspects of the process, such as the kinetics associated with the degradation of pollutants, will be studied in a laboratory-scale experimental photochemical system. The aim is to combine pollutant degradation experiments with the analysis of residual oxidants and organic compounds using colorimetric techniques and liquid chromatography, respectively.

Keywords: Micropollutants, wastewater, Advanced Oxidation Processes, sunlight, chlorine

2. RESUM

Les tecnologies de tractament de les estacions depuradores d'aigües residuals (EDARs) no estan dissenyades per eliminar els anomenats contaminants de preocupació emergent (CPEs). Aquest grup de compostos està format per restes de fàrmacs, hormones, pesticides i productes d'higiene personal, entre d'altres, i es caracteritzen per ser orgànics, d'origen antropogènic, poc biodegradables i per trobar-se a nivells de traça als efluents secundaris. Tot i així, poden representar un perill pel medi ambient i les persones, especialment si s'alliberen al medi aquàtic o si l'aigua de sortida de les depuradores s'utilitza per al reg agrícola o altres possibles aplicacions.

Per tal d'aconseguir una atenuació significativa dels CPEs a les EDARs i reduir els riscos associats a aquest tipus de pol·lució, es fa necessària la implementació de tractaments avançats d'aigües com ara els anomenats processos avançats d'oxidació (PAOs) que es basen en la generació d'espècies molt oxidants que poden destruir químicament una àmplia varietat de contaminants orgànics.

Alguns dels PAOs més prometedors són els basats en la utilització de llum ultraviolada (UV) i oxidants febles, tot i que els costos d'operació d'aquests tractaments són elevats degut en bona part als requeriments d'electricitat per al funcionament de les làmpades. Per això, des de fa algun temps s'intenta substituir la radiació ultraviolada per llum natural procedent del Sol.

L'objectiu del projecte és avaluar la viabilitat, tant econòmica com química, d'un possible nou PAO que combini clor i l'ús de llum solar com a font de radiació per l'eliminació de CPEs de les aigües residuals. S'estudiaran els aspectes bàsics del procés, en un sistema fotoquímic experimental a escala de laboratori. Es pretén combinar experiments de degradació de contaminants amb anàlisis d'oxidants residuals i compostos orgànics mitjançant, respectivament, tècniques colorimètriques i cromatografia líquida.

Keywords: Microcontaminants, aigua residual, Processos d'Oxidació Avançada, llum solar, clor.

3. INTRODUCTION

3.1. WATER RESOURCES

During the last century, the world's population has been growing exponentially. According to the United Nations (UN) in 1950 there were a total of 2500 million people in the world while today, in 2022, there are already more than 7900 million and this number is expected to continue to increase [2]. Along with other factors such as economic development, this population growth has been responsible for the increase in water use worldwide.

Of all the water found on Earth, only 1% is fresh water in a liquid state [3]. This small amount is normally used by the population daily, giving it all kinds of uses and, therefore, making it a very valuable and scarce resource.

Water use has grown to more than double compared to the population increase in recent decades. This, together with an uneven distribution of freshwater resources across the planet (Figure 1) [4] has caused almost half of the global population to live in areas where there is water scarcity at least once a month per year. This fact may affect between 4,800 and 5,700 million people in 2050 and, therefore, water scarcity has been classified as a global risk [5]

Volume of liquid freshwater x 1000 km3

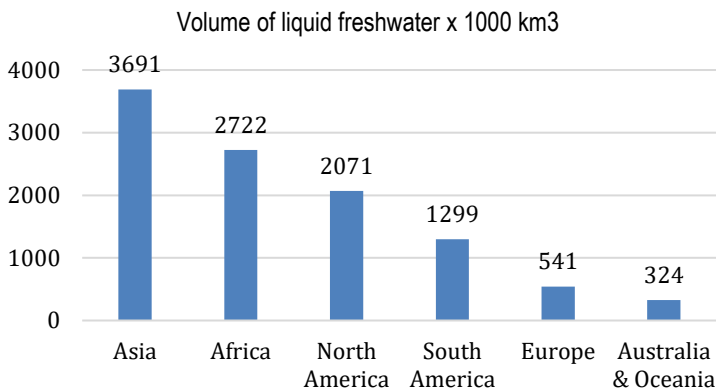| Continent	Value
Asia	3691
Africa	2722
North America	2071
South America	1299
Europe	541
Australia & Oceania	324

Figure 1. The estimated total amount of freshwater is x1000 km^3 per continent [4].

The lack of fresh water and its supply is currently one of the great problems of the 21st century, so it is necessary to find a way to solve it. One possible solution is to reuse water through wastewater treatment plants (WWTPs).

3.2. WASTEWATER TREATMENT

Wastewater (WW) is water that has been used in industrial, domestic, or municipal activities, in which changes in its composition, temperature, and/or quality are perceived compared to drinking water. Wastewater is no longer apt for human consumption and given its content in several classes of contaminants it has to be treated before returning to the aquatic environment. This is usually done in WWTPs.

WWTPs are usually divided into four stages of treatment (see Fig. 2):

· First, dirty water goes through a pre-treatment stage. This stage serves to separate the solid components that the water may have. It consists of various processes depending on the size of the solid to be separated: Roughing, where the bulkiest elements are removed; dilacerating, where the remaining solids of the water are crushed; sieving, which removes the smallest solid particles; or the sandblaster, which removes particles by gravity, are some of the most important processes of pre-treatment.

· Once the solids have been removed, the water moves to the primary treatment stage. This stage consists of evacuating all possible remaining solid particles by physicochemical processes. Coagulation-flocculation is one of the most typical processes to this end, which aims to eliminate turbidity, suspended organic matter, and increase the sedimentation rate. At the end of this stage, the sludge formed is removed by decantation, filtration, and/or sedimentation in the primary settler.

· The second treatment stage of a WWTP is based on aerobic biological treatments to degrade organic matter. It can also be combined with anoxic and anaerobic processes and serves to biologically eliminate the chemical oxygen demand (COD) and nutrients (Nitrogen and Phosphorus). Among available secondary or biological treatments, the Conventional Activated Sludge (CAS) process is the most common option [6]. After secondary treatment, the treated effluent can in general be released into the aquatic environment (e.g., a river or the sea).

· The last stage of a WWTP is the tertiary treatment, which consists of improving the effluent quality of wastewater coming out of WWTP's secondary treatments. They are based on additional physical, chemical, or biological processes and allow to eliminate a large percentage of the

remaining contaminants, making it possible to resend the effluent to the aquatic environment with an even lower impact or reuse the treated wastewater in certain non-potable applications. In Spain, for instance, 70% of the reused wastewater is employed in agricultural irrigation, 17% is destined for the maintenance of the environment, 7% is given to recreational use, and 5% is dedicated to urban and industrial use. In any case, tertiary treatments are only present in some WWTPs, especially in countries such as the United States, Germany, Switzerland, or Australia [7].

Figure 2 shows schematically how a WWTP could be divided through all its stages.
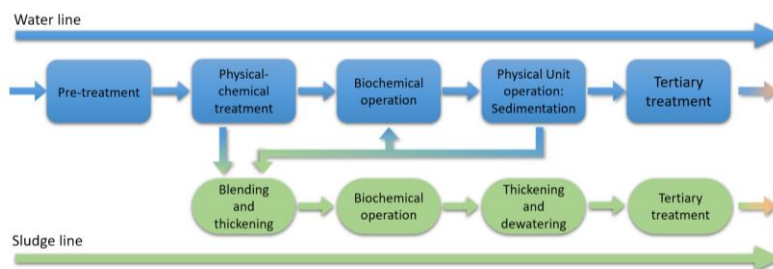

Figure 2. Operating diagram of WWTPs. Adapted from [8].

Even though not all WWTPs have tertiary treatments, they are especially important because can remove very minority compounds present in wastewater that even though are harmful to both humans and the environment. These pollutants are known as contaminants of emerging concern [8], [9].

3.3. CONTAMINANTS OF EMERGING CONCERN

Contaminants of emerging concern (CEC) are organic compounds of different anthropogenic origins. Normally they do not usually have a precise regulation and are present in waters in very low concentrations, between (pg–μg L^{-1}) [10]. Because of these low concentration ranges, they can also be called micropollutants. Those compounds are usually difficult to degrade in biological systems and typically are released into the environment from WWTPs' secondary effluents, thus potentially posing risks to both human health and the environment.

CECs can be classified as emerging contaminants, all those new compounds whose existence was unknown and because of which their possible effects on health and the environment must be studied; contaminants of emerging interest, which are those that have

existed for a long time, but have not been until relatively recently that their existence has been concerned; and old contaminants with emerging issues, which include all those substances that were already classified as contaminants some time ago, but for which due to recent studies new information has been found regarding their dangerousness [11]. Table 1 shows some of the most common CECs in wastewater classified by use.

Group of CEC	Subclasses	Source of origin of the CEC
Illicit drugs	Amphetamine Cocaine Heroin Methamphetamine MDMA Morphine	Human excretion after illegal consumption or disposal in clandestine drug laboratories.
Industrial chemicals	Flame retardants Food additives Plasticizers	Leaching of material in domestic wastewater
"Lifestyle" compounds	Caffeine Nicotine	Human excretion and domestic discharge
Pharmaceuticals	Analgesics Antibiotics Lipid regulator Non-steroidal Anti-inflammatory Drugs	Human excretion, hospital effluence, disposal of unused products, and agricultural use
Personal care products	Perfumes and fragrances Sun protection agents Insect repellents	Domestic wastewater
Pesticides	Fungicides Herbicides and Insecticides	Domestic wastewater and agricultural use

Group of CEC	Subclasses	Source of origin of the CEC
Steroid hormones	Oestrogens	Human excretion
Surfactants	Non-ionic surfactants	Domestic and industrial wastewater

Table 1. Main CECs in aquatics environments [12], [13]

When a possible new emerging contaminant is discovered, its possible human toxicity and ecotoxicity are studied to have enough knowledge about these aspects. From this information, governments can establish criteria for adequate protection of public health and the environment. In addition, those already regulated contaminants are subject to continuous evaluation based on new information to ensure that they are not harmful [11].

Because these compounds are difficult to remove by conventional treatment technologies typically implemented in WWTPs, specific technologies, such as Advanced Oxidation Processes, can be used.

3.4. ADVANCED OXIDATION PROCESSES

Advanced oxidation processes (AOPs) are tertiary treatment techniques capable of removing micropollutants and CECs that conventional WWTPs processes cannot eliminate. These processes are based on the in-situ generation of different highly reactive species, mainly hydroxyl radical (HO·) [14]. Due to its high reactivity and lack of selectivity hydroxyl radical can undergo degradation reactions with most organic molecules.

AOPs can be divided according to whether the hydroxyl radical is generated by photochemical processes, in which it is necessary to provide light during the process, or by non-photochemical processes [15]. In Figure 3 some of the most typical classes of AOPs are schematized according to this classification:
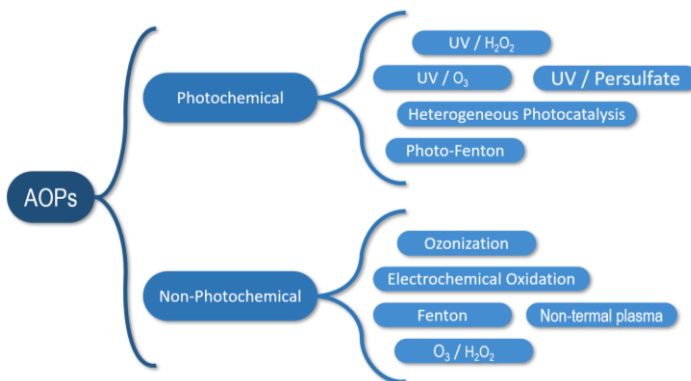
Figure 3. Classification of some AOPs

3.4.1. Photochemical AOPs

Although the efficacy of photochemical AOPs has been demonstrated, some of them involve a high expenditure of resources in terms of electric energy and oxidizing agents and catalysts, and some of them are very expensive or difficult to handle/separate from treated wastewater after treatment objectives are achieved (e.g., in heterogeneous photocatalytic AOPs). It is also quite expensive to rely on the use of ultraviolet lamps for the relatively long reaction times required by some AOPs to attain the degradation of CECs present in WW or to add huge amounts of reagents to maintain the reaction medium under particular pH conditions which sometimes are necessary for the process to work, as in the case of the homogeneous Photo-Fenton system [16]. For these reasons, alternative AOPs that use sunlight combined with relatively cheaper and less harmful reagents, such as free available chlorine (FAC) are nowadays being investigated intensively.

3.4.1.1. Combination of sunlight and chlorine

Free available chlorine (HOCl/OCl⁻) is one of the most used disinfectants in WWTPs since it is very effective against a wide range of bacteria and viruses, among other pathogens. However, it can only partially degrade some of the present organic compounds. The photolysis of FAC generates highly reactive species such as hydroxyl radicals and chlorine radicals (Cl·) following the following reactions [17]:

$$HOCl \leftrightarrow OCl^- + H^+ \tag{1}$$

$$HOCl \xrightarrow{h\nu} HO\cdot + Cl^- \tag{2}$$

$$OCl^- \xrightarrow{h\nu} O\cdot^- + Cl\cdot \tag{3}$$
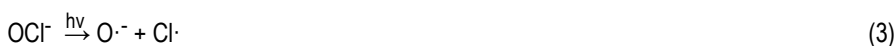
From the formation of these species, $Cl_2^{\cdot-}$ and $ClO\cdot$ are generated as secondary radicals and are expected to also participate in the degradation of CECs during the process. The reactions which are formed are the following ones [17]:

$$Cl\cdot + Cl^- \rightarrow Cl_2 \tag{4}$$

$$HOCl + HO\cdot \rightarrow H_2O + OCl\cdot \tag{5}$$

$$HOCl + Cl\cdot \rightarrow HCl + OCl\cdot \tag{6}$$

The FAC absorption spectrum overlaps in a good range with the sun's emission spectrum and, due to this, it is thought that the solar-Cl_2 combination can work to generate these reactive species [18]. Therefore, this new method could be used as a new AOP to remove CECs from wastewater. In this way, it could be possible to save large amounts of money on the electricity needed for the use of lamps (UV_{254}) that usually work to decompose the FAC into radicals.

4. OBJECTIVES

The reuse of WW is necessary to partially solve the looming problem of water scarcity. Many AOPs have been developed and used in this process, but many of them involve high energy and monetary costs. Therefore, new processes based on the generation of hydroxyl and chlorine radicals from sunlight are being studied, as they can be a more economical option and, therefore, would facilitate their incorporation as a tertiary treatment in WWTPs.

The main objective of this work is to develop a method capable of eliminating CECs based on the formation of reactive oxygen and chlorine species of by direct sunlight irradiation and to check if the process can be efficient enough to merit further investigation on its applicability to wastewater treatment.

To achieve this general objective, the following specific objectives were defined:

• To set up a working methodology in the laboratory for the study of the solar/Cl_2 process because, although the process has been studied in a theoretical way, there is not much experience at an experimental level.

• To study the possible application of this method for the degradation of a resistant, model contaminant, Atrazine, both in MiliQ water and in wastewater, to establish the working conditions and make a first approximation to the effectiveness of the process. In addition, some experiments were carried out to verify that all the free available chlorine came to react.

• Trying to understand the mechanisms responsible for the overall degradation process. To this end, different radical probe experiments were carried out to study the formation of hydroxyl radicals ($\cdot$ OH), ozone (O_3), and chlorine radicals ($Cl\cdot$).

• Conducting a preliminary economic estimate for the possible application of this oxidation process to evaluate the possibility of introducing the process on an industrial scale in a WWTP.

5. MATERIALS AND METHODS

5.1. CHEMICALS

Table 2 shows a summary of all the chemical reagents used during the work, indicating their CAS number, their purity, their formula, their purity, their use, and where they were acquired.

Name	CAS No.	Formula	Company	Purity (%)	Used in/for
Acetonitrile	75-05-8	CH_3CN	PanReac Chemical	99.9%	HPLC analysis
Atrazine	1912-24-9	$C_8H_{14}ClN_5$	Sigma-Aldrich	-	Test contaminant
Benzaldehyde	100-52-7	C7H6O	Sigma-Aldrich	≥99%	Detection of O_3 formation
Benzoic acid	65-85-0	$(C_6H_5)CO_2H$	Sigma-Aldrich	≥99.5%	Detection of ·Cl· formation
Chlorohydric Acid	7647-01-0	HCl	PanReac Chemical	37%	Measure WW alkalinity
Cinnamic acid	140-10-3	$C_9H_8O_2$	Merck	-	Detection of O_3 formation
DPD	6283-63-2	$C_{10}H_{16}N_2*H_2O_4S$	Sigma-Aldrich	≥98.0%	Chlorine indicator
EDTA-Na2	6381-92-6	$C_{10}H_{14}N_2O_8Na_2$ * 2 H_2O	Sigma-Aldrich	99.0-101.0%	Chlorine indicator

Name	CAS No.	Formula	Company	Purity (%)	Used in/for
Mercury dichloride	7487-94-7	$HgCl_2$	PanReac Chemical	-	Buffer in free chlorine determination
Methanol	67-56-1	CH_3OH	PanReac Chemical	99.9%	Solid-phase extraction
Nitrobenzene	98-95-3	$C_6H_5NO_2$	Sigma-Aldrich	99%	Detection of HO· formation
Orthophosphoric Acid	7664-38-2	H_3PO_4	PanReac Chemical	-	HPLC analysis
Potassium hydrogen phosphate	7758-11-4	KH_2PO_4	PanReac Chemical	-	Buffer in free chlorine determination
Sodium hydrogen phosphate	7558-79-4	Na_2HPO_4	PanReac Chemical	-	Buffer in free chlorine determination
Sodium hypochlorite	7681-52-9	$NaClO$	LabKem	10% w/w	Chlorine experiments
Sodium thiosulfate anhydrous	7772-98-7	$Na_2O_3S_2$	Fluka	≥98%	To stop reactions
Sulfuric Acid	7664-93-9	H_2SO_4	PanReac Chemical	98%	Buffer in free chlorine determination

Table 2. Chemicals reagents that were used and some chemical data.

5.2. WASTEWATER SAMPLES

The wastewater samples used in this work were collected in February 2022 at the WWTP in Vallvidrera which, being the smallest in Catalonia, is capable of treating 1,200 m^3 of WW/day. This WWTP applies a primary treatment followed by membrane bioreactor stage for simultaneous organic matter degradation and effluent clarification. Before doing the experiments, some water parameters were studied, Table 4.

Parameter	Measurement
Total Organic Carbon (TOC)	11 mg/L
Cl^-	181 mg/L
NO_2^-	Not detected
NO_3^-	51.6 mg/L
Br^-	Not detected
pH	7.42
Alkalinity	134.772 mg/L of Ca_2CO_3
Conductivity	960 µS/cm
Turbidity	0.031
UV_{254}	0.208 cm^{-1}

Table 3. Characteristics of the used WW sample

The turbidity value of the water was taken directly from a sensor implemented at the WWTP. Both for the measurement of TOC and for that of the different ions, two vials were prepared with 35 ml of the water sample, and they were taken to a laboratory at the Scientific-Technological Services of the University of Barcelona for analysis. Alkalinity, pH, and conductivity were measured in the laboratory using a SensION™ + MM374 pH multimeter. Water absorbance was measured at λ=254 nm using the Spectrophotometer UV-Vis Hach Lange DR6000.

5.3. CHLORINE-BASED OXIDATION EXPERIMENTS

To perform the chlorine-based oxidation experiments studied in this thesis, a method had to be developed. For these experiments, an ATLAS SUNTEST CPS+ was used along with a Xenon lamp (1500 W) equipped with a UV-C filter (cutting off radiation wavelengths < 290 nm) to simulate sunlight.

The assembly was done as outlined in Figure 4. The ATLAS SUNTEST CPS+ (1) was placed on top of wooden studs (2). Just below the instrument was mounted a platform consisting of four metal legs (3) that held and raised a magnetic stirrer (4) on which there was a chiller plate (5) that served to cool and prevent evaporation of the sample. To achieve direct and more easily quantifiable irradiation (i.e., quasi-collimated beam), it was decided to add a tube inside the instrument through which the beam of direct light would come out to the sample (6).
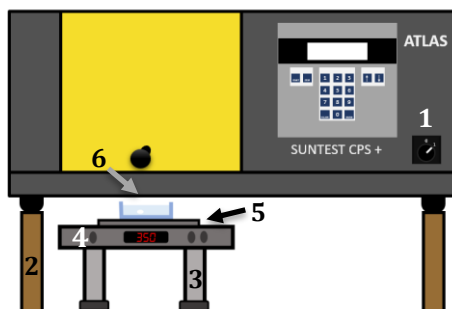

Figure 4. Scheme of the setup made for the experiments.

The instrument was configured for all experiments carried out by setting the irradiation at 765 W/m^2 and the black standard temperature at 35ºC (i.e., the minimum possible).

To carry out the experiments, the following procedure was followed:

First, a 100 mL solution of the matrix used in each case is prepared, either MiliQ or WW water, previously filtered with a 0.45 µm cellulose acetate membrane filter to avoid the presence of any solid not belonging to the effluent sample. Known concentrations of the contaminants studied in each experiment are added to this solution. Then, the solution is transferred to a reactor (6) and a magnetic bar is added to it.

In addition, for each experiment, a fresh solution of HClO is prepared. Finally, a known concentration of HClO is added to the water solution, the reactor is put under the SUNTEST CPS+, in a magnetic agitator at 350 rpm and the experiment is started.

Each experiment lasted six hours. To keep the solution temperature at 22±2ºC and avoid evaporation of the sample as much as possible, a cooling plate was placed at 15ºC under the reactor. In order to correctly study the kinetics of the reaction, it was decided to collect samples for their further analysis in High-Performance Liquid Chromatography (HPLC) 0, 5, 15, 30, 60, 90, 120, 180, 240, 300, and 360 minutes, respectively.

After collecting a sample, a stoichiometric amount of a 10 g/L solution of sodium thiosulfate was added to stop the reaction by Cl_2 quenching.

5.3.1. Determination of micropollutants degradation

The degradation of micropollutants in the solution was quantified by HPLC Infinity Series, Agilent Technologies using a Teknokroma Mediterranea Sea 18 (5 µL 25x0.46) HPLC Column. The flow rate was fixed at 1 mL min⁻¹ and the injection volume was set to 100 µL. These analyses have been carried out according to the absorbance of the different compounds studied. Table 4 shows the different working conditions:

Compound	Wavelength (nm)	Acetonitrile (%)	H2O MiliQ pH=3 (%)
Atrazine	220	70	30
Nitrobenzene	264.4	40	60
Benzoic Acid	230.4	60	40
Benzaldehyde	248.4	50	50

Table 4. Working conditions of the HPLC analyses

5.3.2. Determination of residual chlorine

In order to verify that all the added chlorine reacts with the matrix, its consumption was monitored by a colorimetric method using DPD as an indicator and measuring its concentration with a spectrophotometric procedure, as described in the literature [19].

This method consists of reacting the FAC of the WW sample with a DPD solution, giving a reddish-violet color. Apart from that, is needed to add a phosphate buffer to maintain the pH between 6.2 and 6.5, since if the pH were higher, the dissolved oxygen would give color, interfering with the determination.

The procedure followed consisted of adding 1 mL of WW sample to a solution of 9 mL of MiliQ water, 0.5 mL of the DPD solution, and 0.5 mL of the phosphate buffer. Finally, the absorbance of the sample color was measured at 515 nm using a 1 cm quartz cuvette in a Hach Lange DR600 UV-Vis spectrophotometer (Figure 5).

Figure 5. Spectrophotometer UV-Vis Hach Lange DR6000.

6. RESULTS AND DISCUSSION

6.1. SETTING WORKING CONDITIONS

6.1.1. Experimental conditions

Not much information is found in the literature on the methodology to be followed to study the Solar-Cl_2 process. Therefore, the first thing that had to be done was to carry out various experiments to set the working parameters.

The first thing that was fixed was the time that the experiments would last. It was decided that they would last six hours to see the maximum possible degradation of the micropollutants and to be able to carry out a broader study of the kinetics of the reactions.

Next, it had to be decided at what temperature the cooling plate would be set to avoid evaporation of the sample. For this, an experiment was carried out with the SUNTEST CPS+ as indicated in section 5.3, using 100 mL of MiliQ water as a sample and the temperature of the reactor was measured every 15 minutes. Table 5 shows the temperatures obtained.

Time (minutes)	0	15	30	45	60	75	90	105
Temperature (ºC)	21.4	22.8	24.6	25.9	26.5	26.7	26.8	26.7

Table 5. Preliminary control of the working temperature.

As can be seen, the sample rose in temperature due to the incident light beam. Its volume was checked at the end of the experiment, and it was obtained that about 10 mL had evaporated. To avoid this evaporation, it was found that setting the temperature of the refrigerant plate to 15 ºC would allow keeping the solution temperature at 22±2 ºC.

6.1.2. Determination of the chlorine concentration used

First, it was necessary to quantify what concentration of chlorine (Cl_2) had the purchased bottle of sodium hypochlorite. Three solutions were prepared with 9.9 mL of MiliQ water and 0.1 mL of commercial NaClO. From them, other elucidations were obtained by taking 1 mL of these solutions and 9 mL of MiliQ water. Finally, the absorbance of these solutions was measured at 292 nm. Considering that at this wavelength the hypochlorite anion has a molar absorption

coefficient (ε_{OCl^-}) of 365 $M^{-1}cm^{-1}$ [20] and that the quartz cuvette used was l=1cm, the Lambert-Beer law was applied to calculate the concentration of this reagent in the commercial bottle (Calculations in Appendix 1).

To know which concentration of chlorine would be necessary to be able to correctly degrade the micro contaminants, some experiments were carried out using 100 mL of MiliQ water as a matrix and 0.5 mL of a previously prepared solution of Atrazine 20 mg /L. In one of them, a concentration of 10 mg· L^{-1} of Cl_2 while in the other 20 mg· L^{-1} of Cl_2.´

Atrazine was chosen for this study because it is a compound relatively resistant to oxidation treatments. This is because it has kinetic constants with the radical species present of $3.9 \cdot 10^9$ and $6.9 \cdot 10^9$ M^{-1} s^{-1} for HO· and Cl· respectively [21], while other compounds have kinetic constants with these radicals that can be up to an order of magnitude higher.
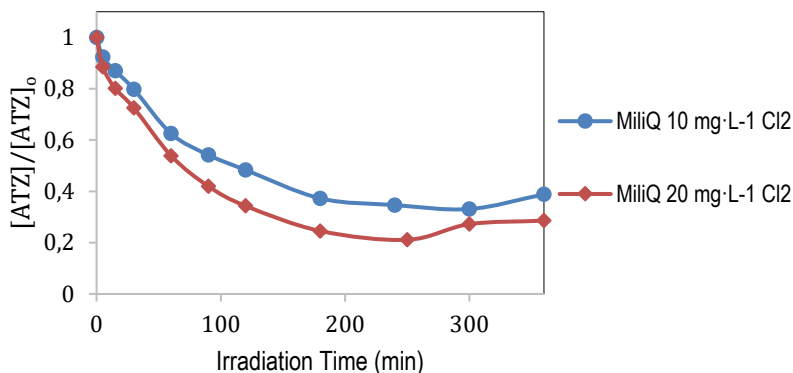

Figure 6. Comparison between degradation of Atrazine using solar light
and various concentrations of chlorine in MiliQ samples.

As can be seen in the graph in Figure 6, using a higher concentration of chlorine also leads to a higher percentage of degradation, to be more specific, with 20 ppm a 78.9% maximum degradation is achieved while with 10 ppm 66.9% is achieved.

Given these values, it was decided to do similar tests, but using in this case wastewater as the water matrix. As has already been seen in the analysis of wastewater, different types of compounds are present in high concentrations in the water, such as carbonates, nitrates, or organic matter. These compounds can generate a situation of competition between them for reactive species, thus reducing the efficiency of the process. Therefore, when using a more complex matrix, a higher concentration of reagents is required, so a third experiment was carried out using a concentration of Cl_2 of 50 mg· L^{-1}.
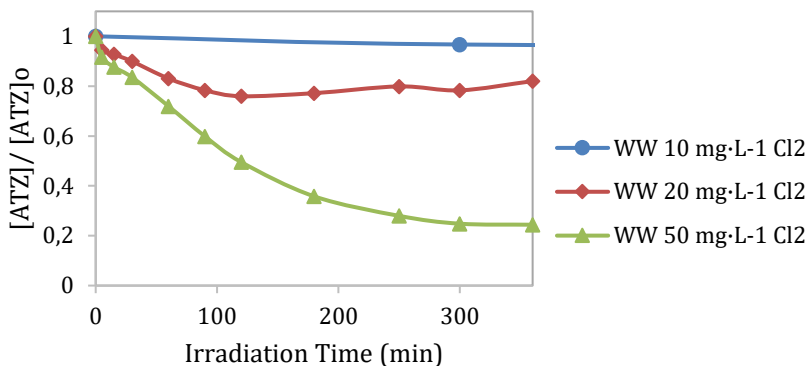
Figure 7. Comparison between degradation of Atrazine using solar light
and various concentrations of chlorine in wastewater samples.

As can be seen in Figure 7, by using a higher concentration of chlorine, a greater degradation is obtained. If the graph is observed, it will be possible to see that for 10 mg L^{-1} and 20 mg L^{-1} the percentage of degradation of atrazine has decreased considerably compared to that obtained using MiliQ water, this being 5.76% and 24.04% respectively. On the other hand, when using 50 mg·L^{-1} of Cl$_2$, a 75.59% degradation is obtained, for which it was decided to carry out the other experiments using this same concentration of Cl$_2$.

6.2. STUDY OF THE REACTIVE SPECIES

As discussed in section 3.4.1.1, chlorine radicals (Cl·) is expected not be the only reactive species that may be participating in the degradation reactions of micro contaminants. The formation of hydroxyl radicals (HO·), ozone (O$_3$), or even the effect of light could affect the kinetics of the reaction, so its contribution had to be studied.

6.2.1. Contribution of chlorine and incident light

First, the contribution of NaClO added to the samples without the participation of light was evaluated, doing experiments with 100 mL of WW, 0.5 mL of Atrazine 20 mg·L^{-1}, and 50 mg·L^{-1} of Cl$_2$ but without turning on the SUNTEST CPS+.

On the other hand, it was also wanted to evaluate the direct contribution of the irradiated light to the sample, so other experiments were carried out where the conditions were the same as those described above, except that no chlorine was added.

As can be seen in Figure 8, neither chlorine nor incident light alone makes a significant contribution to degrading atrazine. Even so, it will be considered later for the study of the kinetics of the reactions.
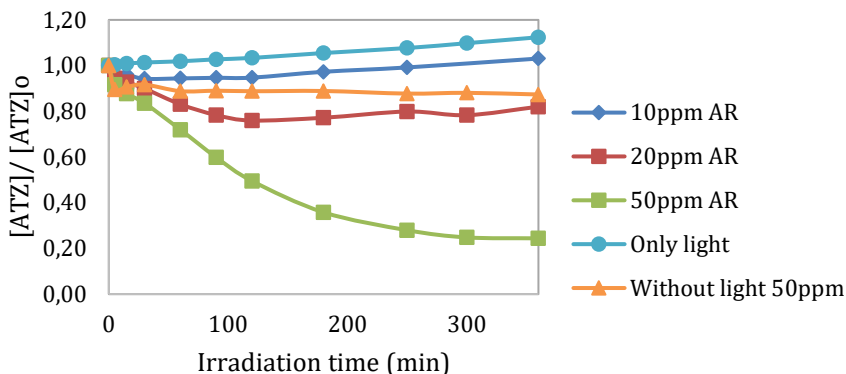

Figure 8. Degradation of Atrazine in WW using 10, 20, 50 ppm of Cl_2, 50ppm
of Cl_2 without light and only light

Assuming that the degradation reactions used in this section follow first-order kinetics (Eq. 1), their observed kinetic constants (k_{obs}) can be found from the graphical representation of the natural logarithm of the atrazine concentration concerning the time between initial atrazine concentration versus time in seconds. Once represented, the equation of the line is drawn and the slope of this is the k_{obs}.

$$-\ln\left(\frac{[ATZ]_t}{[ATZ]_o}\right) = k_{obs} \cdot t \qquad\qquad \text{(Eq. 1)}$$

The observed kinetic constants are $-5 \cdot 10^{-6}$ $M^{-1}s^{-1}$ in the case of light-only white; and $1 \cdot 10^{-6}$ $M^{-1}s^{-1}$ for the non-light experiment. The negative value obtained is due to a small increase in concentration. This does not make sense so it may be due to an analytical issue.. These contributions are very small so they will not have great weight when calculating the kinetics of the reaction. It should be noted that the constant of the case without chlorine is negative, which does not make sense because it would imply that atrazine is being generated instead of degrading.

6.2.2. Contribution of hydroxyl radical

As seen in section 3.4.1.1 hydroxyl radicals are generated as by-products of the reaction of chlorine with light so, being such a reactive species, it can be assumed that it will have a high contribution to the kinetics of the reaction. Therefore, it is necessary to study the amount of HO· that is generated during the process and calculate its kinetic constant for this process.

To study the contribution of HO·, it was chosen to do so through a nitrobenzene (NB) degradation experiment instead of atrazine, since NB does not react with chlorinated radicals, but rather with hydroxyl radicals [22]. Reaction 7 shows how nitrobenzene reacts with HO· to give nitro hydroxy cyclohexadienyl radical.
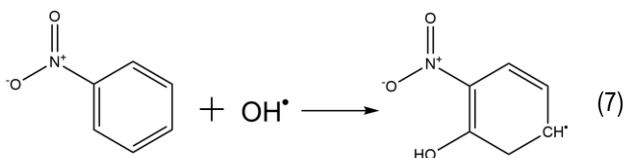
(7)

Three replicates of an experiment consisting of a sample of 100 mL of WW, 50 ppm of Cl_2, and 0.2 ppm of a previously prepared solution of NB were made. The samples were placed under solar-artificial irradiation for 6 hours and the following results were obtained.
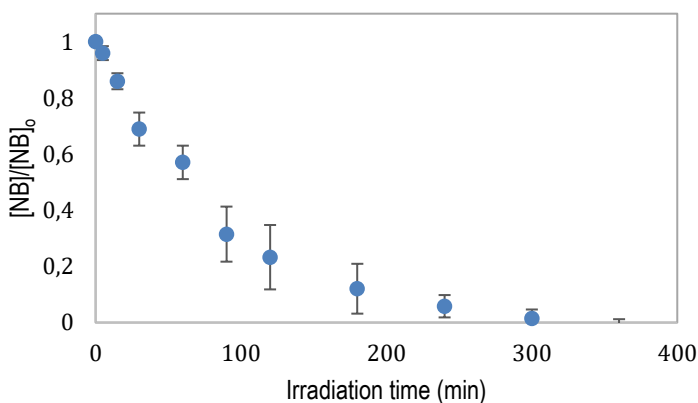

Figure 9. Degradation of Nitrobenzene with 50ppm of Cl_2 and light

Figure 9 shows how there is a total degradation of nitrobenzene. As nitrobenzene absorbs in the range in which it is being worked, it had to be checked if all this degradation was due to

hydroxyl radicals or if the incident light also had to do with it. This was done by repeating the experiment but this time without adding the 50 ppm of Cl_2 to prevent the formation of $\cdot$ OH radicals.
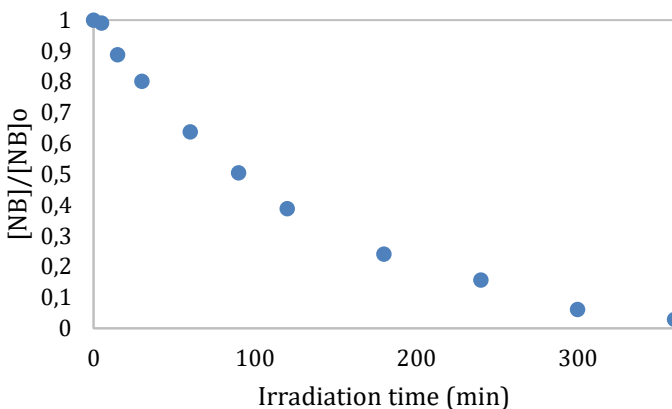

Figure 10. Degradation of Nitrobenzene with only light

As can be seen, Figure 10 shows that Nitrobenzene is a compound that can also be degraded only with light, achieving up to 97% in the six hours that the experiment lasted. These results, together with those in sections 6.2.3 and 6.2.4, will be considered for further study of the kinetics of the reaction (section 6.3), particularly the contribution of each species in the ATZ degradation process.

6.2.3. Contribution of chlorine radical

To study the contribution of chlorine radicals in the advancement of reaction, it was chosen to use benzoic acid (BA) to do the degradation experiments, because the conjugate base of benzoic acid, benzoate anion, has a high affinity with hydroxyl radicals and chlorine radicals [22].

Having studied in the previous section the participation of the $\cdot$ OH in the reaction and, knowing that BA reacts with both Cl$\cdot$ and $\cdot$ OH, the kinetic constants of both species can be isolated.

Three replicas of an experiment consisting of a sample of 100 mL of WW, 50 ppm of Cl_2, and 0.2 ppm of a previously prepared solution of BA were made. The samples were placed under solar-artificial irradiation for 6 hours and the following results were obtained.
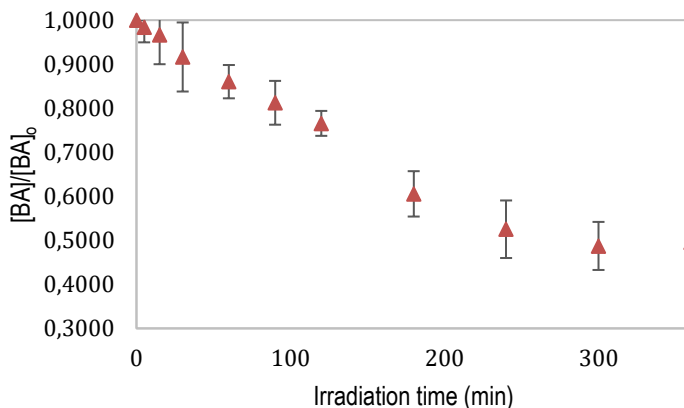
Figure 11. Degradation of Benzoic acid with 50pp, of Cl_2 and light

Figure 11 shows how, despite having a great affinity for both radical species and having kinetic constants greater than those of NB, BA has not completely degraded, reaffirming, a priori, the idea that, in the degradation of NB, light plays an important role.

6.2.4. Determination of ozone formation

Although ozone ($O3$) is not the main reactive species of this method, it has been reported that it can be formed as a secondary product of the photochemical decomposition of hypochlorite [17]. Being so, it was decided to study if its formation throughout the reaction would have a significant weight in order to contribute to the total degradation of micropollutants during the application of the solar/Cl_2 process.

Ozone formation was determined indirectly using cinnamic acid. Cinnamic acid reacts with O3 resulting in benzaldehyde (8).

$$(8)$$
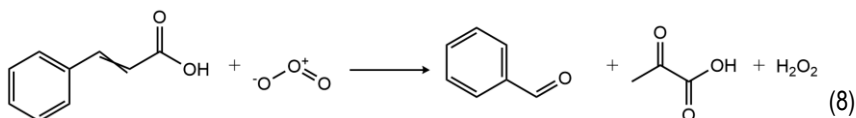
So, by performing a pattern of the signal obtained in the HPLC instrument of various concentrations of benzaldehyde, it was possible to measure the amount of ozone that was formed. Three replicates of an experiment consisting of a sample of 100 mL of WW, 50 ppm of Cl_2, and 0.2 ppm of a previously prepared solution of BA were made. The samples were placed under solar-artificial irradiation for 6 hours and the following results were obtained.
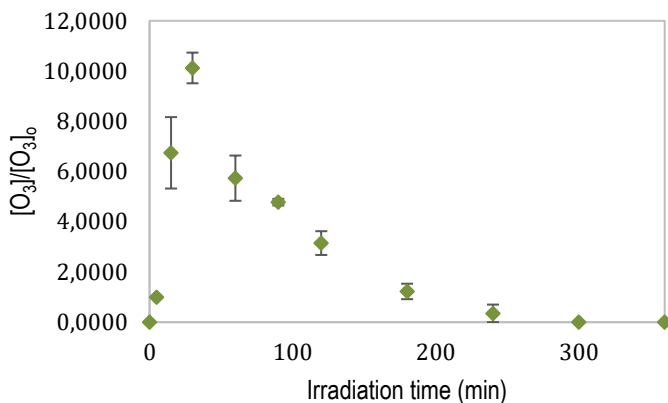
Figure 12. Formation of Ozone from cinnamic acid, chlorine, and light

It can be seen in Figure 12 how, although if some ozone is generated, it seems that from a certain point during the experiment, this species is consumed faster than it is generated so its involvement in the reaction cannot be correctly evaluated following this method.

This method was used because it was the one that some authors use in the literature to determine the amount of O3 formed [17]. Despite this, it was possible to conclude that some drawbacks are present in the method. The most concerning one is the fact that since extremely reactive species were generated during the process, such as hydroxyl radical, these could attack the added cinnamic acid and the benzaldehyde formed, thus interfering with the analysys of formed ozone. Therefore, it can be concluded that there are doubts regarding the reliability of the method to quantify ozone. Alternatives should be sought for the determination of this species during the process.

Fortunately, not being able to correctly assess the formation of ozone will not influence when calculating the kinetics of the reaction because Atrazine is a molecule that resists the attack of ozone [23].

6.2.5. Determination of residual chlorine

Chlorinated compounds are highly toxic, so it must be ensured that these species are not left at the end of the process [24]. For this, three experiments were carried out following the method explained in section 5.3.2. for colorimetric determination of FACs and the following results were obtained.
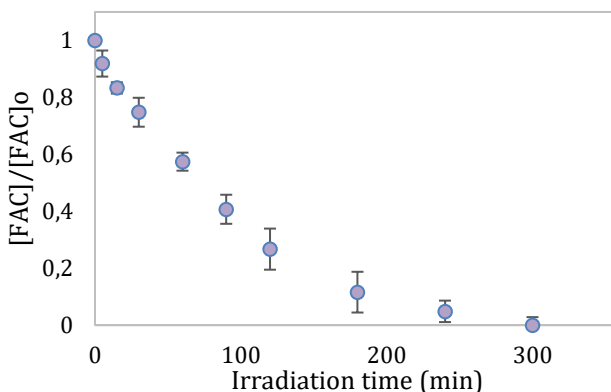
Figure 13. The disappearance of the FAC as a function of time

Looking at Figure 13, all the chlorine added ends up disappearing. On the one hand, this is positive because there is no free chlorine left in the medium, decreasing the toxicity of the samples.

In any case, it should be studied in the future if a large amount of disinfection by-products (DBPs) is generated during the degradation of micro contaminants and evaluate their toxicity. In this sense, the solar/Cl_2 process has not been yet well studied, but it can be seen in the literature that in similar processes such as UV/Cl_2, the generated DBPs do not imply high toxicity. Considering that the process with sunlight involves radiation of different properties, a different generation of DBPs could be expected than with UV. Thus, it is the toxicity of the products and the viability of the solar/Cl_2 process from an ecotoxicological point of view should be studied [25].

6.3. KINETIC STUDY OF THE REACTION

The calculation followed to determine which reactive species are the ones that have the greatest weight when it comes to degrading micropollutants is detailed below. It should be clarified that for this work there was only time to carry out experiments with Atrazine, thus only the kinetics of the solar/Cl_2 process with a matrix of residual water and Atrazine was be studied.

To carry out the kinetic study of the process, the degradation rate constants observed during the different experiments will be considered.

The main kinetic equation (Eq. 2) depends on the rate constant observed during the Atrazine degradation experiments with wastewater in $M^{-1}s^{-1}$ (k_{obsATZ}), on the concentration of Atrazine at a specific time, in mol·L^{-1}, ($[ATZ]_t$).

$$-\frac{d[ATZ]}{dt} = k_{obs} \cdot [ATZ]_t \qquad \text{(Eq. 2)}$$

By integrating the Eq. 2, Eq 3 is obtained, where $[ATZ]_o$ represents the initial concentration of Atrazine in mol · L^{-1} and t represent the reaction time in seconds:

$$-\ln\left(\frac{[ATZ]_t}{[ATZ]_o}\right) = k_{obs} \cdot t \qquad \text{(Eq. 3)}$$

Experimentally it was found that k_{obsATZ} had a value of $9.00 \cdot 10^{-5}$ $M^{-1}s^{-1}$. This observed kinetic constant will depend on various factors since, apart from the involvement of various reactive species, such as HO· or Cl·, there will also be a contribution from free Cl_2 and the effect of light. Besides, when working with a complex matrix in which not all the possible species that can contribute to the kinetics of the reaction are being monitored, a kinetic constant called k_{others} has had to be dedicated to all the possible contributions that have not been considered when carrying out this work.

In Eq. 4 the breakdown of the k_{obsATZ} made for these calculations is shown.

$$k_{obsATZ} \cdot t = k_{HO\cdot} \int_0^t [HO\cdot]\, dt + k_{Cl\cdot} \int_0^t [Cl\cdot]\, dt + k_{obsCl_2} \cdot t + k_{obs\ sunlight} \cdot t + k_{others} \cdot t$$
$$\text{(Eq. 4)}$$

Where $k_{HO\cdot}$ is the kinetic constant of atrazine with the hydroxyl radical and has a value of $3 \cdot 10^9$ M^{-1} s^{-1} [21]; $k_{Cl\cdot}$ is the kinetic constant of atrazine with the Cl radical that has a value of $6.87 \cdot 10^9$ $M^{-1}s^{-1}$ [21]; K_{obsCl2} is the kinetic constant obtained in the degradation experiment without the presence of light, and $k_{obs\ sunlight}$ is the constant observed in the degradation experiment without Cl_2, having values of $1.03 \cdot 10^{-6}$ s^{-1} and $-5.19 \cdot 10^{-6}$ s^{-1}, respectively.

To determine which species are the ones that most affect the reaction, the k_{others} must first be calculated. To do this, it will be necessary to isolate the terms of the definite integrals from 0 to t of the concentrations of HO· and Cl· ($\int_0^t [HO\cdot]\, dt$ y $\int_0^t [Cl\cdot]\, dt$) from experiments with nitrobenzene and benzoic acid. These experiments have been previously presented in sections 6.2.2 and 6.2.3.

Since nitrobenzene does not react with chlorine radicals and is only degraded by HO· and light, the definite integral of the HO· concentration can be calculated by isolating it from Eq. 5.

$$-\ln\left(\frac{[NB]_t}{[NB]_o}\right) = k_{HO\cdot,NB} \int_0^t [HO \cdot]\, dt + k_{light,NB} \cdot t \qquad \text{(Eq. 5)}$$

The kinetic constant of nitrobenzene with the hydroxyl radical, $k_{HO\cdot,NB}$, was taken from the literature and has a value of $3.9 \cdot 10^9$ M^{-1} s^{-1} [22]. Instead, the $k_{light,NB}$ was determined experimentally and a value of $1.56 \cdot 10^{-4}$ s^{-1} was obtained.

Once the integral has been calculated, it can be substituted in Eq.6, where the definite integral of the Cl· concentration will be isolated for later use (i.e., in Eq. 4).

$$-\ln\left(\frac{[BA]_t}{[BA]_o}\right) = k_{HO\cdot,BA} \int_0^t [HO \cdot]\, dt + k_{Cl\cdot,BA} \int_0^t [Cl \cdot]\, dt \qquad \text{(Eq. 6)}$$

Both $k_{HO\cdot,BA}$ and $k_{Cl\cdot,BA}$ have been collected from the literature [22] and have values of $5.9 \cdot 10^9$ $M^{-1} \cdot s^{-1}$ and $1.8 \cdot 10^{10}$ $M^{-1} \cdot s^{-1}$, respectively and represent the kinetic constants of the reactions of benzaldehyde with radical hydroxyl and with the radical chlorine.

Thanks to these calculations and following Eq. 4 the following values were obtained for the kinetic constants:

Kinetic constant	k_{obsATZ}	$k_{HO\cdot}$ [21]	$k_{Cl\cdot}$ [21]	k_{obsCl2}	$k_{obs\ sunlight}$	k_{others}
Value	$9.23 \cdot 10^{-5}$ s^{-1}	$3 \cdot 10^9$ $M^{-1} \cdot s^{-1}$	$6.9 \cdot 10^9$ $M^{-1} \cdot s^{-1}$	$1.03 \cdot 10^{-6}$ s^{-1}	$-5.19 \cdot 10^{-6}$ s^{-1}	$6.31 \cdot 10^{-5}$ $M^{-1} \cdot s^{-1}$

Table 6. Values of the kinetic constants involved in the Atrazine

degradation reaction using the Solar/Cl_2 method.

Once all the constants have been obtained, the percentage of contribution that each of the species has to the overall observed degradation of ATZ can be calculated. As an example, Eq. 7 shows the calculation for hydroxyl radical contribution.

$$Contribution\ HO\cdot = \frac{k_{HO\cdot}\cdot[HO\cdot]}{k_{obsATZ}}\cdot 100\ \ \text{(Eq. 7)}$$

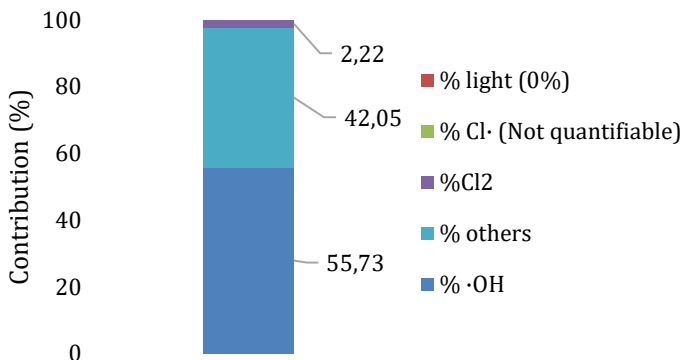The results of the calculation of the contribution of each species are shown in Figure 14.

Figure 14. Contribution of each reactive species to the degradation
of Atrazine with the Solar/Cl2 process

As can be seen in Figure 14, the species that contributes the most to the degradation of Atrazine is the hydroxyl radical, with 55.73%; followed by the rest of the non-determined species, with 42.05% and finally it has been seen that free Cl_2 is also capable of slightly degrading the sample, with 2.22%. This last contribution is probably much lower in a real experiment, since it was derived from a control experiment where the Cl_2 had no light present and therefore there was a lot of free chlorine. Under real conditions, this chlorine would react rapidly with light, drastically reducing its contribution.

In the case of the other undetermined reagents, it has been seen in the literature that the reactive species that are acting could be both $ClO\cdot$ and $CO_3\cdot^-$ [21]. In subsequent works, the impact of these possible reactive species would have to be evaluated.

It should be clarified that when calculating the contribution of $Cl\cdot$ a negative percentage was obtained. Therefore, it has been concluded that the contribution of the $Cl\cdot$ radical must be such a small percentage that it is not quantifiable by the method used. The fact that the result is negative and not just a small positive number may be due to the various uncertainties that may arise, such

as the fact that the conditions of the experiments to isolate the terms of the definite integrals of HO· and Cl· and of the degradation of NB were not the same or, even, that the kinetic constants collected from the literature presented small deviations with respect to true values that could lead to errors. These uncertainties could have larger weight in the described calculation procedure than the Cl· contribution itself, and therefore this contribution percentage cannot be quantitatively estimated reliably.

It is also important to note that when making the calculation, the term of the kinetic constant obtained for the case of the light-only control experiment has been ignored. This decision was made when seeing that experimentally the constant obtained was slightly negative, which does not make physical sense and probably has to do with analytical issues, so it could be deduced that light *per se* does not influence the degradation of Atrazine.

Even though there is a part of the study of contributions that is not conclusive, that is the contribution of Cl·, the mechanism must continue to be investigated in order to fully understand the chemistry behind the process. This could be done by replacing some of the experimental methods or assumptions made, or perhaps by introducing additional experiments aiming at detecting the presence of other reactive chlorine species potentially contributing to the overall degradation of micropollutants. In any case, and regardless of the lack of current understanding, it can be concluded that the process can become interesting to apply it to effluent treatments provided that degradation of resistant pollutants such as ATZ is attained.

6.4. ECONOMIC ESTIMATION OF THE PROCESS

To finish the study of the possible application of this treatment to wastewater treatment, the cost of the process per cubic meter of treated water has been calculated. For this, an approximate estimate of the economic cost of the solar/Cl_2 process has been made and it has been compared with the costs of the UV/H_2O_2 and O_3 processes, since they are the most used or technologically ready AOPs nowadays [26]. This estimate includes the cost of reagents per cubic meter of treated wastewater and the cost of the energy needed to carry out the treatment of the same volume of water.

For the UV/H_2O_2 process, both the energy cost of the process and the amount of reagents per cubic meter treated must be calculated. Following Eq. 7 the amount of energy required, EN, can be calculated from the applied UV doses, in J/m^2; of the optical path L and of the efficacy of the lamp η_{lamp}.

$$EN = \frac{UV_{dose}}{L*\eta_{lamp}}$$ (Eq. 7)

The efficiency of industrial lamps is 30% and the UV doses used in the calculation have been 1,000 J/m^2 and 30,000 J/m^2, as it is the typical range of doses used in industrial processes. On the other hand, three different optical paths (i.e. 1, 5, and 10 cm), have been used. Finally, the different results of EN were converted from J/m^3 to kWh/m^3.

Once the EN has been calculated, it is necessary to calculate the cost of the reagents to obtain the total cost of the process operation. The concentrations of H_2O_2 used in industrial processes range from 5 mg/L to 10 mg/L of H_2O_2 [27]. Knowing that the average consumption is of 10 kWh/H_2O_2 and taking the average price of electricity in Spain at 06-10-2022 of 0.27194 €/kWh [28], the total cost of the process can be estimated. The following costs has been obtained:

	Min L=1 cm	Min L=5 cm	Min L=10 cm	Max L=1 cm	Max L=5 cm	Max L=10 cm
Total cost using 5mg/L (€/m³)	0,0387	0,0186	0,0161	0,7478	0,1631	0,0870
Total cost using 10mg/L (€/m³)	0,0523	0,0322	0,0297	0,7614	0,1767	0,1006

Table 7. Total operation cost for the UV/H_2O_2 process.

Min means minimum UV_{dose} (1,000 J/m^2) and Max means maximum UV_{dose} (30,000 J/m^2).

As can be seen in Table 7, the UV/H_2O_2 process has an approximate cost ranging from 0.0161 to 0.7614 €/m³ of treated wastewater.

In the case of ozone AOP, it has been found that 15 kWh/kg O_3 are required. Average intakes for this process are usually between 0.25 and 1 mg O_3/mg TOC. Knowing that the water treated in this work has a TOC of 11 mg/L, a consumption of between 2.75 and 11 mg O_3/L of treated WW can be estimated. From all these data it ends up obtaining that the total cost of this process will go from 0.0112 €/m^3 to 0.0449 [27].

Finally, the economic estimation of the Solar/Cl_2 process was calculated. Sodium hypochlorite has a cost of 0.6-0.9 $/gallon, which in exchange is 0.124-0.186 €/L [29]. Knowing that in this work concentrations of 50 mg/L have been used for the treatment of WW, it has been obtained that the cost estimate for this process ranges from 0.0053 to 0.0080 €/m^3 of treated water.

With this approximation to the work costs, it can be concluded that the Solar/Cl_2 process might be cheaper than both the UV/H_2O_2 and ozonation. Since there is no energy factor, the price falls mainly on the cost of the reagents, thus lowering costs.

Also, it is important to note that to implement this technology in a WWTP it would be necessary to build reactors with a large surface area and a shallow depth in order to optimize the long treatment times. Although it may be a large initial investment, in the long term it may become an economically optimal process for the degradation of CECs present in wastewater.

7. CONCLUSIONS

Once this work on the study of the process of combining sunlight with Cl_2 to degrade CECs has been completed, the following conclusions have been reached:

• Due to the experiments carried out for this work, it has been possible to verify that the Solar/Cl_2 process can achieve a high level of degradation of CECs present in a complex wastewater matrix, even those presenting a higher recalcitrant character such as atrazine. Thus, this solar-based AOP might merit further study. It has also been concluded that wastewater treatments based on this process would probably require relatively high reaction times. This issue can be solved by building larger full-scale reactors allowing the entire volume of water to be irradiated by sunlight.

• Regarding the study of the kinetics of the reaction, it has been seen that the hydroxyl radical is the main reactive species, with a contribution greater than 55%. The rest of degradation observed in the model pollutant is tentatively suggested to be caused by other chlorine and carbonate reactive species different than $Cl\cdot$, whose contribution should be experimentally verified in future works. It has also been possible to reach the conclusion that the contribution of $Cl\cdot$, although probably very small, should be evaluated by a different method.

• According to the economic estimation made for the UV/H_2O_2 and O_3 processes and its subsequent comparison with the application cost for solar/Cl_2, it has been possible to conclude that the solar/Cl_2 process studied is considerably cheaper than currently most technological mature AOPs. To this cost, however, the value of the initial investment necessary to build the reactors necessary for this application would have to be added in a future study. Despite this, it can be affirmed that in the long term it can become a good substitute for these AOPs due to the low application cost.

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12. ACRONYMS

Advanced Oxidation Process	AOP
Atrazine	ATZ
Benzoic acid	BA
Contaminants of emerging concern	CEC
Chlorine radical	Cl·
Chemical demand for oxygen	COD
Disinfection by-products	DBPs
Hydroxyl radical	HO·
Nitrobenzene	NB
Wastewater	WW
Wastewater treatment plant	WWTP

APPENDICES

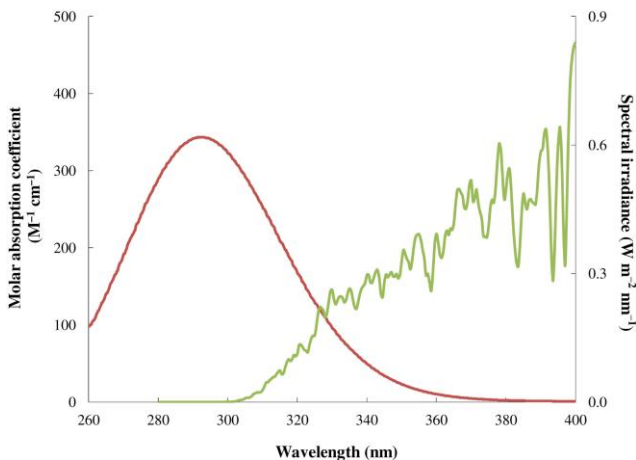# APPENDIX 1: COMPARISON BETWEEN CLO⁻ ABSORPTION AND SOLAR IRRADIANCE SPECTRUM

Figure A1. Comparison between the OCl⁻ molar absorption coefficient absorption spectrum (red line) and the solar spectral irradiance spectrum (green line). Retrieved from [18].

APPENDIX 2: CHLORINE CONCENTRATION

When measuring the absorbance (A) of the dilute solutions of hypochlorite at 292 nm, the following values were obtained: 0.590, 0.629, and 0.584.

Starting from these values, following the Beer-Lambert law (Eq A.1) and, knowing that the molar absorptivity coefficient (ε) at wavelength λ = 292nm is 365 M^{-1} cm^{-1} and that the length of light path (l) is 1cm, the concentrations of the samples (C) can be calculated.

$$A = \varepsilon \cdot l \cdot C \qquad \text{(Eq A.1)}$$

Following these steps, the following concentration results were obtained for each sample. (Table A.1).

	Sample 1	Sample 2	Sample 3
Absorbance	0.590	0.629	0.584
Concentration (mol·L⁻¹)	$1.616 \cdot 10^{-3}$	$1.723 \cdot 10^{-3}$	$1.600 \cdot 10^{-3}$

Table A.1. Concentrations of diluted samples of HClO.

The samples were diluted twice before the absorbance measurement was made, so it was necessary to calculate what concentration of HClO was originally in the commercial bottle. As the process we are studying in the Solar-Cl$_2$, the concentration of Cl$_2$ was calculated and passed to ppm because it is a unit of measurement more comfortable to use because of the low concentrations that have been used.

$$[Sample] \frac{mol}{L} \cdot \frac{10 \; mL}{1 \; mL} \cdot \frac{10 \; mL}{1 \; mL} \cdot \frac{1 \; mol \; Cl_2}{1 \; mol \; HClO} \cdot \frac{70.906 \; g \; Cl_2}{1 \; mol \; Cl_2} \cdot \frac{1000 \; mg \; Cl_2}{1 \; g \; Cl_2} = [Cl_2] \frac{mg}{L} \quad \text{(Eq A.2)}$$

The Cl$_2$ concentration values presented in Table A.2 were obtained.

	Sample 1	Sample 2	Sample 3
Concentration Cl$_2$ (mg·L⁻¹)	114615.18	122191.44	113449.60

Table A.2. Concentrations of Cl$_2$.

The average between these three terms was calculated, 116752.071 mg·L⁻¹, and this value was used as a reference to calculate the HClO concentrations needed to perform each experiment. Finally, the standard deviation was calculated, obtaining a value of 4746.542 mg·L⁻¹ and giving an error of 4.07%.