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Performance of a hybrid system combining constructed wetland and solar photo-Fenton for micropollutant removal in aquaculture farms.

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SUMMARY

One of the biggest threats to human society is the scarcity of fresh water. Approximately 40 % of world population does not have access to fresh water. Agriculture is the sector that uses the most, approximately 70 %. This is the reason why the reuse of water derived from aquaculture could be a solution for this big challenge.

Aquaculture is based on the cultivation of aquatic organisms. Organic compounds such as antibiotics are commonly added to the medium to improve the production. Micropollutants are within these types of organic compounds and are found at low concentrations in aquatic environments used for aquaculture. Micropollutants are very difficult to remove by the conventional wastewater treatment plants. In this study, several micropollutants were evaluated such as antibiotics (e.g. sulfamethoxazole, ciprofloxacin and metronidazole), pesticides (e.g. acetamiprid) and the estrogen, estradiol. On the one hand, estradiol, metronidazole and ciprofloxacin are widely used in the aquaculture sector. On the other hand, acetamiprid and sulfamethoxazole have been found in river water.

Constructed wetlands are spaces built by humans in which micropollutants can be absorbed under controlled conditions. However, they require an extensive land area and time. Contrary, advanced oxidation processes are a more efficient technology that removes these contaminants from wastewater. Although compared to constructed wetlands, they are more expensive and less environmentally friendly.

This work aimed at finding a more effective, economic and sustainable process to remove micropollutants from wastewater. For this purpose, a hybrid system that combines advanced oxidation processes and constructed wetlands was evaluated. Among advanced oxidation processes, solar photo-Fenton at neutral pH using organic fertilizers as iron source was selected. For the constructed wetlands two different plants *Phragmites australis* and *Cyperus* *haspan* were chosen. Besides the effect of this hybrid system at different hydraulic retention times (e.g. 0, 2, 4, 7 and 14 days) was studied.

A higher degradation of micropollutants was observed in the hybrid system when after 4 days in plants, the photo-Fenton method was applied using a concentration of 2.5 mg/L of iron and 25 mg/L of hydrogen peroxide as compared to the photo-Fenton method alone (using double the concentration of reagents). This degradation was also higher as compared to the use of the constructed wetland alone after 7 days without any additional treatment. Acetamiprid was the contaminant most difficult to remove. In the hybrid system, after 4 days in the constructed wetland and using the aforementioned concentrations of iron and hydrogen peroxide in photo-Fenton process, 79.10 % and 67.82 % of acetamiprd was removed in the presence of *C.haspan* and *P.australis*, respectively. The remaining pollutants were completely degraded under these conditions.

The outcome of this study showed that a hybrid system is a more sustainable, efficient and economic process to reuse the water derived from aquaculture.

Keywords: constructed wetlands, advanced oxidation processes, micropollutants, water reuse, aquaculture, hybrid system.

RESUMEN

La escasez de agua dulce en el mundo es uno de los problemas más graves a los que se tiene que enfrentar la sociedad. Aproximadamente un 40 % de la población mundial no tiene acceso a agua dulce. En este sentido, la agricultura es el sector que más agua dulce consume, aproximadamente un 70 %. Es por ello que la reutilización de aguas procedentes de la acuicultura para la irrigación podría ser una de las posibles soluciones a este contratiempo.

La acuicultura consiste en el cultivo de organismos acuáticos, en el que se añaden compuestos orgánicos, tales como antibióticos para mejorar la producción. Los microcontaminantes son un tipo de estos compuestos orgánicos que se encuentran en los compartimientos acuáticos utilizados para el sector de la acuicultura y radican a muy bajas concentraciones (μg/L). Se caracterizan por su carácter recalcitrante por lo que resulta muy difícil eliminarlos por las plantas de tratamientos residuales.

Los microcontaminantes estudiados en este trabajo son los antibióticos metronidazol, sulfametoxazol y ciprofloxacina, el pesticida acetamiprid y el estrógeno estradiol. Este último, junto con el metronidazol y la ciprofloxacina son utilizados frecuentemente en el sector de la acuicultura. Mientras que, el acetamiprid y sulfametoxazol son dos de los contaminantes cuya presencia se ha reportado en aguas de río.

Los humedales artificiales son zonas construidas por el hombre en el que se pueden absorber los microcontaminantes de forma controlada. Sin embargo, requieren mucha área de trabajo y tiempo. No obstante, los procesos de oxidación avanzada son la tecnología más eficiente a la hora de eliminar estos contaminantes de las aguas residuales, aunque a diferencia de los humedales artificiales tienden a ser más caros y menos respetuosos con el medio ambiente.

En este estudio se ha pensado estudiar un sistema híbrido combinando los procesos de oxidación avanzada con los humedales artificiales, para investigar la posibilidad de promover un proceso más eficiente, económico y respetuoso con el medio ambiente. Dentro de los procesos de oxidación avanzada se ha escogido el foto-Fenton solar a pH neutro y utilizando fertilizantes orgánicos como fuente de hierro. En los humedales artificiales se han seleccionado dos plantas *Phragmites australis* y *Cyperus haspan.* Además, se han estudiado diferentes tiempos de retención hidráulicos: 2,4,7 y 14 días.

Con el sistema híbrido en 4 días y posterior foto-Fenton utilizando 2.5 mg/L de hierro y 25 mg/L de peróxido de hidrógeno, se observó una mayor degradación de contaminantes que con el doble de concentración de reactivos en el foto-Fenton solo y en el humedal artificial a 7 días sin tratamiento posterior. El acetamiprid fue el contaminante que más se resistió a ser degradado. En el sistema híbrido, después de 4 días en el humedal artificial con las concentraciones de hierro y peróxido ya mencionadas, se eliminó el 79.10 % en la *C.haspan* y 67.82 % en *P.australis*, mientras que se consiguió una eliminación total en el resto de los contaminantes.

De esta forma el sistema híbrido posiblemente es un método más sostenible, eficiente y económico para la reutilización de agua en el sector de la agricultura.

Palabras clave: Humedales artificiales, procesos de oxidación avanzada, microcontaminantes, reúso del agua, acuicultura, sistema híbrido

1. INTRODUCTION

Water has an immeasurable value in economic, social and environmental aspects which makes it an essential resource on the Earth. Water is the main compound of the planet Earth (71.00 %), nonetheless only 3.00 % corresponds to fresh water and within this value, 66.00 % comes from frozen glaciers, meaning it's not useful [1]. Water is an essential resource for the development of life. However, water is also present in our daily life in other ways such as personal care, cooking or washing clothes. It is estimated that at the end of the day person from western countries can consume up to 150-200L of fresh water [2].

On the other hand, water can also be used in other way in the industrial sector, for example as refrigerant or dissolvent. In Spain, the water used for industrial processes is around 965 hm^3 and water production in Spain is expected to increase in the coming years [3]. Nevertheless, its domestic and industrial use is almost irrelevant compared to its agricultural use (Figure 1). For all the above mentioned, water becomes a resource of immense value and an essential element in our daily life.

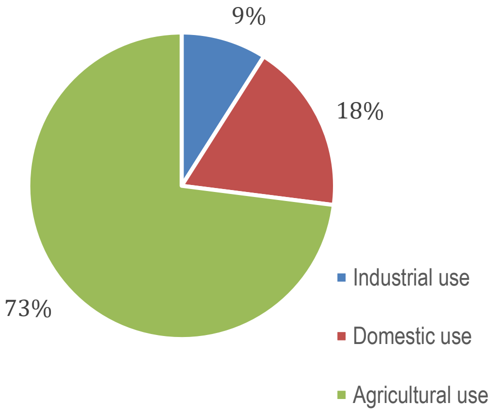


Figure 1. Water consumed in Catalunya in 2020. Source: Agencia Catalana del Agua

1.1. WATER PROBLEM

Nowadays, the scarce availability and high demand of fresh water is considered as a global and important issue for all of us. FAO (Food and Agriculture Organization of the United Nations) research estimated that one in five developing countries will face water scarcity problems by 2030 [4]. This global uncertainty occurs by the combination of two main factors, the population growth and socio-economic development, in other words, improvement in life's quality. That is why, ensuring water security and quality has become one of the most concerning environmental aspects.

1.2. WASTEWATER TREATMENT AND REUSE

Simultaneously to an increasing demand for water usage, there is also an increase in the resulting waterwaste (WW). Untreated domestic water contains, pathogens and organics, although, industrial water has more dangerous substances such us metals, some organic compounds, and other pollutants. If this type of water is not treated correctly and it is dumped to the environment, it can be a dangerous risk for the ecosystems and human health. The WW reuse is an activity which lately is gaining more attention among the scientific community. This is because is a new reliable resource, independent from atmospheric drought, that also competes against water scarcity and at the same time cuts down the spilling of pollutants substances. [5]

In 2019, 7.5 million m^3/day of new water reuse capacity was reported [6]. Meanwhile, this quantity only represents less than 1.00 % of the global water use. It is predicted that this percentage will increase reaching 1.66 % by 2030 [7]. Despite all the advantages from this resource, water reuse has been a subject of very few studies, mainly because of its high capital costs (financial issue), technologies and legacy. Currently, the policies for reclaimed water are strongly fragmented and, in many countries, incomplete. The necessity of developing an appropriate legislation, regulations and planning framework for governments is essential to adopt reused wastewater as a future supply of water.

1.3. OCCURRENCE OF MICRPOLLUTANTS IN WATER COMPARMENTS

Since the period of industrial revolution, by the middle of the eighteenth century, the amount and production of numerous organic chemicals has been rising. The production of some of these organic chemicals generates compounds that can reach the aquatic environment. In many cases, these compounds can be harmful for human health and ecosystems [8]. Currently, more than 100.000 compounds in European Community (EC) countries are derived from human activity in industrial, domestic and agricultural applications [9]. One example are antibiotics that may be present and represent an acute threat to aquatic systems and human health. This is due to its ineffective long-term biodegradation [10].

The effluents from Wastewater Treatment Plant (WWTP) have been identified as a major point source pollution [11]. These effluents may contain micropollutants (MPs) which are found in low concentrations in aquatic environment, usually between ng/L and µg/L. MPs are bio accumulative and recalcitrant. MPs, also referred as to emerging contaminants (EC), can be anthropogenic or natural substances and include several pharmaceuticals, personal care products, industrial chemicals, pesticides, steroid hormones and endocrine disrupting compounds [12].

In the recent years, MPs have gained attention because they are difficult to remove by using the conventional WWTP [13]. These systems commonly consist of a primary (physicochemical) and secondary (biological) treatments, which are not effective in removing MPs due to their trace concentrations and their biological resistance. Therefore, solutions are needed to fulfil the increasing demands for water as well as provide an effective WW management. In the following section, the MPs studied in this work are described.

1.3.1. Sulfamethoxazole

Sulfamethoxazole (SMX) is a sulphonamide antibiotic used for humans and animals (Figure 2). It is used for treating bacterial infections such as acute bronchitis, urinary tract infections and prostatitis. SMX inhibits bacterial enzyme dihydropteroate and as consequence generates folic acid which is necessary for acid nucleic formation. SMX is soluble in water (0.46 mg/mL) and presents low hydrophobicity (octanol-water partition coefficient, log K_{OW} = 0.27). Its presence in aquatic environment is frequent and has been reported in many effluents of WWTPs [14].

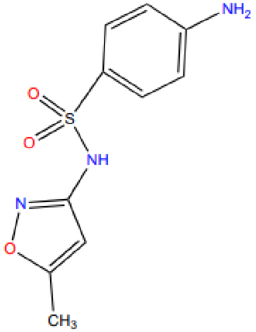


Figure 2. Structural formulate of SMX Source: ChemDraw.

1.3.2. Acetamiprid

Acetamiprid (ACMP) is an odourless neonicotinoid insecticide used for controlling sucking insects on crops such as leafy vegetables, pome fruits, grapes, cotton, etc. Its structure is depicted in Figure 3. It affects the central nervous system of insects causing paralysis and subsequent death. Nonetheless, negative effects have been also observed in humans and aquatic organisms. ACMP is slightly soluble in water (4.30 mg/mL) and presents low hydrophobicity (log K_{OW} = 0.80). ACMP has been detected in different water systems worldwide, including some in Europe, presenting concentrations up to 380.00 ng/L. Currently its use is not banned, but it is under vigilance in Europe by 2018/840/EU directive [15].

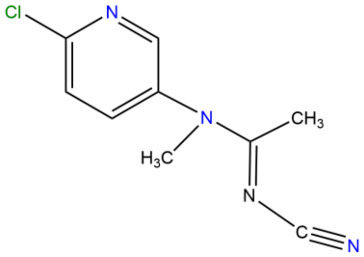


Figure 3. Structural formulate of ACMP Source: ChemDraw.

1.3.3. Estradiol

Estradiol (E2) is an estrogenic steroid female hormone with the following structure (Figure 4). It plays important roles in the development and differentiation of the gonads and the central nervous system in vertebrates. It is also used for advanced cancer treatment and estrogenic deficiency. E2 can be used as feed for aquatic organisms as well. E2 has low solubility in water 0.0036 mg/mL and is hydrophobic (log K_{OW} = 4.01). Several studies have reported that E2 occurrence is high in fresh water, even in drinking water [16]. Moreover, E2 may have an acute risk in human health and they could be transferred from parental generations.

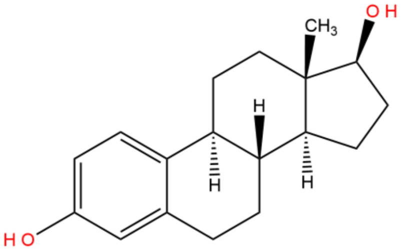


Figure 4. Structural formulate of E2 Source: ChemDraw.

1.3.4. Metronidazole

Metronidazole (MET) is an antibacterial and antiprotozoal medicine derived from the group of nitroimidazole (5-Nitromidazole). Figure 5 shows its structure. It can be used either alone or with other antibiotics to treat endocarditis, bacterial vaginosis and pelvic inflammatory disease. It is effective against anaerobic bacteria [17]. MET is one of the most used treatments in the aquaculture industry [18]. MET is soluble in water (0.0257 mg/mL) and hydrophilic (log K_{OW} = 0.02).

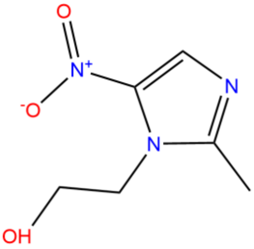


Figure 5. Structural formulate of MET Source: ChemDraw.

1.3.5. Ciprofloxacin

Ciprofloxacin (CIPR) is an antibiotic of fluoroquinolone group used to treat bacterial infections, such us bone, intra-abdominal, skin or respiratory tract infections. Its structure is shown in Figure 6. CIPR is the most used antibiotic in animal and human to control infections. This antibiotic was detected in the last years in aquatic environments causing a threat due to its adverse effects in the ecological systems by inducing bacterial resistance [19]. CIP is soluble (36.00 mg/mL) and presents low hydrophobicity (log K_{OW} = 0.28).

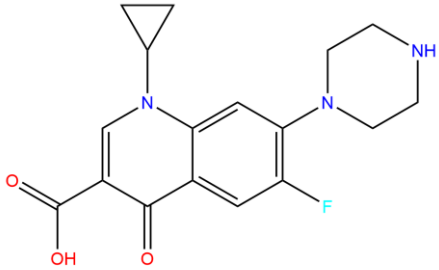


Figure 6. Structural formulate of CIPR Source: ChemDraw.

1.4. AQUACULTURE

Aquaculture, often called the “Blue Revolution,” represents an important strategy to support the current growth of food demand [20]. Aquaculture farm’s purpose is the cultivation and growth of aquatic organisms such as fish, crustaceans, molluscs, algae or aquatic plants under fully controlled conditions. These conditions simulate an optimal aquatic environment for the growth and reproduction of aquatic organisms. There are different aquaculture systems depending on the type of water used to grow the aquatic organisms. For example, fresh water (inland water) or salt water (marine water). Inland waters are aquatic-influenced environments located within land boundaries which include those located in coastal areas. On the other hand, marine waters are derived from the sea or the ocean water and they are different due to their higher salt content.

Nowadays, half of the consumed aquatic organisms are derived from aquaculture production (Figure 7). This percentage has been increasing in the last years as compared to capture fisheries. For example, in China, the aquaculture production has tripled fishing production in the last decade. Nonetheless in the rest of the world, capture fisheries are still superior, but the difference is decreasing annually. [6]

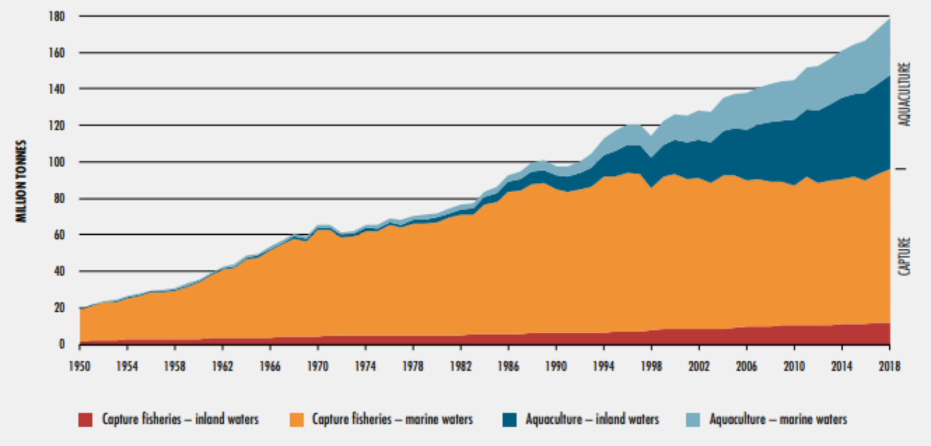


Figure 7. World capture fisheries and aquaculture production.

(Picture extracted from FAO. 2020. The State of World Fisheries and Aquaculture 2020. Sustainability in action. Rome. https://doi.org/10.4060/ca9229en)[6]

Aquaculture farms are commonly classified according to their intensity (e.g. extensive, semi-intensive or intensive), water exchange (e.g. open, semi-closed, closed), culture structure (e.g. cages, race ways or concrete/fiberglass tanks) and farming methods (e.g. mono- or poly-culture).

To guarantee aquatic animals' reproduction several substances are used such as veterinary drugs, disinfectants and antifoulants which are MPs and might afterwards be released into the effluents derived of farming activity. [21]

Moreover, with the increasing intensification of aquaculture, finding sustainable production practices that minimize ecological impacts are currently a priority in research.

1.5. GENERAL FRAMWORK OF WATER

There is a global concern about the release of MPs into the environment because they are a risk to human health and aquatic ecosystems. This is the reason why the European regulatory administration has been seeking for the development of water quality policies. Some regulations were published in the recent years.

For example, the Water Framework Directive (WFD), dated in 2008, has the objective to protect water by the identifying of substances that may represent a risk to aquatic ecosystems and human health.

In 2000 the first European Water policy was implemented, Directive 2000/60/EC. Its aim was to evaluate a list of substances which were considered potentially hazardous to the aquatic environment [22]. Moreover, European Environmental Quality Standards (EQSs) were also defined. The following year, in 2001, the Decision 2455/2001/EC was published, where a list of 33 priority substances (PSs) had to be controlled at European Union (EU) countries, based on the amount of production, environmental risk and the presence of these substances on environment [23].

Afterwards, this directive was replaced by the 2008/850/EC in which 8 additional PSs were included [24]. From this report EU countries can supervise these pollutants in aquatic ecosystems and compare the date they got with EQS values, to have a reference of water quality in aquatic environmental and take necessary steps.

In the Directive 2013/39/EU [25], new PSs were included reaching 45 substances in total. EQSs became more restrictive and it was warned that there was a necessity for improving water treatment undesirable these pollutants.

1.6. WETLANDS AND CONSTRUCTED WETLANDS

A wetland consists of a flat land area, where the surface is permanently or seasonally flooded. By covering itself by water, soil saturates and consequently oxygen concentration goes down, causing a hybrid ecosystem between aquatics and terrestrial ecosystems. Due to the shallow water, wetland soil undergoes variations. Hydrophilic plants act as water filters, storing and releasing water. Wetland waters are considered among the most biologically diverse of all ecosystems, being the sole ecosystem to live for a wide range of unique plant and animal species.

Wetlands benefit humans in several ways such as water purification, groundwater replenishment, water storage or food control. However, this type of lands suffers degradation or even disappearance because of aquaculture, agriculture, and industrial development. Therefore, policies and measures that seek to protect these types of ecosystems are now being implemented worldwide. [26]

Constructed wetlands (CW) are engineered systems. CW are controlled environments aiming to create mechanisms for the removal of pollutants and organic matter, NO_3^- and NO_2^- from wastewater through physical, biological, and chemical processes simultaneously such as adsorption, photolysis or microbial degradation. CWs recreate the conditions and processes of natural wetlands. Microbial degradation and absorption by plants are the main natural processes for the removal of contaminants from water through CWs. These systems are easy to maintain and handle, have a low cost and achieve a high-quality effluent. That is why this is the most sustainable resource to battle against MPs in water ecosystems. [27]

Nevertheless, they have disadvantage too. The biological process occurring in CWs are highly dependent on diverse factors, such as the environmental conditions and the compound (pollutant) properties. In relation to environmental conditions, parameters such as pH, temperature and oxygen availability contribute to adsorption or microbial degradation processes. Meanwhile, pollutants characteristics, such as vapor pressure or chemical polarity can widely vary in each contaminant hindering the effectiveness of the method. [28]

1.7. **AOPS**

Advanced Oxidation Processes (AOPs) are an oxidation technology based on the production of highly reactive species under soft temperature and pressure conditions. These reactions resulut in the mineralizeation of pollutants into carbon dioxide (CO_2), water (H_2O) and inorganic ions [29]. These processes degrade pollutants and other organics compound into non-toxic biodegradable products. The hydroxyl radical (HO•) is the main specie formed by AOPs. Other radicals can be also generated depending on the type of oxidant and the mechanisms of reactions. Examples of the formed radicals are the oxide anion (O2•-), hydroperoxyl (HO2•), ozonide anion (O3•-), sulphate (SO4•-) and chlorine (Cl•) radicals [24]. HO• radical is very reactive and has one of the highest oxidative capacities of all oxidate agents (E0=2.80V) which causes a fast breakdown of molecule bands. This shortens reaction time and therefore results in a lower environmental impact.

Within AOPs there are different categories of processes which are distinguished depending on the number of phases involved in the oxidation (homogenous or heterogenous processes) or the generation of reactive species (chemical, electrochemical or photochemical) (Figure 8).

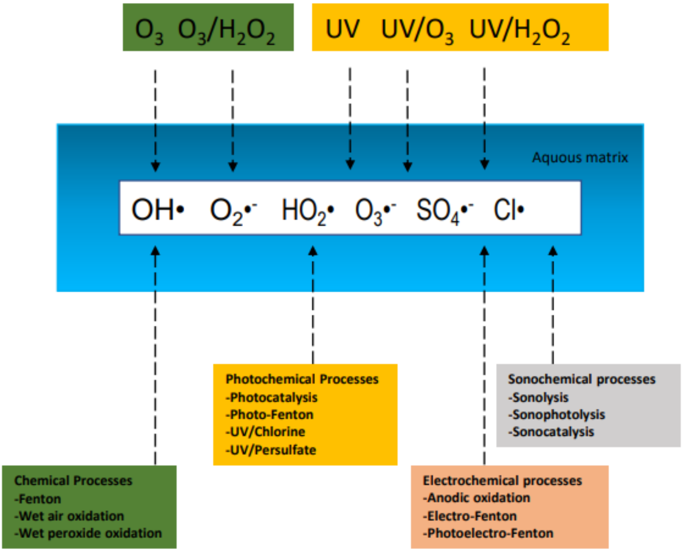


Figure 8. AOPs general mechanism for removing organic MPs from aqueous matrices (chemical, photochemical, electrochemical and sonochemical processes).

These chemical processes require oxidants, such as ozone (O_3), hydrogen peroxide (H_2O_2) or catalytic mixtures. On the other hand, in photochemical processes radiation is necessary (UV/O_3 or UV/Fenton). In electrochemical processes electrical currents are required, being a more complex process. A positive aspect of these processes compared with other chemical processes is that hazardous subproducts for water are not generated when the oxidation is completed. Besides, treating almost all organics, it can also deal with some heavy metals due to its high oxidation capacity.

The main disadvantage of AOPs are their relatively high capital costs. Operating costs are the most significant costs because of the continuous requirement of chemicals and energy [29].

1.7.1. Fenton

Fenton's reaction, named after its discoverer in 1894 H.J.H. Fenton is an AOP in which HO• are generated. This reaction occurs at room temperature and pressure and in an acidic environment (pH 2.80). Under these conditions, iron (Fe) does not precipitate. H_2O_2 is used as an oxidant with transition metals, usually iron (catalyst). The following reactions take place during Fenton's reaction.

$$Fe\ (II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO^{\cdot} \tag{1.1}$$

$$Fe\ (III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\cdot} + H^+ \tag{1.2}$$

$$HO + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \tag{1.3}$$

$$HO_{\cdot} + Fe\ (II) \rightarrow Fe\ (III) + OH^- \tag{1.4}$$

$$Fe\ (III) + HO_2^{\cdot} \rightarrow Fe\ (II) + O_2 + H^+ \tag{1.5}$$

$$Fe\ (II) + HO_2^{\cdot} + H^+ \rightarrow Fe\ (III) + H_2O_2 \tag{1.6}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{1.7}$$

The first two reactions are the most important ones. The first one describes how a radical and a hydroxyl ion are generated while iron is oxidated. The second one explains the recovery of iron using the same hydrogen peroxide and producing a radical. Iron cation stands on a cycle between both oxidation states II and III. The appropriate pH should be close to 3. Under this condition the $[Fe(H_2O)_5(OH)]^+$ complex is the stable specie, being the catalyst of the reaction. If the pH, is lower than 3, Fe (III) ion is predominant and it is not suitable for the kinetic of the reaction. On the other hand, if the pH is above 3, iron precipitates resulting in the formation of iron precipitates e.g. $Fe(OH)^{2+}$ and $Fe2(OH)_2^{4+}$.

1.7.2. Photo-Fenton

Photo-Fenton is a modification of Fenton reaction and includes irradiation (UV or UV/Visible light), that enhances the generation of HO• thereby, gaining a higher efficiency in the removal of organic pollutants from water. This occurs due to the Fe catalytic-cycle, Fe (III) reduces to Fe (II) by the photo-reduction. There are three main mechanisms in this process.

The first one is the decomposition of hydrogen peroxide with Fe(II) catalyst (2.1).The second, results in H_2O_2 decomposition into hydroxyl radical (2.2) in the presence of UV radiation. An additional production of HO• radicals upon Fe(II) regeneration occurs (2.3-2.4) and finally, in the last reaction Fe(II) is regenerated (2.5) [30].

$$\mathrm{Fe\ (II)} + H_2O_2 \longrightarrow \mathrm{Fe\ (III)} + OH^- + HO^\cdot \qquad 2.1$$

$$H_2O_2 + h\nu \rightarrow 2HO^\cdot \qquad 2.2$$

$$\mathrm{Fe\ (III)} + H_2O_2 + h\nu \rightarrow \mathrm{Fe\ (II)} + HO^\cdot + H^+ \qquad 2.3$$

$$\mathrm{Fe(OH)}^2 + h\nu \rightarrow \mathrm{Fe\ (II)} + HO^\cdot \qquad 2.4$$

$$[\mathrm{Fe}(\mathrm{RCO}_2)]^{2+} + h\nu \rightarrow \mathrm{Fe\ (II)} + CO_2 + R^\cdot \qquad 2.5$$

At neutral pH some of these reactions may take place. Fe (II) reacts with H_2O_2, consequently Fe (II) oxidates to Fe (III) and HO• is generated. Fe (III) chelate in presence of solar irradiation can reduce to Fe (II). Chelating agents are employed to keep iron in solution and to prevent from working at acid ph. DTPA and EDTA are the organic fertilizers used in this study. Afterwards this organic fertilizer can employ in water irrigation for agriculture. [31]

2. JUSTIFICATION

2.1. HYBRID SYSTEM

The aquaculture production is growing in the whole world, that is why new policies are being implemented for ensuring the use of water on a safe way. The reuse of water in this type of farming may be the solution for the lack of fresh water in agriculture. However, MPs and other pollutants must be removed first to make this water useful. AOPs and CWs are the most studied processes to remove pollutants in aquaculture. Over the last years the study of AOPs for MPs removal have gained attention among researchers (Figure 9). The implementation of CWs for the removal of MPs has been less studied but some articles have been published in the recent years. The combination of these processes has not been widely studied until now. Up to date, only 8 publications can be found in literature [32-39]. To the best of our knowledge, there are not yet available reports studying a hybrid system combining solar photo-Fenton at neutral pH (7.5-8) using organic fertilizers and CWs processes. The best way to study this hybrid system is simulating environmental conditions (e.g. solar light, temperature, humidity) similar to those of wetlands. Additionally, photo-Fenton process was selected because at natural condition of pH it is not as efficient as ozone (O3) or UV/H2O2 treatments but it is more eco-friendly technique. The published reports studying the effectivity of a hybrid system compared to a single process showed that hybrid systems are more effective. [40] [41]

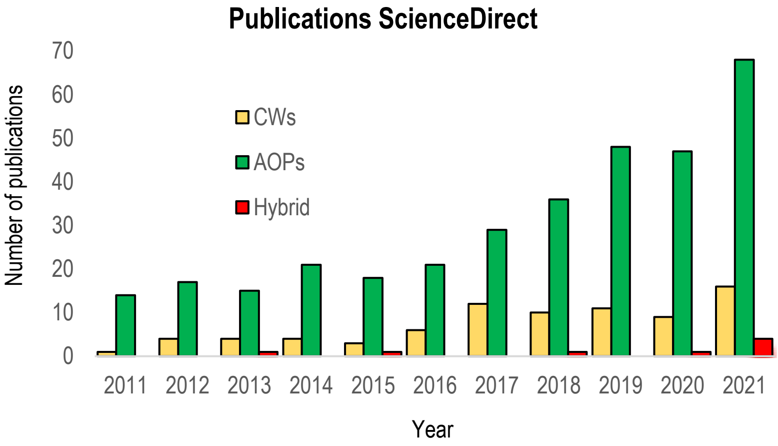


Figure 9. Increase of papers related to MPs removal by CWs, AOPs and Hybrid system in the last 10 years. Source: ScienceDirect

2.2. MICROPOLLUTANT SELECTION

The selection of MPs was made according to the log K_{OW}, retention time and type of pollutant. The selected MPs are E2, SMX, MET, CIP and ACMP. All of them, except E2, have a low partition coefficient (below one). This means that these pollutants have a high tendency to dissolve in water, which is necessary for the analysis of these pollutants in the samples by high liquid performance chromatography (HPLC). Ethinylestradiol (EE2) and oxytetracycline were selected in this work too. Nonetheless, they were discarded from the study because of their poor solubility in water and difficult to analyse in the HPLC.

2.3. ECONOMIC AND SUSTAINABILITY

CWs have the advantage that are low-cost biological systems for the removal of organic MPs. These systems should be built in rural areas to optimize its performance. Therefore, an ecosystem can be developed in a sustainable way where different species can cohabit and reproduce. CWs relies on the environmental conditions (humidity temperature, and sunlight exposure) saving costs related to control and maintenance. AOPs requires less area and are more effective to remove MPs in WWs (Figure 10). Among AOPs, photo-Fenton may be the most sustainable one. Besides, the use of CWs and AOPs simultaneously could potentially reduce costs. At the same time more MPs can be removed by a hybrid method than by a single process while respecting the environment.

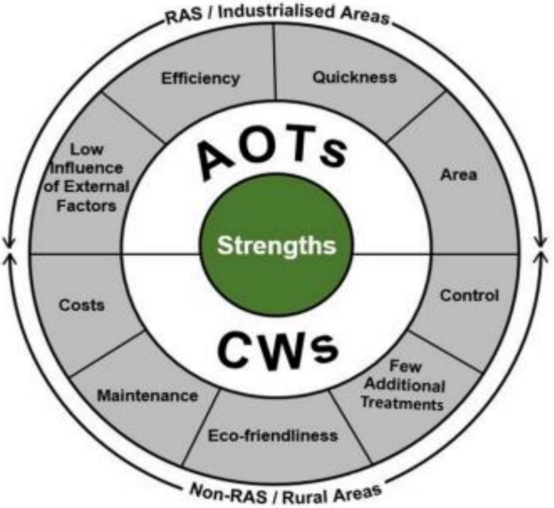


Figure 10. Main strengths of AOTs (AOPs in this study and CWs, and suitable application according to the type of aquaculture (i.e., RAS in industrialized areas and non-RAS in rural areas). (Picture extracted from (Gorito et al., 2022) [32]

3. OBJECTIVES

The main objective of this project was focused on the study of ACMP, SMX, MET, CIPR and E2 removal by a hybrid system combining CW with a simulated solar photo-Fenton process at natural pH using organic fertilizers as an iron chelates. The aim of this combination (hybrid system) was to make the treatment more efficient and environmentally friendly. Besides, explore the possibility to reuse the treated effluents for agricultural purposes.

4. MATERIALS AND METHOD

4.1. REAGENTS

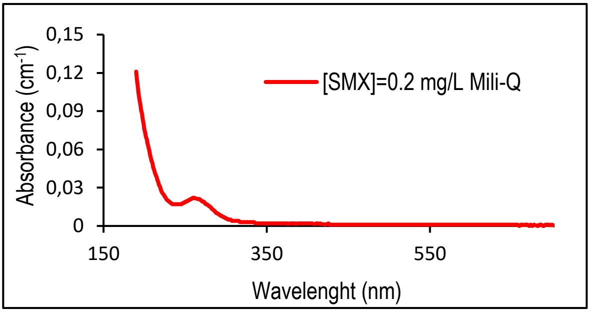
4.1.1. Micropollutants (MPs)

In the following section the properties of each studied pollutant are described (Table 1-5). Additionally, the chemicals used in this study are listed in Table 6.

4.1.1.1. Sulfamethoxazole

Table 1. SMX properties [42]

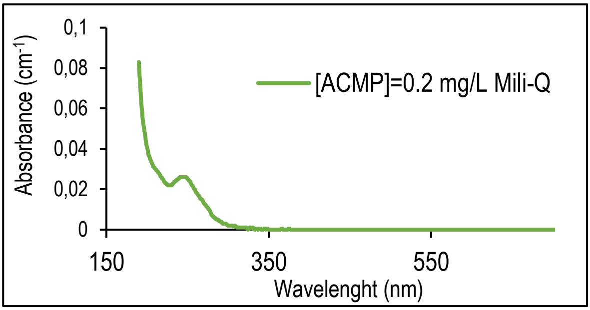
Propriety	Value
Molecular formula	$C_{10}H_{11}N_3O_3S$
IUPAC name	4-amino-N-(5-methyl-1,2-oxazol-3-yl)benzenesulfonamide
Type	Antibiotic
Molecular weight (g/mole)	253.28
CAS No.	129378-89-8
EC No.	211-963-3
Melting Point (ºC)	167
Solubility (mg/mL)	0.459
pKa_1	1.60
pKa_2	5.70
log K_{OW}	0.89

Hazard Symbol	-
Company	SIGMA
Absorption spectrum (0.2 mg/L in Milli-Q water)	

4.1.1.2. *Acetamiprid*

Table 2. ACMP properties [43]

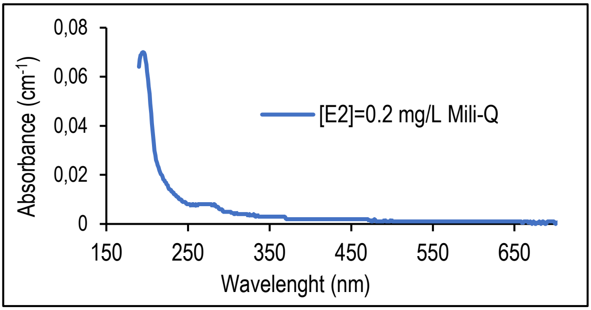
Propriety	Value
Molecular formula	$C_{10}H_{11}ClN_4$
IUPAC name	N-[(6-chloropyridin-3-yl)methyl]-N'-cyano-N-methylethanimidamide
Type	Pesticide
Molecular weight (g/mole)	222.67
CAS No.	160430-64-8
EC No.	603-921-1
Melting Point (ºC)	98.9
Solubility (mg/mL)	0.425
pKa_1	0.70
log K_{OW}	0.80
Hazard Symbol	
Company	SIGMA ALRICH

Absorption spectrum (0.2 mg/L in Milli-Q water)	

4.1.1.3. Estradiol

Table 3. E2 properties [44]

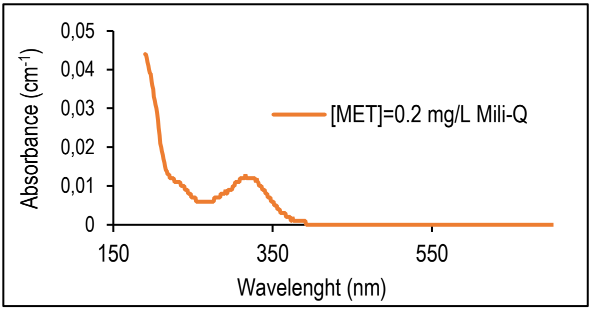
Propriety	**Value**
Molecular formula	$C_{18}H_{24}O_2$
IUPAC name	(8R,9S,13S,14S,17S)-13-methyl-6,7,8,9,11,12,14,15,16,17-decahydrocyclopenta[a]phenanthrene-3,17-diol
Type	Estrogen
Molecular weight (g/mole)	272.4
CAS No.	17916-67-5
EC No.	200-023-8
Melting Point (ºC)	173-200
Solubility (mg/mL)	0.0036
pKa$_1$	10.46
log K_{OW}	4.01
Hazard Symbol	
Company	SIGMA

Absorption spectrum (0.2 mg/L in Milli-Q water)	

4.1.1.4. Metronidazole

Table 4. MET properties [45]

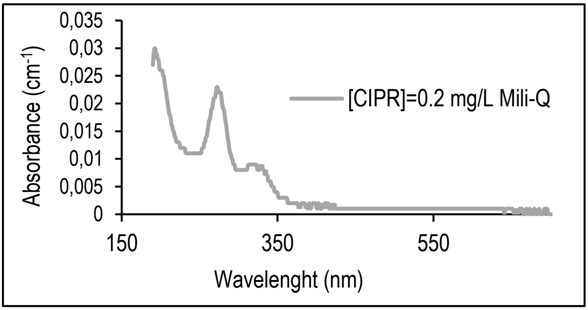
Propriety	Value
Molecular formula	$C_6H_9N_3O_3$
IUPAC name	2-(2-methyl-5-nitroimidazol-1-yl)ethanol
Type	Antibiotic
Molecular weight (g/mole)	171.15
CAS No.	443-48-1
EC No.	207-136-1
Melting Point (ºC)	157-160
Solubility (mg/mL)	0.0257
pKa$_1$	2.38
log K_{OW}	-0.02
Hazard Symbol	-
Company	SIGMA ALRICH

Absorption spectrum (0.2 mg/L in Milli-Q water)	

4.1.1.5. Ciprofloxacin

Table 5. CIPR properties [46]

Propriety	Value
Molecular formula	$C_{17}H_{18}FN_3O_3$
IUPAC name	1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid
Type	Antibiotic
Molecular weight (g/mole)	331.34
CAS No.	85721-33-1
EC No.	
Melting Point (ºC)	225-257
Solubility (mg/mL)	36.00
pKa$_1$	6.09
log K$_{OW}$	0.28
Hazard Symbol	
COMPANY	Riedel-de Haën

Absorption spectrum **(0.2 mg/L in Milli-Q water)**	

4.1.2. Other chemicals reagents

The following table (Table 6) illustrates other reagents used during experiments.

Table 6. Information about reagents

Name	Formula	Company	Purity (%)	Used in/for
Acetonitrile	CH_3CN	Fischer Chemical	99.80	HPLC analysis
Acetic acid glacial	CH_3COOH	Panraec Química	95	Bisulphite preparation for Fe determination
Amonium acetate	$CH_3COOONH_4$	Panreac Química	99	Bisulphite preparation for Fe determination
Ammonium metavanadate	H_4NO_3V	Sigma Aldrich	99	H_2O_2 determination
Ascorbic acid	$C_6H_8O_6$	Panreac Química	91	Totally Fe determination
DTPA-Fe	$C_{14}H_{18}N_3O_{10}FeNa_2$	Pyhgenera	7	Photo-Fenton
EDTA-Fe	$C_{10}H_{12}N_2O_8FeNa \cdot 3H_2O$	phygenera	13.3	Photo-Fenton
Hydrogen peroxide	H_2O_2	Merck	30 w/w	Photo-Fenton
Liver bovine catalase	$C_9H_{10}O_3$	Sigma Aldrich	-	To avoid further reactions

Orthophosphoric acid	H_3PO_4	Panreac Química	85	HPLC analysis
Sodium bisulphite	$NaHSO_3$	Panreac Química	40	Stop the reaction with peroxide
1,10-phenanthroline	$C_{12}H_8N_2$	Panreac Quimica	99	Fe^{2+} determination

4.2. WATER MATRIX

4.2.1. Milli-Q water

Milli-Q water is purified water using a Millipore Milli-Q lab water system. Milli-Q water, also known as ultrapure water (UPW) is made by passing the source water through mixed bed ion exchange and organics cartridges. The purity of the water is monitored by measuring the conductivity. The higher resistance, the fewer ions in the water. American Society for Testing and Materials (ASTM) International and the International Organization for Standardization (ISO) have both set standards for defining and categorizing water purity in laboratory-grade water [47]. According to these standards, it is considered UPW when it has been purified to 18.2 MΩ·cm of resistivity. The Mili-Q water used in this study exhibited a pH of 4.8, resistivity of 18.2 MΩ·cm and TOC of 2bbp (Table 7).

Table 7. Mili-Q water characteristics

pH	Resistivity (MΩ·cm)	TOC (ng/L)	Temperature (ºC)
4.8	18.2	2.0	19.7

4.2.2. Real water matrix

The water used in the experiments and to irrigate the plants was taken in Llobregat river in Sant Vicenç dels Horts. The properties of this water are described in Table 8

Table 8. River water characterization

pH	UV_{254} [cm^{-1}]	Cl^- [mg/L]	SO_4^{2-} [mg/L]	NO_2^- [mg/L]	NO_3^- [mg/L]
8.13	0.11	210.00	118.60	0.40	6.60

4.3. ANALYTICAL METHODS

4.3.1. High Performance Liquid Chromatograph

MPs concentration was measured by HLPC (1260 Infinity from waters by Agilent Technologies). MET, ACMP, SMX and CIPR were analysed in the same sample as they required the same working conditions and had different HRT (Hydraulic Retention Time). However, E2 was analysed separately, as a previous dilution with acetonitrile (50:50) had to be made in order not to remain absorbed in the syringe filters used for HPLC analysis. The column and HPLC method conditions (pressure, detection, mobile phase as well as the flow rate) for each pollutant, except E2, are shown in Table 9. The details for the analysis of E2 can be seen in Table 10.

Table 9. Mix Method characterization

	Detection (nm)	Column	Pressure (bar)	Mobile phase	Flow-rate (mL/min)
MET	220	SEA18 Teknokroma (250 x 4.6 mm i.d.;5µm particle size).	110	80% H_2O (with H_3PO_4 pH = 3) 20% acetonitrile	1
SMX	270				
ACMP	250				
CIRPR	280				

Table 10. E2 Method characterization

	Detection (nm)	**Column**	**Pressure (bar)**	**Mobile phase**	**Flow-rate (mL/min)**
E2	200	SEA18 Teknokroma (250 x 4.6 mm i.d.;5µm particle size).	110	50% H_2O (with H_3PO_4 pH = 3) 50% acetonitrile	1

4.3.2. Determination of iron precipitation

Ferrous iron (Fe(II)) was measured by the complexation with 1,10-phenanthroline according to standardized procedure (ISO 6332) (International Organization for Standardization 1988) [48]. 4 mL of sample were mixed with 1 mL of phenanthroline solution (1 g/L) and 1 mL of acetic/acetate buffer (62.5 g of ammonium acetate are dissolved in 175 mL of acetic acid and flushed until 250 mL with ultrapure water). The complex exhibited a red colour, which was measured by a spectrophotometer (Hach Lange DR 6000) at 510 nm. Total iron (Fe_{tot}) concentration was evaluated after ferric iron reduction to ferrous form by ascorbic acid (4.1). In the experiments performed with iron chelates at circumneutral pH, since the iron is already chelated, the differentiation between ferrous or ferric forms it is not possible. Thus, only total iron can be measured. In these cases, samples were filtered with 0.20 µm PVDF filter to ensure a good read of soluble (chelated and not) iron.

$$Fe^{2+} + 3(\text{1,10-Phenantroline}) \rightarrow Fe(\text{1,10-phenantroline})_3^{2+} \tag{4.1}$$

4.3.3. Determination of Hydrogen Peroxide consumption

Hydrogen peroxide concentration was determined by metavanadate colorimetric method. 1.50 mL of sample was mixed with 1.50 mL of ammonium metavandate solution (5.14 g/L) in acidic medium [49]. When reaction 4.2 took place, peroxovanidium cation is formed. The resulting solution presents an orange coloration which was measured by spectrophotometer (Hach Lange DR 6000) at 450 nm. The concentration of H_2O_2 was determined from a calibration curve between the absorbance and concentration of H_2O_2.

$$VO_3^- + 4H^+ + H_2O_2 \longrightarrow 3H_2O + VO_2^{3+} \qquad (4.2)$$

4.3.4. pH measurement

pH was measured in a CRISON GLP 22 pH meter correctly calibrated each day with pH 7.00 and pH 4.00 buffers.

4.4. EXPERIMENTAL DEVICE

4.4.1. CW System

The plants selected for the CWs were *Phragmites australis* and *Cyperus haspan. P.australis*, also known as the common reed. It is a gramineous plant. Is native to wetland ecosystem all over the world. *P. australis* is a plant species also grown in natural wetlands. It is commonly used for in pollutants reparation systems [50]. It can grow up to 4m high and forms extensive stands, known as reed beds [51].

C.haspan is an aquatic plant species of the Cyperus genus. It grows well in the subtropical and tropical climates, and it is among the most productive plants of wetlands for bioremediation processes [52]. The species vary greatly in size, with small species only 5 cm tall, while others can reach up to 5 m in height.

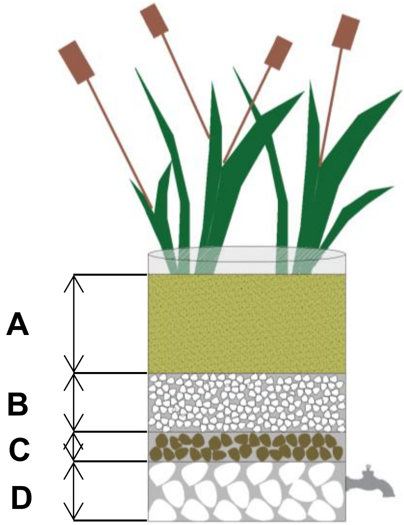


Figure 11. CW microcosm set up. (A) Roots bed substrate layer, 10cm. (B) Gravel layer 5cm. (C) Lava rock layer 2 cm. (D) Cobbles layer 5 cm.

Microcosms are artificial, simplified ecosystems that are used to simulate and predict the behaviour of natural ecosystems under controlled conditions. Microcosms were set up using plastic containers (22.5 cm high and d=9.5 cm) filled first with a layer of Cobbles stones (5 cm of layer), followed by a second layer of lava rock (2 cm of layer), a third sand layer of Gravel (5 cm of layer) and a last a fourth covering consisting of roots and sands as bed substrate (10 cm of layer) (Figure 11). *Two P.australis* and two *C.haspan* were transplanted in four different containers. The outlet of the container was ubicated at the bottom to recirculate the maximum water every day. Cobbles were applied at the bottom of the container to prevent clogging. On the other hand, lava rock was used in the middle to increase the porosity of the substrate, promote the retention of contaminants and to improve the biofilms development. Gravel was applied at the top to help the further filtration. This filtration is done starting in the layers with lower porosity. Sand was used as bed substrate for the CWs microcosms A visual representation of sand, gravel, volcanic rock and cobbles and their size (in mm) is shown in Figure 12.

Sand Ø=0.5mm Gravel Ø=12-30mm

Volcanic Rock Ø=25-50mm Cobbles Ø=60-120mm

Figure 12. Rock layers diameter

4.4.2. Photo-Fenton experiments

All photo-Fenton experiments were carried out in a bench solar simulator (SUNTEST CPS, Hereaus) equipped with a 1500-W Xenon lamp with infrared and UV-C cut off-filters. The irradiance was set at 500 W/m^2. The simulator was connected to a thermostatic bath at 10 ºC to maintain the temperature within the device at around 21-23 ºC (Figure 13). To perform the experiments cylindrical Pyrex glass reactors (D=9.0 cm h=4.5 cm) was used under a constant stirring (200 rpm).

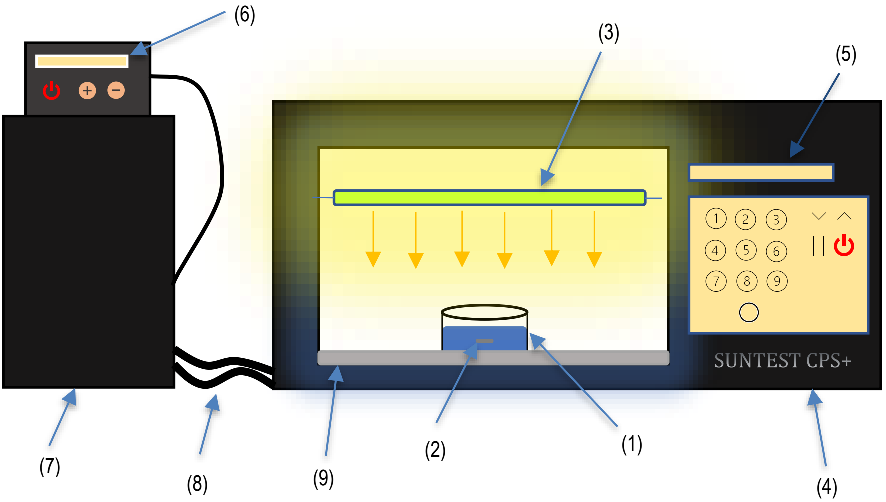


Figure 13. Experimental Device. (1) Reactor glass, (2) Magnetic stirrer, (3) Xenon Lamp, (4) Suntest CPS+, (5) Suntest controller, (6) Thermostatic bath temperature controller, (7) Thermostatic bath, (8) IN/OUT thermostatic bath, (9) Cooling plate.

4.5. EXPERIMENTAL PROCEDURE

The plants were irrigated with 1.5 L river water containing diluted pollutants. The MPs were in a concentration of 0.2 mg/L (Figure 14). Every day the water from the microcosm was recirculated and filled up to 1.5L (water was absorbed and evaporated) with tap water. This was done so that the total organic carbon (TOC) and NO_2^- and NO_3^- concentrations analysed was not affected. Tap water was chosen instead of Milli-Q water because it contains several minerals that are beneficial to plant.

The MPs degradation by photo-Fenton process was measured for one hour. The iron content was set at 2.5 or 5 mg/L and the selected H_2O_2 concentrations were 25 or 50 mg/L, depending on the experiment. The tests were always performed using an optimal ratio of 1:10 for Fe(II)/ H_2O_2 (Section 5.3.1.). Samples for HLPC were taken inside the reactor at 0, 0.5, 2.5, 5, 10, 15, 20, 25, 30, 45 and 60 min. About 3 mL of each sample was taken, as 1 mL was necessary for each HLPC analysis method (Mix method and E2 method) (Table 9 and Table10). At 0 and 60 min more volume was sampled for Fe(II) and H_2O_2 initial and final determination.

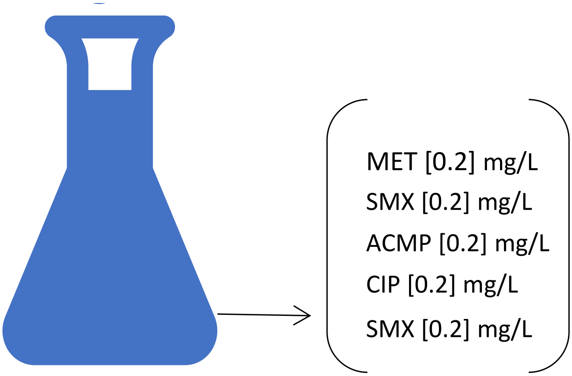


Figure 14. Irrigation water dilution's preparation

Every experiment had the following procedure:

Preparation for only AOPs tests

1. Twenty HLPC vials (ten for E2 method and ten for MIX method) for each sampling time were tagged.
2. A drop of catalase (≈ 0.1 mL) is added in each HPLC MIX vial and in each 20 mL vials for E2.
3. 1 mL of acetonitrile was added in a 10 mL vial for E2 and was closed to avoid evaporation.
4. Preparation of Fe- Ethylenediaminetetraacetic acid (EDTA) solution, A solution containing Fe-EDTA concentration of 50 mg/L was prepared with river to prevent the water matrix dilution.

5. Preparation of Fe-diethylenetriaminepentaacetic acid (DTPA) solution, A solution containing Fe-DTPA concentration of 50 mg/L was prepared with river to prevent the water matrix dilution.
6. Preparation of MPs solutions with Fe-EDTA and Fe-DTPA. A 200 mL water river solution was prepared containing 0.20 mg/L of MET, ACMP, CIP, E2 and SMX, and 1.25 mg/L of Fe-DTPA and 1.25 mg/L of Fe-DTPA.
7. A volume of 150 mL of the solution above was separated and introduced into the reactor.
8. The remaining 50 mL are to sample MPs and Fe at time 0. Once the experiment is set, only 10% of volume from the reactor can be taken to not affect the volume/radiation ratio.
9. After the addition of the solution, the reactor was heated up to 22 ºC.
10. The Suntest device was set to 500W/m^2 and 60 minutes.
11. The reactor was agitated and homogenized with a magnetic stirrer.
12. 25 mg/L of H_2O_2 was added to the reactor and immediately the Suntest and the timer started.
13. For each sampling time, 3mL were taken using a syringe.
14. From these 3 mL, 1 mL of sample was passed through a 0.45µm syringe filter to the HLPC MIX vial. This vial was then analysed with the MIX method in HLPC (Table 9).
15. The rest of the sample was added into a vial containing catalase.
16. 1 mL of sample from this vial was taken and transferred into a 10 mL vial containing acetonitrile with a dilution factor of 50%.
17. From the acetonitrile vial, a volume of 1.5 mL was taken and was passed through a 0.45 µm syringe filter to the HPLC E2 vial. This sample was then analysed following the E2 method in the HLPC (Table 10).
18. The steps 13-17 are repeated for each sampling time.
19. After 60 minutes, the experiment finalized by turning off the light, disconnecting the thermostatic bath and the agitation.

20. Fe and H_2O_2 determination were done as explained in section 4.3.2 and 4.3.3 respectively.

Preparation of Hybrid system experiments:

1. The first five steps from only AOPs procedure were repeated.
2. Preparation of the solution of outlet water from CWs with EDTA and DTPA. A 200 mL solution containing 1.25 mg/L of Fe-EDTA , 1.25 mg/L of DTPA-Fe and the outlet water from CWs in a 200mL volumetric flask.
3. The 7-20 steps from only AOPs were repeated.

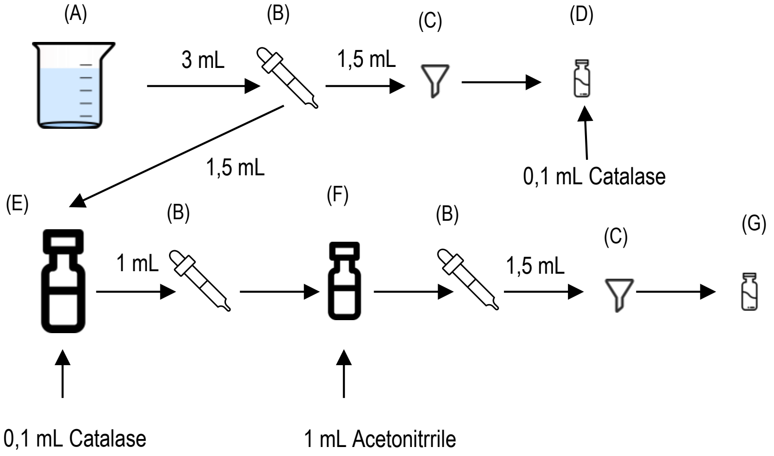


Figure 15. Experimental procedure of AOPs. (A) Reactor glass, (B) Plastic syringe, (C) Syringe filtre, (D) HLPC MIX vial, (E) 20 mL vial, (F) 10 mL vial, (G) HLPC E2 vial.

5. RESULTS AND DISCUSSION

5.1. PREVIOUS CONTROL AND TEST

5.1.1. Adsorption tests

The removal of MPs from CWs is mainly performed by the absorption of the pollutant by plants. After absorption, MPs are removed by biological processes. However, MPs can be adsorbed by different materials present in CW or used during the analysis, such as the plastic container, HLPC filters or syringes.

The partition coefficient P is the ratio between the concentrations of a substance in the two phases of the mixture formed by two immiscible solvents in equilibrium. This coefficient therefore measures the differences in solubility of a substance in these two solvents. It indicates the hydrophilic or hydrophobic character of a substance.

The partition coefficient between n-Octanol and water is known as the n-octanol-water partition coefficient, or K_{OW}.

$$K_{ow} = \frac{C_{op}}{C_w} \tag{5.1}$$

Where Cop and Cw are the concentrations, in g/L, of the species in the octanol-rich phase and in the water-rich phase respectively [53]. If the value is above one, the substance is lipophilicity i.e. soluble in fats and lipids solvents. On the other hand, if the value is below one the substance is hydrophilic i.e. soluble in water. Within the MPs selected the E2 was the only one with a log K_{OW} higher than one, thus it should be insoluble in water.

5.1.1.1. Adsorption of MPs from the plastic wetland

The adsorption was measured every 24 hours for each MP. To do this, plastic pieces from the CWs (the container in which the plant was grown) were placed in a bottle containing each MP at 0.2 mg/L. In total, five bottles were prepared, each containing one MP. The concentration of the MPs in the bottle was measured on a daily basis. On all the days for all MPs the concentration decreased less than 5%, meaning that there was hardly any adsorption of MPs from the plastic material.

5.1.1.2. Adsorption of MPs from plastic syringe

MPs were not adsorbed by the syringe used in the experiments

5.1.1.3. Adsorption of MPs from HLPC filter

At first, the adsorption was studied in a nylon filter of 0.22 µm. It presented a value close to 5.00 % of adsorption in all MPs except for E2, where everything was adsorbed. The nylon filter of 0.45 µm was also studied, and the adsorption percentage of E2 was reduced to 42.00 %. This value was still high. That is why it was decided to make a 50:50 dilution with acetonitrile before filtering to avoid this adsorption of E2 in the filter. As a result, only 5.00 % of E2 adsorption was obtained when passing that pollutant through a nylon filter of 0.45 µm which was valid for experiments.

5.1.2. Photolysis control

The MPs could be degraded by sunlight. Therefore, it was carried out a photolysis test. This experiment was made by following the same steps as for a photo-Fenton experiment (Section 4.4.2) without adding Fe-Complex and H_2O_2. Catalase was added to keep the same minimum dilutions in all samples for the HPLC analysis. However, the enzyme would not have any effect as there is no chemical reaction happening due to the absence of reactants (e.g. H_2O_2). In Figure 16. it is presented the removal of each MP by simulated solar light.

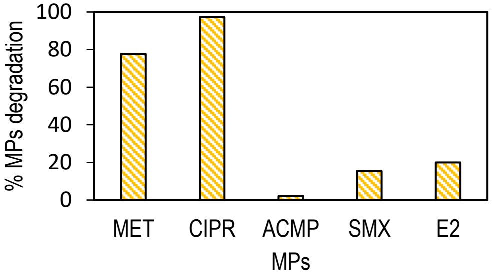


Figure 16. MPs abatement by photolysis. Power (P)=500 W/m2. $[ACMP]_0$= $[SMX]_0$ = $[E2]_0$= $[CIPR]_0$ = $[MET]_0$=0.2 mg/L

The antibiotics CIPR and MET were the most affected by photolysis (Figure 16). CIPR was degraded by 97.30 % while MET by 77.30 %. On the other hand, solar radiation hardly affected to ACMP, only 2.00 % was degraded. These values are logical as we know the absorbance of MPs for each wavelength (Figure 17) in the Suntest ranges, in wavelength between 290 and 400 nm. MET and CIPR are the only ones containing its wavelengths peak within this rage. Shorter wavelengths exhibit greater energy than longer wavelengths, which could explain why CIPR degradation is 20.00 % higher than MET.

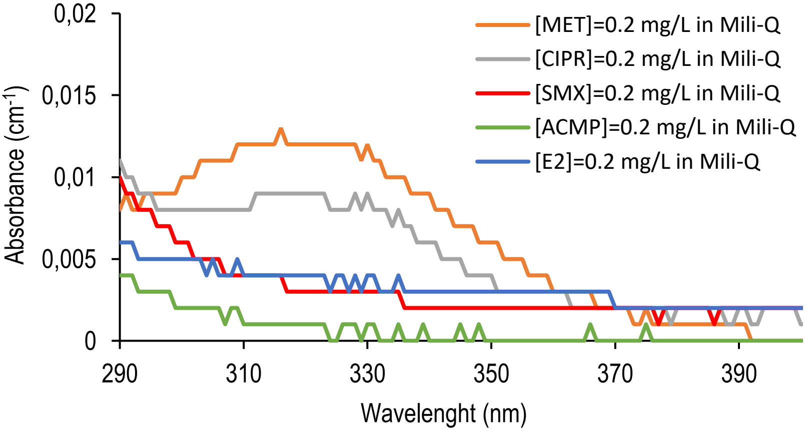


Figure 17. Absorbance vs wavelength between 290-390 nm. P = 500 W/m^2. $[ACMP]_0$= $[SMX]_0$ = $[E2]_0$= $[CIPR]_0$ = $[MET]_0$=0.2 mg/L

This would also explain why ACMP was hardly removed. Its absorbance in Suntest wavelengths is almost zero.

5.1.3. H_2O_2 + hv control

Regarding the effect of H_2O_2 and irradiation MPs removal, the second order reaction rate constant (M^{-1} s^{-1}) of the hydroxyl radical reaction with a compound i, is the limiting factor to consider. H_2O_2 absorbs at a maximum wavelength of 250 nm when the reaction took place (5.2).

$$H_2O_2 + hv \rightarrow 2HO^{\bullet} \qquad 5.2$$

The two-hydroxyl radical formed during this reaction can attack any type of substance depending on its hydroxyl radical rate constant. As the Suntest works in wavelengths between 290 and 400 nm (above the maximum wavelength of H_2O_2) not many hydroxyls radical should be generated. The few radicals released attack mostly CIPR and SMX 100.00 % and 30.86 % of degradation respectively, as these are the MPs with a higher constant rate (Table 11). CIPR degradation is completed with H_2O_2 and photolysis while SMX degradation doubles its value compared to only photolysis. In the case of ACMP, degradation increases up to 150.00 % compared to only photolysis. The major part of ACMP degradation, is due to hydroxyl radical as H_2O_2, competed for solar radiation which does not occur in the photolysis control (Figure 18). The degradation of this contaminant by photolysis was only 2.07 % but in H_2O_2 control was twice bigger 5.22 % (Table 12). This control was made as the one described above (Section 5.1.2) for photolysis, but for this case, 25 mg/L of H_2O_2 was added.

Table 11. MPs hydroxyl radical rate constant values

[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
$1.98 \cdot 10^9$ M^{-1} s^{-1}	$6.07 \cdot 10^9$ M^{-1} s^{-1}	$2.1 \cdot 10^9$ M^{-1} s^{-1}	$5.5 \cdot 10^9$ M^{-1} s^{-1}	$3.7 \cdot 10^9$ M^{-1} s^{-1}

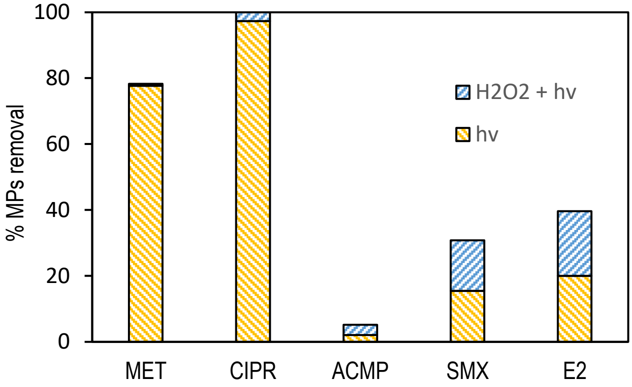


Figure 18. MPs degradation by photolysis and H_2O_2. P = 500 W/m^2. $[ACMP]_0$= $[SMX]_0$ = $[E2]_0$= $[CIPR]_0$ = $[MET]_0$=0.2 mg/L. $[H_2O_2]$=100 mg/L

5.1.4. Fe-Complex control

The removal of MPs by adding a Fe-Complex can be related to the existence of a photoexcitation of iron chelates under solar radiation, which could generate hydroxyl radicals without presence of H_2O_2 [54]. In presence of solar light, the photo redox cycle, reduces iron chelates from Fe (III) to Fe(II), that results in the generation of hydroxyl radicals (5.3) (Ligand applicable to DTPA and EDTA). This reaction is the same as photo-Fenton one without chelates, but the reaction is slow.

According to the study Lopez-Vinent [54] and co-workers the irradiation of Fe-EDTA does not affect MPs degradation. However, through photodegradation the DTPA-Fe complex gets excited following reactions (5.5-5.6). In these reaction hydroxyl radicals are release and react with the MPs resulting in their degradation.

$$Fe(III){-}Ligand + hv + H_2O \rightarrow Fe(II){-}Ligand + HO\bullet + H^+ \quad 5.3$$

$$[Fe(II) - \mathrm{DTPA}]^{2-} + O_2^{\bullet-} + 2H_2O \rightarrow [Fe(III) - \mathrm{DTPA}]^{-} + H_2O_2 + 2HO^{-} \quad 5.4$$

$$[\mathrm{Fe(III)} - \mathrm{DTPA}]^{*-} + \mathrm{O}_2 \rightarrow [\mathrm{Fe(III)} - \mathrm{DTPA}^{\bullet 3-}] + \mathrm{O}_2^{\bullet -} \quad 5.5$$

$$[\mathrm{Fe(III)}\text{-}\mathrm{DTPA}^{\bullet 3-}] + \mathrm{HO}^{-} \rightarrow [\mathrm{Fe(III)}\text{-}\mathrm{DTPA}]^{-} + \mathrm{HO}^{\bullet} \quad 5.6$$

For DTPA, the electron transfer to molecular oxygen would proceed through the excited Fe(III)-complex ([Fe(III)-DTPA]*-). In this reaction superoxide radical (5.5) is formed, which can be involved in further reactions resulting in the production of hydroxyl radicals. However, the reduction of $[Fe(III)\text{-}DTPA]^-$ to $[Fe(II)\text{-}DTPA]^{2-}$ is possible following the reaction (5.3), and subsequent formation of H_2O_2 according to (5.4).

The evolution of MPs concentration during the experiment of Fe-Complex + hv was similar to H_2O_2 + hv experiment. This is because the degradation of MPs strongly depends on the rate constant of the hydroxyl radical (that is characteristic for each MPs). CIPR was totally degraded (Table 12). The removal of SMX was more effective using the Fe-Complex than photolysis, but it was less effective than hv + H_2O_2. This test was made according to the procedure described in section 5.5 for AOPs, but in this one H_2O_2 was not added. That is why all hydroxyl radicals formed are due to photo-excitation of Fe-Complex.

Table 12. Summary of MPs abatement for each control. P=500 W/m^2

Control	MET	CIPR	ACMP	SMX	E2
hv	77.73	97.30	2.07	15.46	20.07
H202 +hv	78.30	100.00	5.22	30.86	30.86
Fe +hv	72.75	100.00	6.5	25.50	46.61

5.1.5. Kinetics

The degradation of all the MPs studied (Figure 19) was modelled following a pseudo first order kinetics (5.1) and linearized afterwards (5.2). Figure 19 represents the fittings for the three experiments, i.e. Photolysis, H_2O_2 + hv and Fe-Complex + hv.

$$C_{MPs}=C_{MPs,o}\cdot\exp(-k\cdot t) \qquad 5.1$$

$$LN([MPs]/[MPs_0]) = kx + b \qquad 5.2$$

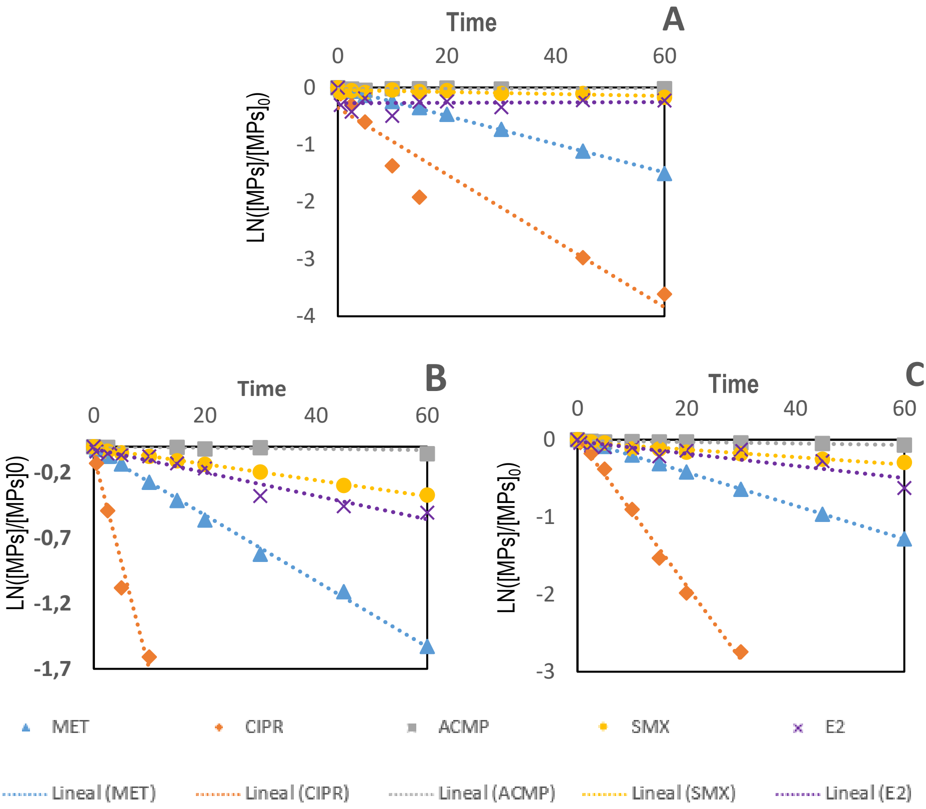


Figure 19. Pseudo first order kinetic of each MP [A] Photolysis [B] Hydrogen perxoide test, [C] Fe-Complex test

Degradation of all MPs could be modelled to the pseudo first order kinetics, however CIPR did not get a good adjust (Table 13). This is due to the fact that this MP barely decreased i.e. was not degraded during the 60 minutes of experiment, being its degradation almost constant over time. It has to keep in mind that in this study samples were analysed only once. Therefore, for a better study of the kinetic more repetitions (at least two) of the measurements should be performed. In the photolysis, E2 could not modelled. However, most of the kinetics studied can be consider reliable as their coefficient of determination is > 0.9 (Table 13). As expected, the higher degradation constant rates were observed in CIPR followed by MET in the three treatments (hv, H2O2 + hv and Fe-Complex+hv).(Table 13)

Table 13. Kinetics characterization

Treatment	MPs	k (min^{-1})	Removal (%)	R^2
hv	MET	-2.47E^{-03}	77.73	9.99E^{-01}
	CIPR	-5.80E^{-02}	97.30	9.27E^{-01}
	ACMP	3.00E^{-04}	2.07	1.42E^{-01}
	SMX	-1.80E^{-03}	15.46	6.29E^{-01}
	E2		20.07	
H_2O_2 + hv	MET	-2.52E^{-02}	78.3	9.97E^{-01}
	CIPR	-1.63E^{-01}	100.00	9.72E^{-01}
	ACMP	-5.50E^{-04}	5.22	2.54E^{-01}
	SMX	-9.00E^{-03}	30.86	9.52E^{-01}
	E2	-6.10E^{-03}	39.65	9.96E^{-01}
Fe-Complex + hv	MET	-2.16E^{-02}	72.75	1.00E^{+00}
	CIPR	-9.54E^{-02}	100.00	9.94E^{-01}
	ACMP	-1.00E^{-03}	6.5.00	8.76E^{-01}
	SMX	-4.90E^{-03}	25.50	9.37E^{-01}
	E2	-7.90E^{-03}	46.61	8.12E^{-01}

5.1.6. CWs control

Part of MPs decrease could also be related to the adsorption and the evaporation in the microcosm. This was studied by weighting the container and measuring the water each day for 5 days. The microcosm lost 100 g every 24 hours. Furthermore, the water retained by the sand and the substrate could be considered negligible, observing differences in the first day when sand was dried. Considering that river waters density is approx. to 1000 kg/m^3. A volume of 100 mL the water in the container was evaporated (6.66 % of total water) for 24 hours.

The degradation of MPs in the CWs without plants was also studied, showing different results among the MPs (Figure 20). Four samples 2 HRT, 4 HRT, 7 HRT and 14 HRT were analysed. E2 and CIPR were totally removed in the microcosm after 14 days. However, the trend between both pollutants was different. Whereas E2 was totally removed after the first two days, CIPR was completely degraded after seven days. This can be explained with the property of adsorption (log K_{OW}). E2 have the highest one so it was adsorbed by the rocks. However, the CIPR is not hydrophobic its log K_{OW} is below one, thus it should not be adsorbed by the microcosm. In this case, CIPR degradation may be due to photolysis. CIPR was the most removed MPs in photolysis control (Figure 16). The container was not completely covered with aluminium foil. In the top layer i.e. the part was not covered, the water was saturated and this could have affected the degradation by solar irradiation.

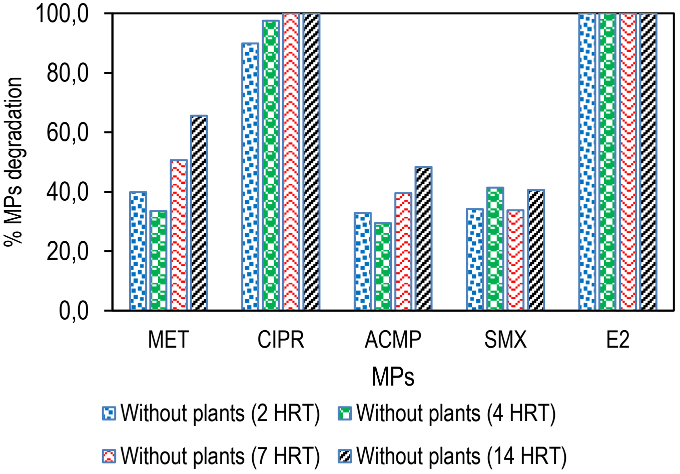


Figure 20. MPs degradation in microcosm without plants at different HRT. $[ACMP]_0 = [SMX]_0 = [E2]_0 = [CIPR]_0 = [MET]_0 = 0.2$ mg/L

Of the remaining three MPs, MET was the one that degraded most despite having the lowest log K_{OW} of all MPs studied. For this case, it is hypothesized that the removal of pollutants can be associated to photolysis as well. No big differences were appreciated between HRTs for each MPs, which indicated that most of the degradation was achieved at the beginning (Figure

20). ACMP and SMX were most degraded after 2 HRT. After 14 HRT only 15.40 % more ACMP was removed compared after 2 HRT. SMX was only removed 6.40 % more after 14 HRT compared to 2 HRT.

5.2. CONSTRUCTED WETLAND SYSTEM

5.2.1. CWs characterization

The Microcosm have been developing throughout the study due to the biological processes occurring in the plants. Regarding the height of the plants, *P.australis* or *C.haspan* grew few centimetres (1-3 cm). In contrary to the height, there were differences in the number of sprouts. *P.australis* P1 increased from 16 to 19 sprouts (18.75 %) and in Phragmites australis P2 the quantity of sprouts increased from 24 to 30 (25.00 %). The increase was more significant in *C.haspan* C1, from 90 to 117 cm (an increase of 30.00 %) and in C2 from 91 to 130 cm (and increase of 42.00 %). At the end of the experiments the number of sprouts per square meter was approximately three times more in C1 and C2 than in P1 and P2. This means that *C.haspan* absorbed more water and resulted in a more effective biological process for the removal of MPs. At the end of the experiment, algae appeared in the container in all plant's microcosm. Bacteria and algae are known to promote the degradation of MPs in CWs. [55]

5.2.2. MPs degradation

The results from the degradation of MPs in CWs justified this study. In the presence of plants, all MPs degraded faster than without the plants indicating (Figure 20) that CWs are a useful biological process to remove MPs from ecosystems. Among MPs, E2 and CIPR were hardly removed by plants biological processes as all their degradation is due to the adsorption by rocks as seen in section 5.1.6. (Figure 21).

Table 14. MPs removal by CWs *in P.australis* and *C.haspan* after 2,4,7 and 14 HRT.

	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
P2	54.10	93.46	32.31	24.92	100.00
C2	50.90	97.50	51.04	51.61	100.00

P7	93.60	10.00	63.95	55.17	100.00
C7	92.23	100.00	80.79	74.51	100.00
P4	69.44	90.83	59.00	60.66	100.00
C4	80.16	94.86	74.66	66.00	100.00
P14	100.00	100.00	76.02	75.31	100.00
C14	100.00	100.00	100.00	100.00	100.00

On the other hand, a big amount of SMX, ACMP and MET was removed by plants (Table 14). In *P.australis* and *C.haspan* the MET removal increased by 116.00 % and by 139.00 % respectively compared to the container without the plants. But the biggest difference was observed in ACMP, in the presence of *C.haspan* the removal of this MPs increased up to 149.00 % compared to the container without the plants. SMX exhibited higher percentages of removal in both plants, but smaller than MET and ACMP (59.10 % in *P.australis* and 63.80 % in *C.haspan*. All MPs were more degraded in the presence of *C.haspan* than in *P.australis.* This is because *C.haspan* had more number of sprouts per square meter.

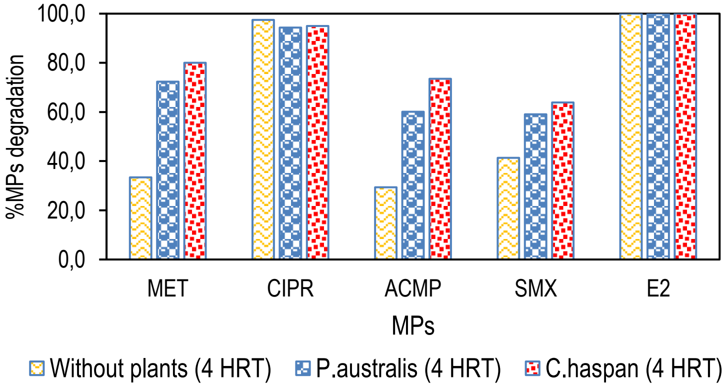


Figure 21. MPs degradation at 4 HRT in *P.Australis*, *C.Haspan* and micrccosm without plant. $[ACMP]_0$= $[SMX]_0$ = $[E2]_0$= $[CIPR]_0$ = $[MET]_0$=0.2 mg/L

An increase of MPs removal was observed after 7 HRT respect to 2 HRT in MET, ACMP and SMX. E2 and CIPR were almost completely degraded after 2 HRT. After 2 HRT different percentages of removal between *C.haspan* and *P.australis* can be appreciated for the contaminants ACMP and SMX (Table 14). However, this percentage is similar after 7 HRT for the five MPs. At the beginning of the experiment, the number of sprouts per square metre was a limiting factor as the environment was not established and plants could not absorb much. After 2 HRT, ACMP was removed by 32.30 % in the presence of *P.australis* and 51.40 % when *C.haspan* was present (Figure 22). However, in the control made without plants, ACMP degradation was 29.40% (Figure 20). This means that plants require time to absorb MPs.

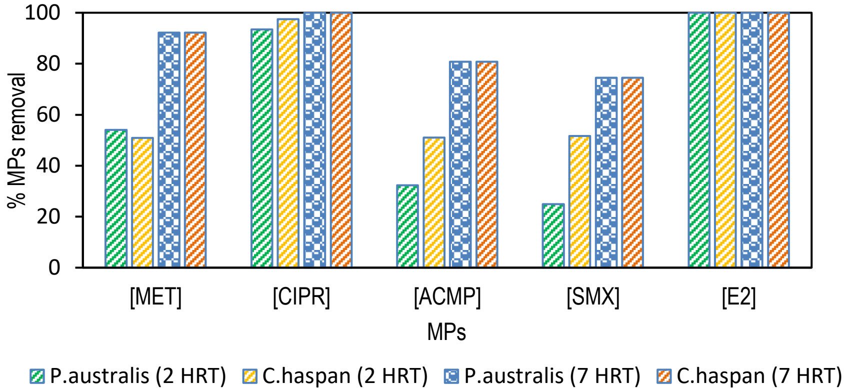


Figure 22. MPs degradation in 2 HRT and 7 HRT. $[ACMP]_0 = [SMX]_0 = [E2]_0 = [CIPR]_0 = [MET]_0 = 0.2$ mg/L

5.3. ADVANCED OXIDATION PROCESS SYSTEM

5.3.1. Reagents concentration selection

An appropriate ratio between iron (II) and H_2O_2 concentrations is essential to maximize the HO• production, so that the performance of the oxidation process improves. A higher concentration of Fe (II) and H_2O_2 results in a higher hydroxyl radical generation [56]. The ideal concentration ratio of reagents depends on the effluent's characteristics. For instance, 5 mg/L is the maximum concentration of iron emission in irrigation permitted by international regulations. [57]

In this work a ratio of 1:10 (Fe:H_2O_2) was chosen in accordance with the study of López-Vinent and co-workers [58] where the optimal concentration were 10 mg/L and 150 mg/L for Fe (II) and H_2O_2 respectively. According to this ratio, HO• production was assured without limiting the reactants and avoiding the scavenging of hydroxyl radicals by H_2O_2. Figure 23 shows the MPs abatement by photo-Fenton using different H_2O_2 and Fe-Complex concentrations with a ratio of 1:10 (Fe:H_2O_2).

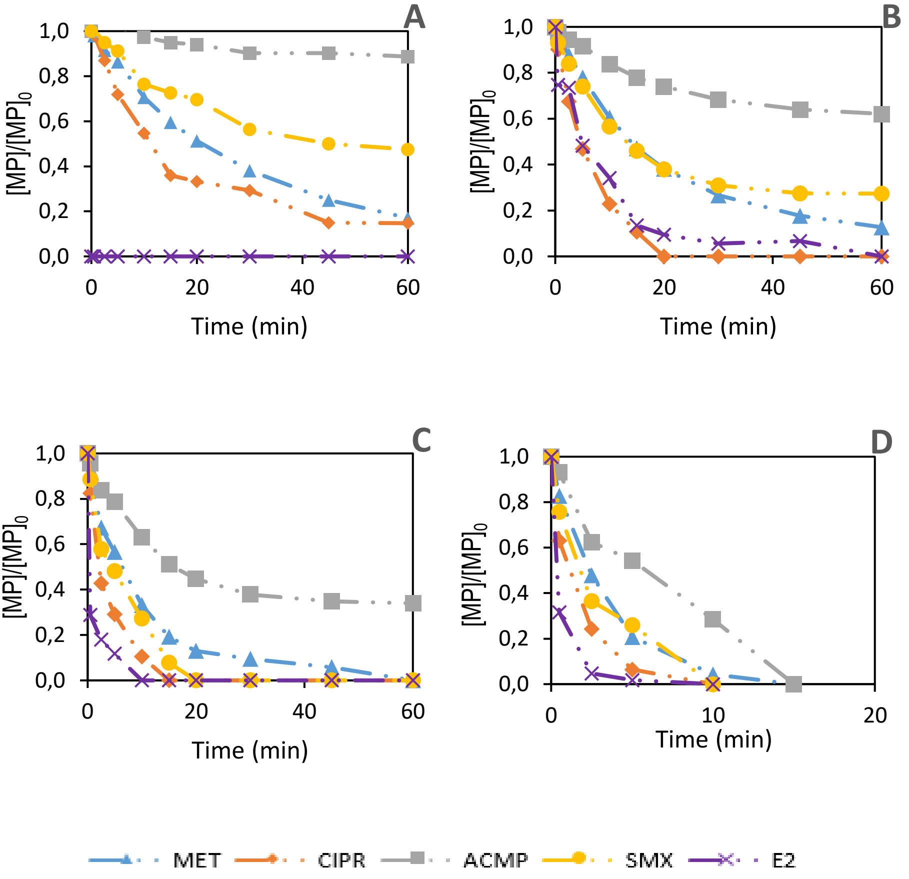


Figure 23. MPs degradations by photo-Fenton at neutral pH using a mixture of EDTA-DTPA-Fe at (A) [Fe-EDTA-DTPA]=1.25 mg/L [H_2O_2]=12.5 mg/L, (B) [Fe-EDTA-DTPA]]=2.5 mg/L [H_2O_2]=25 mg/L, (C) [Fe-EDTA-DTPA]=5 mg/L [H_2O_2]=50 mg/L, (D) [Fe-EDTA-DTPA]=10 mg/L [H_2O_2]=100 mg/L. Suntest power = 500 W/m^2 . $[ACMP]_0$= $[SMX]_0$ = $[E2]_0$= $[CIPR]_0$ = $[MET]_0$=0.2 mg/L

As it was expected, in the experiments with a major concentration of reagents a faster and higher removal of MPs was observed (Figure 23). In Figure 23 D, it can be observed that all the MPs were eliminated in the first 15 minutes when the concentration of the reagents was the highest ([Fe-Complex] =10 mg/L [H_2O_2] =100 mg/L). In Figure 23 C almost all MPs (except for ACMP) were removed after 60 minutes. These results indicate that AOP processes are useful for removing MPs but only when using high concentrations of reactants. This is the reason why the combination of both AOP and CWs processes could be advantageous in reducing the reagents of AOP while achieving a complete MPs removal. Using lower amounts of reagents would also minimize the environmental impact. Based on these results, we chose a concentration of [Fe-Complex]=2.5 mg/L and [H_2O_2]=25 mg/L.

5.3.2. Power selection

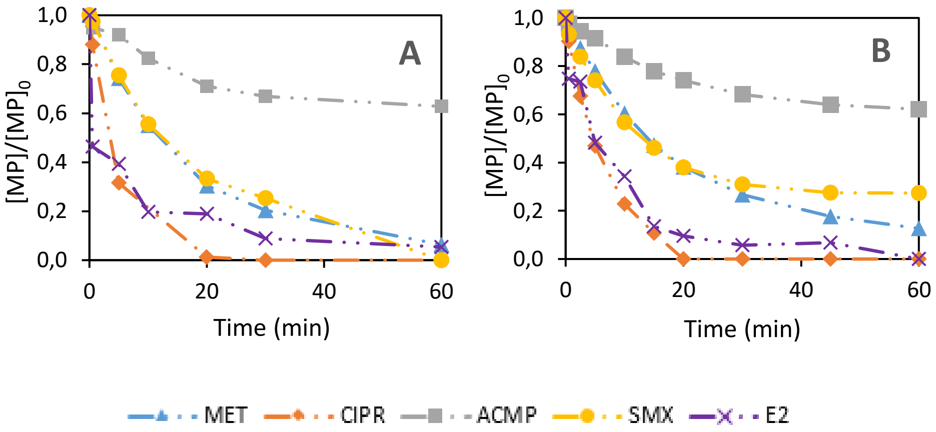


Figure 24. MPs degradations by photo-Fenton at neutral pH using a mixture of EDTA-DTPA-Fe at (A) P = 765W/m^2, (B) P=500 W/m^2. [Fe-EDTA-DTPA]=2.5 mg/L, [H_2O_2]=25 mg/L [ACMP]$_0$= [SMX]$_0$ = [E2]$_0$= [CIPR]$_0$ = [MET]$_0$=0.2 mg/L

In Figure 24 is observed how the behaviour of each MPs is practically the same at different power of Suntest. This could be due to the fact that the system is saturated with radiation, then the power is not a limiting factor.

The power of 500 W/m^2 was selected instead of 765 W/m^2 as the efficiency was the same, but Fe precipitation was lower (Figure 25). The lower Fe precipitation, the less environmental impact. The catalytic action may be another factor that alters precipitation. The higher iron chelate may be beneficial for the reuse of WW in agriculture. At 500 W/m^2 there was less Fe precipitation, what it means there is more Fe reacting and consequently more catalytic action.

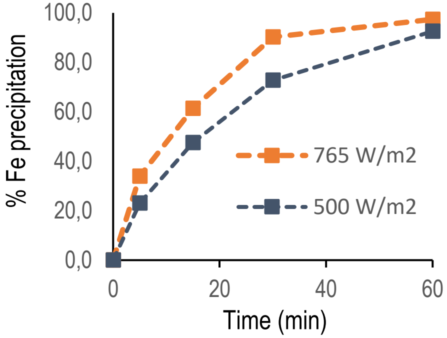


Figure 25. Comparation of Fe precipitation between 765 W/m^2 and 500 W/m^2 working power. [Fe-EDTA-DTPA]=2.5 mg/L. [H_2O_2]=25 mg/L. [MP]$_0$=0.2 mg/L. [ACMP]$_0$= [SMX]$_0$ = [E2]$_0$= [CIPR]$_0$ = [MET]$_0$=0.2 mg/L

5.3.3. MPs degradation

Once we selected the appropriate factors in the AOPs method, the effectivity of this method for removing MPs can be discussed. CIPR and E2 were totally removed by AOPs (Figure 23 B). CIPR degraded the fastest, after 20 minutes. This result was expected as in the previous controls (Photolysis, H_2O_2, Fe-Complex) it was the only MPs that degraded completely. On the other hand, E2 in the previous control was not much degraded, its maximum degradation was observed in Fe-Complex + hv control achieving a 46.60 % degradation (Table 12). This means that its degradation by the photo-Fenton method was 114.59 % higher compared to the Fe-Complex + hv experiment. This increase can be related to the higher hydroxyl radicals release in photo-Fenton process than in the previous controls. E2 did not absorb much at the Suntest wavelength, therefore is hypothesized that its degradation is mainly from hydroxyl radicals. MET had the lowest hydroxyl radical rate constant. That is why in photo-Fenton process it was not totally degraded (87.00 %), despite 78.00 % being removed in the photolysis control. MET was degraded by the photo-Fenton process only 11.00 % more in compared with the photolysis experiment. ACMP was the MP with the lowest degradation in the photo-Fenton (37.89 %), but it was much higher comparing with its degradation in the previous controls (Table 12). In Fe-Complex + hv experiment ACMP degradation was the highest (6.50 %), thus its removal by photo-Fenton increased 582.00 % compared to the Fe-Complex + hv experiment. SMX degradation was 72.60 % when using the photo-Fenton process, but in none of the previous control was higher than 30.00 %. Its higher removal using the AOP process can be related to the higher hydroxyl radical's formation as it has one of the biggest rate constant.

5.3.4. AOPs Kinetics

Degradation of all MPs could be modelled to the pseudo first order Kinetics in AOPs studied at the variables selected (Section 5.1.5). ACMP had the lowest coefficient of determination (0.82). This was expected as it was degraded only by 37.89 % (Table 15). This means that the kinetics in this MPs was low, any point away from the lineal equation would make difficult to linearized. CIPR had the highest kinetic and the best fit to the model (highest R^2 value).

Table 15. Kinetics charaterization at AOP . P=500 W/m^2. [Fe-DTA-EDTA]=2.5 mg/L. [H_2O_2]=25 mg/L

	k (min $^{-1}$)	**Removal (%)**	**R^2**
MET	-0.0465	87.31	0.988
CIPR	-0.2193	100.00	0.999
ACMP	-0.0078	39.89	0.825
SMX	-0.0475	72.66	0.982
E2	-0.0989	100.00	0.964

5.3.5. Fe precipitation and H_2O_2 consumption

The precipitation of iron in the photo-Fenton experiment was close to 90.00 % after 60 minutes. In Figure 23 B, it can be observed how the MPs are not more degraded after 40 minutes. This is related to the iron precipitation. Iron precipitation was 63.40 % after 30 minutes, thus there is less catalytic action and consequently less HO• appear to attack the MPs. H_2O_2 was degraded a 46.66 % by photo-Fenton with the optimal reagents concentration.

5.4. HYBRID SYSTEM

The Hybrid system combining CWs and AOPs processes showed an effective removal of MPs in the presence of both plants i.e. *P.australis* and *C.haspan* (Table 16). CIPR, SMX and E2 were totally degraded after 2 HRT. Nonetheless, MET removal took place after 4 HRT in the presence of C.Haspan and after 7 HRT in P.australis. ACMP was the pollutant that showed the highest resistance to degradation. It can be seen in Table 14 that this contaminant was only degraded completely two weeks later after being added. These results could be expected based on the outcome of section 5.3 3. were ACMP was not degraded to a big extent by AOPs (37.98 %) compared to the other MPs. Moreover, ACMP was only degraded 80.00 % at 7 HRT in the presence of both plants (Table 16). Therefore, a slow degradation could be expected in this pollutant when using a hybrid system.

Table 16. MPs degradation in hybrid systems at differents HRT in the presence of the plants *C.haspan* and *P.Austrlius*. C2 =2 HRT in *C.haspan*. P2= 2 HRT in *P.australis*. C4 =4 HRT in *C.haspan*. P4= 4 HRT in *P.australis*. C7 =7 HRT in *C.haspan*. P7= 7 HRT in *P.australis*. C14 =14 HRT in *C.haspan*. P14= 14 HRT in P.australis.

HRT	**% REMOVAL**				
	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
C2	96.15	100.00	76.98	100.00	100.00
C4	100.00	100.00	79.10	100.00	100.00
C7	100.00	100.00	83.77	100.00	100.00
C14	100.00	100.00	100.00	100.00	100.00

P2	93.56	100.00	53.80	100.00	100.00
P4	93.98	100.00	67.92	100.00	100.00
P7	100.00	100.00	76.21	100.00	100.00
P14	100.00	100.00	100.00	100.00	100.00

After 2 HRT, in *C.haspan* all MPs showed at least 50.00 % of degradation(Figure 26 A).For the same hydraulic retention time, in *P.australis* the pollutants degraded slower.

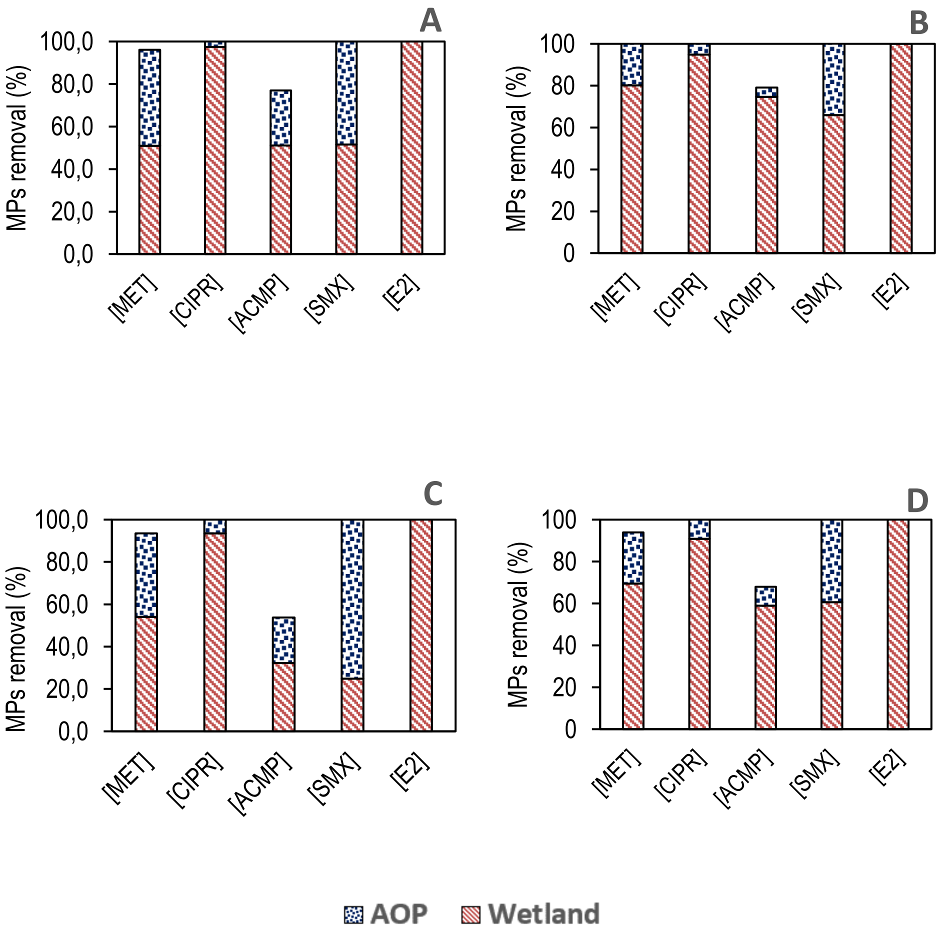


Figure 26. Percentage of removal in a hybrid system for CWs and AOPs in the presence of (A) *C.haspan* 2 HRT. (B) *C.haspan* 4 HRT. (C) P.*australis* 2 HRT (D) *P.australis* 4 HRT.

When the AOPs process was applied after 2 HRT, the degradation of MPs in the hybrid system i.e. *P.australis*-Photo-Fenton and *C.haspan*-Photo-Fenton was similar in the presence of both plants. Contrary, in the absence of AOPs process, the degradation of MPs was higher in *C.haspan*. SMX and ACMP were degraded at least 45.00 % in the presence of *C.haspan*, but when *P.australis* was present none of these MPs were degraded above 36.00 % (Figure 26 A-C).

SMX and CIPR were totally degraded by combining both processes i.e. CWs and AOPs (Figure 26 A). When SMX was degraded in the hybrid system, AOPs process had more influence on removing than CWs. However, in CIPR most of the removal was due to the CWs process. MET could not be totally degraded in the presence of any plant. After 2 HRT, MET removal was distributed equally between photo-Fenton and the plants microcosm. E2 was totally degraded after 2 HRT, that is why AOPs was not necessary for this contaminant. ACMP, as expected seeing the results of CWs and AOPs experiments (Section 5.2.2. Section 5.3.3. respectively), had the lowest degradation. In *C.haspan* hybrid system and *P.australis* hybrid system, ACMP was degraded by 77.00 % and by 54.00 % , respectively after 2 HRT (Table 17). CWs system resulted in a higher degradation of the studied contaminants than AOPs for ACMP in the presence of both plants. 10.00 % more in the presence of *C.haspan* and 37.00 % in *P.australis.*

Regarding the results of MPs removal obtained after 4 HRT, the results are similar to the 2 HRT. However, in this time the hybrid system between *C.haspan* and photo-Fenton achieved a total removal of MET (Figure 26 B). The MPs degradation was similar (in percentages of removal) after 2 HRT in the hybrid system. However, after 4 HRT when using CWs, the degradation was higher as compared to AOPs for all MPs in both hybrid systems. When the HRT increased, the effectivity of CWs for removing the MPs in the hybrid system increased as well (Figure 26 C-D).

After 7 HRT, in the *C.haspan* microcosm all contaminants were totally degraded, except ACMP (Table 17). After applying a photo-Fenton process, the degradation of this pollutant was 83.77 %. On the other hand, after 7 HRT in the presence of *P.australis*, E2, SMX and CIPR were completely degraded. MET was 100% removed when applying photo-Fenton. Nevertheless, after applying photo-Fenton ACMP was degraded 76.21 %. After 14 HRT all MPs were completely degraded in the presence of both plants. However, in the presence of *P.australis* a photo-Fenton method was necessary to remove ACMP completely (Table 17).

Table 17. Time to achieve 100% MPs removal in the hybrid system,

Ranking	MPs-Plant	Time
1.	E2-*C.haspan*	2HRT
2.	E2-*P.australis*	2HRT
3.	CIPR-*P.australis*	2 HRT + 2.5 min
4.	CIPR-*C.haspan*	2 HRT + 5 min
5.	SMX-*C.haspan*	2 HRT + 5 min
6.	SMX-*P.australis*	2 HRT + 30 min
7.	MET-*C.haspan*	4 HRT + 45 min
8.	MET-*P.australis*	7 HRT + 15 min
9.	ACMP-*C.haspan*	14 HRT
10.	ACMP-*P.australis*	14 HRT + 15 min

Table 17. shows the ranking of the fastest MPs to be completely removed in the hybrid system. The results are expected as they are related to Figure 26 where it can be seen that E2, CIPR and SMX were totally removed after 2 HRT. E2 degradation is the fastest because it was adsorbed in bigger amounts by the microcosm, especially by the rocks (Section 5.1.6). In contrast, the absorption by plants of this MP is much slower. CIPR exhibited the second fastest degradation. In this case the hybrid system with the presence of *P.australis* resulted in the most effective degradation process. However, in only CWs, CIPR was degraded faster in the presence of *C.haspan* than in the presence of *P.australis* (Figure 26 A-B). ACMP degradation took 14 HRT to be totally removed, but when *P.australis* was present besides of 14 HRT, additional 15 min of photo-Fenton was necessary to remove the contaminant.

The hybrid system combining 4 HRT in the presence of *C.haspan* and an additional photo-Fenton, showed better removal results than only photo-Fenton with double reagents concentration. This mentioned hybrid system removed completely all pollutants, except ACMP that was degraded by 79.10 %. The photo-Fenton process with the double concentration of reagents showed high percentages of removal for all MPs, except for ACMP. In this experiment, the contaminant was not completely degraded (66.05 %). This means that ACMP was degraded 12.60 % more when the hybrid system was used as compared to only photo-Fenton. Furthermore, the hybrid system mentioned above showed better removal results than in only CWs after 7 HRT in the presence of *C.haspan* (Figure 27). The presence of *C.haspan* could absorb completely MET and E2 after 7 HRT. ACMP was degraded 80.79% in the CWs, an identical value as in the mentioned hybrid system.

Consequently, it is demonstrated that when the two methods are combined better removal results were obtained. In this way, less reagents concentration can be used in the photo-Fenton method. Next to this, the HRT can be reduced in the CWs.

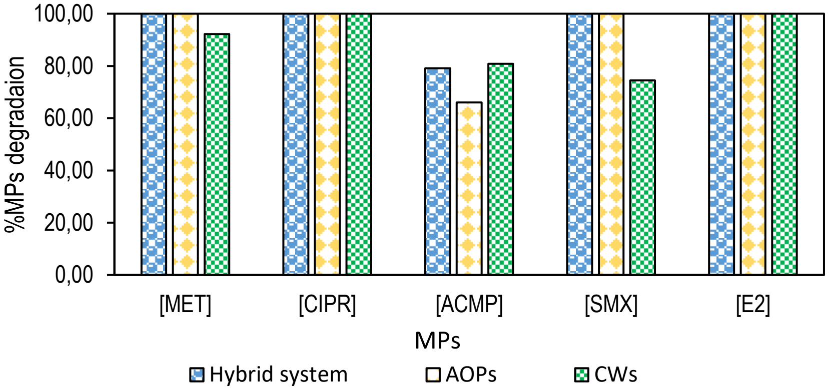


Figure 27. MPs removal in a hybrid system (4 HRT in *C.haspan* $[H_2O_2]$ = 2.5 mg/L [Fe-Complex] = 25 mg/L). AOPs $[H_2O_2]$ = 2.5 mg/L [Fe-Complex] = 25 mg/L). CWs (7 HRT in *C.haspan*)

As ACMP could not be completely removed at lower HRT in the hybrid system, the effect of increasing reagents concentration was studied to improve its removal. This was done by increasing the reagents concentrations i.e. H_2O_2 and Fe-Complex twice. $[H_2O_2]$ = 50 mg/L and [Fe-Complex] = 5 mg/L maintaining the ratio [Fe (II)] / $[H_2O_2]$ (Section 5.3.1).

Duplicating the reagents concentration enhanced MPs degradation in AOPs and in the two-hybrid system in the presence of the two plants. It should be emphasized that the removal of

ACMP in the hybrid system of the *C.haspan*, was completed after 2 HRT (Figure 28). There is also a significant increase of this MP removal in the experiment using the AOP method with high reagents concentration. Removal of 66.00% for ACMP was achieved using a higher concentration of reagents ($[H_2O_2]$ = 50 mg/L and [Fe-Complex] = 5 mg/L).

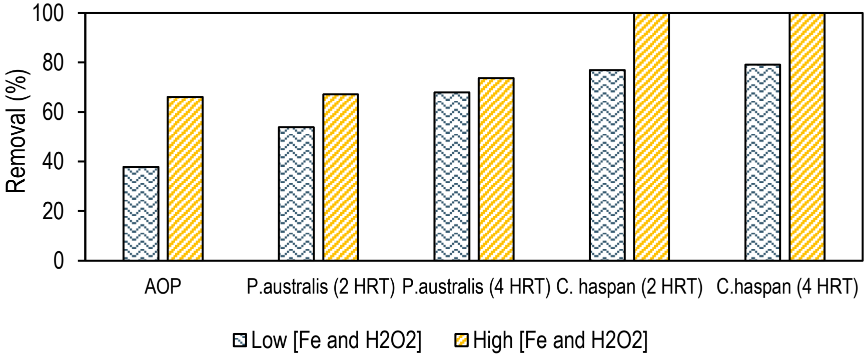


Figure 28. ACMP degradation at different reagents concentration. Low concentration; $[H_2O_2]$ = 2.5 mg/L [Fe-Complex] = 25 mg/L $[H_2O_2]$ = 50 mg/L [Fe-Complex] = 5 mg/L. $[ACMP]_0$=0.2 mg/L

When the concentration of these reagents was two times lower, only 38.00% of ACMP was degraded. Furthermore, in the hybrid system with the presence of *P.australis* big changes were not observed in the percentages of removal in any of the hybrid systems.

6. CONCLUSIONS

This study showed that both processes, CWs and AOPs could be useful methods with high efficiency to remove ACMP, MET, SMX, CIPR and E2 from river water and reuse the resulting water for aquaculture.

CWs require much more time compared with AOPs. After 7 HRT a degradation of at least 75% was achieved for all the contaminants. This is a long time to apply on a large scale. On the other hand, after 2 HRT MET, ACMP and SMX showed degradation below 55% in the presence of both plants. *C.haspan* was the plant with highest number of sprouts and removed faster the contaminants studied. In the presence of *C.haspan*, took 4 HRT to degrade all MPs at least by 65%. However, for the same time (4 HRT) P.*australis* could only remove that amount (65 %) in MET, CIPR and E2.

Among the micropollutants studied, ACMP was the most difficult to remove by the wetland as is a recalcitrant contaminant and presents low hydrophobicity. That is why it was important to select pollutants with different properties to study the efficiency of different processes.

Regarding AOPs, it has been demonstrated that increasing the reagents concentrations, [H_2O_2] and [Fe-Complex], a higher MPs removal was obtained. However, reagents economical costs are the highest of the system. The iron concentration in agriculture water can not exceed a concentration of 5 mg/L. Successful removals (>70%) for all the contaminants were observed by applying the photo-Fenton method using a concentration of 25 mg/L of H_2O_2 and 2.5 mg/L of Fe-Complex. ACMP was an exception as only 37.89% of it was degraded. This is because the photo-Fenton process is more effective with contaminants that have a bigger hydroxyl radical rate constant and wavelengths close to 290-400 nm where solar irradiation exhibits greater energy.

Concerning the hybrid system that combines the use of plants and the photo-Fenton processes (at a concentration of 25 mg/L for H_2O_2 and 2.5 mg/L for Fe-Complex) it took 4 HRT to have a complete degradation in all micropollutants except ACMP (79.1%). This high removal was also observed in only photo-Fenton but when the reagents concentration was two times higher. Nonetheless, in the solar-Fenton process AMCP could be only degraded by 47.66%. This means that the hybrid system resulted in 31.44% more of ACMP removal compared to the photo-Fenton process alone (with double concentration of reagents).

In summary, the hybrid system that combines constructed wetlands and photo-Fenton processes is the most effective system to remove contaminants from wastewater. Moreover, hybrid system could result in a more economic and sustainable method compared with only CWs or AOPs.

7. FUTURE PERSPECTIVES

It has to keep in mind that this work was performed at lab scale and therefore to confirm the effectivity of the hybrid system the study should be performed in a larger scale using different types of container material and different ratio between length and surface. Next to this, in this study only two plants *C.haspan* and *P.australis* were tested. It would be interesting to evaluate the efficiency of other plants for the removal of the studied MPs. For example, *Cordyline fruticosa* and *Hibiscus syriacus* have been reported to be able to remove pesticides such as imidacloropid [59]. In a future work, different types of MPs such as industrial compounds or pharmaceuticals could be tested to evaluate the efficiency of the hybrid system.

Finally, from an economic and sustainability point of view, a Life-Cycle assessment should be performed to see if the hybrid System is more economic and sustainable than CWs and AOPs by separate.

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ACRONYMS

(ACMP)	Acetamiprid
(AOPs)	Advanced Oxidation Processes
(CIPR)	Ciprofloxacin
(CW)	Constructed wetland
(DTPA)	Diethylenetriaminepentaacetic acid
(E2)	Estradiol
(EQSs)	European Environmental Quality Standards
(EDTA)	Ethylenediaminetetraacetic acid
(FAO)	Food and Agriculture Organization of the United Nations
(H_2O_2)	Hydrogen Peroxide
(HO•)	Hydroxyl radicals
(HPLC)	High-Performance Liquid Chromatography
(HRT)	Hydraulic Retention Time
(K_{OW})	Octanol-water partition coefficient, dimensionless
(MET)	Metronidazole
(MPs)	Micropollutants
(PSs)	Priority Substances
(SMX)	Sulfamethoxazole
(UPW)	Ultrapure Water
(WFD)	Water Framwork Directive
(WWTP)	Wastewater Treatment Plant
(WW)	Waste Water

APPENDICES

APPENDIX 1: RESULTS OF MPS DEGRADATION FROM HPLC AND IRON PRECIPITATION FROM SPECTROPHOTOMETER

The results of MPs degradation were obtained from the HPLC analysis, by reading the value of the area of each MPs at their retention time. Iron precipitation data was obtained from the absorbance values from the spectrophotometer for each sample.

Table 18. Experiment 1. MPs degradations by photo-Fenton at neutral pH using a mixture of EDTA-DTPA-Fe at P = 765 W/m^2 [Fe-EDTA-DTPA]=2,5 mg/L, [H_2O_2]=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	277,52	761,96	595,52	435,97	2203,8
0,5	273,05	670,51	565,29	424,98	1022,06
5	206,31	240,21	547,52	329,3	866,96
10	152,92	-	490,5	242,13	435,16
20	84,53	9,36	422,96	144,88	415,94
30	56,56	0	398,37	110,58	194,22
45					118,32
60	17,51	0	373,81	0	0

Table 19. Experiment 2. MPs degradations by photo-Fenton at neutral pH using a mixture of EDTA-DTPA-Fe at P = 765 W/m^2 [Fe-EDTA-DTPA]=5 mg/L, [H_2O_2]=50 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	299.98	809.74	621.52	476.27	1308.54
0.5	272.72	652.84	580.31	410.11	672.56
2.5	212.81	360.36	532.6	306.64	384.74
5	156.48	179.02	467.87	203.65	148.7
10	83.08	59.47	365.95	0	0
15	50.59	0	300.95	0	0
30	22.36	0	222.06	0	0
45	15.29	0	207.89	0	0
60	0	0	203.08	0	0
90	0	0	206.09	0	0
120	0	0	205.1	0	0

Table 20. Experiment 3. MPs degradations by photo-Fenton at neutral pH using a mixture of EDTA-DTPA-Fe at P = 500 W/m^2 [Fe-EDTA-DTPA]=5 mg/L. [H_2O_2]=50 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	234.78	822.75	492.31	389.31	1828.74
0.5	213.84	677.54	470.87	344.89	525.52
2.5	157.98	351.2	412.55	224.92	327.52
5	132.87	238.73	386.49	187.08	214.92
10	77.7	86.29	310.15	105.68	0
15	44.95	0	251.58	30.3	0
20	30.4	0	219.96	0	0
30	22.28	0	186.28	0	0
45	13.49	0	171.24	0	0
60	0	0	167.14	0	0

Table 21. Experiment 4. MPs degradations by photo-Fenton at neutral pH using a mixture of EDTA-DTPA-Fe at P = 500 W/m^2 [Fe-EDTA-DTPA]=2.5 mg/L. [H_2O_2]=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	237.4	823.88	485.58	381.29	1702.9
0.5	229.7	743.93	473.79	355.1	1272.74
2.5	207.77	556.69	458.79	319.94	1251.9
5	185.05	386.03	444.96	282.3	820.78
10	143.53	188.19	406.99	216.14	582.42
15	112.06	88.93	378.25	175.55	230.62
20	90.78	0	359.75	144.63	161.78
30	63.35	0	331.53	117.86	96.34
45	42.05	0	310.82	104.58	114.84
60	30.12	0	301.59	104.25	0

Table 22. Experiment 5. MPs degradations by photo-Fenton at neutral pH using a mixture of EDTA-DTPA-Fe at P = 500 W/m^2 [Fe-EDTA-DTPA]=1.25 mg/L. [H_2O_2]=12.5 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	303.41	962.35	481.21	363.22	936.23
0.5	297.62	946.09	504.59	364.87	690.75
2.5	277.82	836.57	493.51	344.76	615.32
5	262.26	692.18	491.51	331.15	776.56
10	214.32	527.17	468.6	277.73	570.04
15	180.76	345.73	457.03	263.81	730.42
20	155.54	320.63	452.46	253	734.02
30	115.44	281.94	434.29	205.17	663.98
45	75.79	144.17	434.21	181.55	751.98

60	51.81	141.76	426.95	172.48	748.24

Table 23. Experiment 6. MPs degradations by photo-Fenton at neutral pH using a mixture of EDTA-DTPA-Fe at P = 500 W/m^2 [Fe-EDTA-DTPA]=10 mg/L. [H_2O_2]=100 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	309.55	708.79	543.4	363.68	1128.63
0.5	256.26	447.6	506.62	275.75	356.77
2.5	148.24	172.44	339.58	133.11	54.08
5	64.46	45.6	295.49	94.45	20
10	13.52	0	154.87	0	0
15	0	0	0	0	0
20	0	0	0	0	0
30	0	0	0	0	0
45	0	0	0	0	0
60	0	0	0	0	0

Table 24. Experiment 7.1 MPs degradations by photolysis P=500 W/m^2 [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	243.9	773.1	531.97	370.82	936.23
0.5	234.5	693.2	508.05	339.85	690.75
2.5	228.6	569.0	518.16	351.17	615.32
5	212.4	423.61	506.33	340.34	776.56
10	191.6	196.95	522.29	356.3	570.04
15	172.1	114.07	521.7	345.12	730.42
20	152.6	-	526.82	351.83	734.02
30	117.2	-	520.12	334.05	663.98
45	80.2	39.59	534.97	334.32	751.98
60	54.3	20.88	520.97	313.48	748.24

Table 25. Experiment 7.2 MPs degradations by photolysis P=500 W/m^2 [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time	MET	CIPR	ACMP	SMX	E2
0	263.88	918.5	632.42	396.92	1014.76
0.5	260.2	850.78	625.48	377.54	1064.3
2.5	249.67	678.27	624.17	378.81	1024.47
5	236.83	517.55	625.15	393.7	-
10	209.77	306.97	632.48	382.4	988.08
15	186.35	163.44	625.91	377.07	-
20	165.52	80.22	641.92	379.35	-
30	129.37	14.43	648.27	378.23	-

45	87.52	0	666.98	364.17	972.26
60	64.03	0	640.71	350.7	881.24

Table 26. Experiment 8 MPs degradations by photolysis and H_2O_2. P=500 W/m^2 . $[H_2O_2]$=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	236.52	766.47	501.5	368.81	1023.03
0.5	231.19	674.53	502.21	367.53	986.67
2.5	219.9	469.29	499.68	356.48	968.67
5	207.17	260.41	502.36	351.91	960.99
10	180.43	153.21	501.77	342.44	950.1
15	156.68	0	498.95	331.29	900
20	135.05	0	492.86	322.45	865.78
30	103.98	0	498.32	304.11	702.2
45	78.09	0	511.49	273.97	648.83
60	51.27	0	475.31	254.98	617.33

Table 27. Experiment 9 MPs degradations by photolysis and Fe-Complex. P=500 W/m^2 . [Fe-EDTA-DTPA]=2.5 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	247.88	673.54	515.38	370.37	1012.35
0.5	246.4	650.14	515.95	368.2	970.88
2.5	237.96	563.48	506.09	359.66	939.58
5	227.11	461.28	501.61	355.11	920.57
10	203.64	273.85	502.69	328.14	913.96
15	181.63	146.03	502.11	328.15	816.03
20	163.26	92.94	500.3	315.38	880.63
30	130.68	43.33	494.32	309.51	890.08
45	94.48	0	491.14	287.6	767.87
60	68.79	0	481.76	276.01	541.45

Table 28. Experiment 10 MPs degradations by photo-Fenton after 2 HRT in P.australis. P=500 W/m^2. [Fe-EDTA-DTPA]=2.5 mg/L $[H_2O_2]$=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	139.27	62.89	325.75	272.7	0
0.5	136.55	62.09	324.44	267.63	0
2.5	124.82	55.38	318	243.66	0
5	115.11	0	312.32	227.21	0
10	92.88	0	292.77	183.86	0
15	75.83	0	280.45	152.96	0
20	62.01	0	271.62	133.2	0
30	44.59	0	253.77	0	0
45	29.59	0	242.12	0	0
60	19.55	0	222.32	0	0

Table 29. Experiment 11. MPs degradations by photo-Fenton after 2 HRT in C.haspan. P=500 W/m^2. [Fe-EDTA-DTPA]=2.5 mg/L [H_2O_2]=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	148.98	24.04	235.6	175.76	0
0.5	140	23.26	228.23	170	0
2.5	120	21.7	213.29	140.15	0
5	72.7	0	198.24	0	0
10	46.46	0	168.74	0	0
15	32.22	0	148.18	0	0
20	24.3	0	136.14	0	0
30	15.33	0	120.83	0	0
45	0	0	117.77	0	0
60	0	0	110.77	0	0

Table 30. Experiment 12. MPs degradations by photo-Fenton after 4 HRT in P.australis. P=500 W/m^2. [Fe-EDTA-DTPA]=2.5 mg/L [H2O2]=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	76.81	71.21	243.52	173.64	0
0.5	72.54	59.88	239.11	155.59	0
2.5	69.2	0	232.47	156.54	0
5	67	0	231.36	144.53	0
10	66.71	0	223.4	128.58	0
15	56.94	0	219.99	113.94	0
20	49.06	0	202.6	103.03	0
30	37.24	0	200	85.98	0
45	24.63	0	188.28	62.27	0
60	18.16	0	190.58	0	0

Table 31. Experiment 13 MPs degradations by photo-Fenton after 4 HRT in C.haspan. P=500 W/m^2. [Fe-EDTA-DTPA]=2.5 mg/L [H_2O_2]=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	61.32	47.34	133.28	130.76	0
0.5	57.63	0.001	126.13	120.75	0
2.5	55	0	127.13	118.07	0
5	51.62	0	123.45	108.31	0
10	43.24	0	125	94.79	0
15	40	0	116.12	0	0
20	30.48	0	114.82	0	0
30	26.77	0	110.55	0	0
45	17.84	0	109.13	0	0
60	11.9	0	109.92	0	0

Table 32. Experiment 14. MPs degradations by photo-Fenton after 7 HRT in P.australis. P=500 W/m^2. [Fe-EDTA-DTPA]=2.5 mg/L [H_2O_2]=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	18.14	0	193.98	174.89	0
0.5	17.17	0	188.56	181.79	0
2.5	15.65	0	184.39	148.08	0
5	13.66	0	177.37	129.08	0
10	10.75	0	163.79	106.63	0
15	0	0	150.71	0	0
20	0	0	145.63	0	0
30	0	0	136.49	0	0
45	0	0	132.71	0	0
60	0	0	128.09	0	0

Table 33. Experiment 15 MPs degradations by photo-Fenton after 7 HRT in C.haspan. P=500 W/m^2. [Fe-EDTA-DTPA]=2.5 mg/L [H_2O_2]=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	22.02	0	103.45	99.44	0
0.5	21.05	0	100.38	97.02	0
2.5	20.23	0	100.94	93.23	0
5	18.98	0	100.98	0	0
10	16.35	0	96.29	0	0
15	14.06	0	92.79	0	0
20	12.4	0	93.21	0	0
30	0	0	89.74	0	0
45	0	0	89.77	0	0
60	0	0	87.46	0	0

Table 34. Experiment 14. MPs degradations by photo-Fenton after 14 HRT in P.australis. P=500 W/m^2. [Fe-EDTA-DTPA]=2.5 mg/L [H_2O_2]=25 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	0	0	129.12	96.34	0
0.5	0	0	125.78	89.79	0
2.5	0	0	114.43	0	0
5	0	0	100.41	0	0
10	0	0	80	0	0
15	0	0	25	0	0
20	0	0	0	0	0
30	0	0	0	0	0
45	0	0	0	0	0
60	0	0	0	0	0

Table 35. Experiment 15. MPs degradations by photo-Fenton after 2 HRT in P.australis. P=500 W/m2. [Fe-EDTA-DTPA]=5 mg/L [H_2O_2]=50 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	139.27	61.79	301.65	248.83	0
0.5	132.89	15.85	292.82	228.69	0
2.5	116.53	0	288.28	184.89	0
5	99.49	0	274.18	151.36	0
10	69.93	0	241.85	0	0
15	49.73	0	213.77	0	0
20	37.9	0	173.59	0	0
30	24.17	0	162.51	0	0
45	14.15	0	159.86	0	0
60	0	0	157.87	0	0

Table 36. Experiment 16. MPs degradations by photo-Fenton after 2 HRT in C.haspan. P=500 W/m^2. [Fe-EDTA-DTPA]=5 mg/L [H_2O_2]=50 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	117.67	40.68	209.91	177.92	0
0.5	101.59	0.001	200.48	155.43	0
2.5	71.75	0	169.44	0	0
5	44.22	0	139.25	0	0
10	18.58	0	0	0	0
15	0	0	0	0	0
20	0	0	0	0	0
30	0	0	0	0	0
45	0	0	0	0	0
60	0	0	0	0	0

Table 37. Experiment 17. MPs degradations by photo-Fenton after 4 HRT in P.australis. P=500 W/m^2. [Fe-EDTA-DTPA]=5 mg/L [H_2O_2]=50 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	74.73	15.88	231.06	187.71	0
0.5	83.54	0.0001	225.89	177.63	0
2.5	67.19	0	224.42	164.29	0
5	61.11	0	219.12	147.86	0
10	49.48	0	197.44	0	0
15	47.44	0	187.86	0	0
20	38.63	0	172.96	0	0
30	28.35	0	163.76	0	0
45	19.49	0	160.56	0	0
60	14.78	0	156.28	0	0

Table 38. Experiment 18. MPs degradations by photo-Fenton after 4 HRT in *C.haspan*. P=500W/m^2. [Fe-EDTA-DTPA]=5 mg/L [H_2O_2]=50 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

Time (min)	[MET]	[CIPR]	[ACMP]	[SMX]	[E2]
0	61.89	38.11	145.79	136.26	0
0.5	57.9	0.001	135.21	0.001	0
2.5	53.41	0	134.32	0	0
5	53.92	0	127.43	0	0
10	37.41	0	119.69	0	0
15	34.77	0	112.82	0	0
20	28.44	0	103.06	0	0
30	19.88	0	50.25	0	0
45	13.36	0	0	0	0
60	0	0	0	0	0

Table 39. Experiment 19. Iron precipitation in photo-Fenton. At P=765 W/m^2 and P=500 W/m^2. [Fe-EDTA-DTPA]=5 mg/L [H_2O_2]=50 mg/L [ACMP]0= [SMX]0 = [E2]0= [CIPR]0 = [MET]0=0.2 mg/L

P=765 W/m2		P=500 W/m2	
Time (min)	**Abs (510 nm)**	**Time (min)**	**Abs (510 nm)**
0	0.732	0	0.726
5	0.484	5	0.559
15	0.283	15	0.381
30	0.072	30	0.198
60	0.019	60	0.054