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Analytical Chemistry



# **Treball Final de Grau**

Removal of micropollutants contained in wastewaters by a hybrid system: Constructed wetland and Advanced oxidation process

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Cualquiera que pueda resolver los problemas del agua estará mereciendo dos premios Nobel: uno por la paz y otro por la ciencia.

John F Kennedy

Estos meses han sido intensos, agotadores y estresantes, pero puedo decir que estoy satisfecho y orgulloso del trabajo que he realizado. Sin duda, esto no lo podría haber conseguido sin la ayuda de ciertas personas.

Primero de todo, me gustaría darle las gracias al Dr. Alberto Cruz Alcalde "el capo" por haberme acogido para realizar el TFG, en cuanto me enteré de que podía ser mi tutor, tenía clarísimo que lo iba a hacer con él. Además, me ayudó en la decisión de elección de si hacerlo experimental o teórico y la verdad que sigo sin saber cómo me convenció para trabajar más y meterme en el laboratorio. Me ha ayudado mucho durante el trabajo y siempre ha estado allí cuando me ha hecho falta.

Después tuve la suerte de conocer a la Dr. Núria Lopez Vinent, "la patrona". Ya la había tenido en seguridad, pero no tenía el placer de conocerla a ella. Es una persona trabajadora, generosa, amable, inteligente que es feliz compartiendo sus conocimientos y que siempre que empezábamos un proceso importante nuevo ha estado allí para asegurarse de que sabíamos lo que teníamos que hacer, y que lo hacíamos correctamente.

Ambos han sido unos grandes tutores porque sé que otros no se hubieran puesto a limpiar las arenas conmigo, a pegar el metacrilato, a recogerme la última muestra de los AOPs o vigilar los CW que estaban en biología. Su trabajo era simplemente guiarme, pero sin su ayuda no hubiera conseguido tan buenos resultados experimentales. También me gustaría agradecerle la ayuda a Iván Diaz Redondo," el salvador". Siempre que no estaban mis tutores en la universidad y hemos tenido algún problema no ha dudado en ayudarnos y meterse en el laboratorio para encontrarnos un reactivo perdido o aconsejarnos para que todo saliera bien. No tenía la obligación de hacerlo y por eso se lo agradezco tanto.

Además, me gustaría darle las gracias a Pol Sabina," mi compañero de laboratorio" ya lo conocía de antes pero no de esta manera. Si no llega a ser por él no se si tendría tan buenos resultados. Compartimos muchas horas de laboratorio y menos mal que también tenía que construir los CW porque no sé qué hubiera hecho si tuviera que haber estado limpiando todas las arenas, pegando toda la estructura, vaciando y llenando todos los ciclos yo solo. Hubo un día que estuve enfermo y fue él a vaciar y llenar sus CW y los míos y eso no se me olvidará nunca.

Por último, pero no menos importante, darle las gracias a mi familia y amigos que me han estado apoyando, preocupándose por mi memoria y aguantándome todos los días de estrés y cansancio. En especial a mis padres y a Irati por su ayuda final.

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# SUMMARY

Water is a vital resource for life on Earth, with incalculable economic, social and environmental value. However, due to the ever-increasing demand for water and ongoing climate change, water scarcity has become the main challenge we face in the 21st century. Against this critical backdrop, it is expected that wastewater reuse will continue to be necessary to ensure that water demand is met for the foreseeable future.

Water for agriculture accounts for approximately 70 % of total freshwater demand, and this percentage is as high as 90 % in some developing countries. Therefore, the reuse of wastewater in agriculture appears to be essential to reduce the share of freshwater used in this sector. However, the quality of this reclaimed wastewater must meet some minimum requirements to ensure its safe use as an alternative resource for crop irrigation, such as biochemical oxygen demand (BOD), turbidity and pathogens are defined as the main parameters to be monitored. However, wastewater may also contain micropollutants (MPs), as wastewater treatment plants are not designed to remove them. Moreover, they are not fully regulated.

However, since the presence of these substances in water can be harmful to ecosystems and human health, it is expected that new quality criteria will soon be included in water reuse regulations related to this type of pollution.

Due to this scenario, specific treatments are needed to remove these MPs and preserve the environment. Advanced Oxidation Processes (AOPs) are chemical processes that involve the generation of transient species, mainly the hydroxyl radical (•OH), and have demonstrated their efficiency in removing MPs. However, they are costly options. Constructed wetlands, on the other hand, are engineered systems that recreate conditions and processes occurring in nature and have been shown to be effective in improving water quality. These involve lower implementation and operating costs, but require more space, treatment time but are less efficient.

In some cases, no studies have been carried out on the possible efficiency of a hybrid process combining AOP and constructed wetlands (CWs). For this purpose, this study will investigate a

hybrid process combining a constructed wetland with different advanced oxidation processes (solar photo-Fenton at neutral pH and UVC/H<sub>2</sub>O<sub>2</sub>) to treat different types of effluents (different physicochemical characteristics) containing MCP from different families.

To carry out the research, 3 laboratory-scale wetlands were constructed, one for each waste effluent to be studied (MBR, MIX, IFAS). The effluents resulting from this first stage (CWs) will be used to carry out the two advanced oxidation processes. In addition, these processes will also be carried out without pretreatment of the CWs in order to investigate which would be the most efficient combination depending on the wastewater to be treated. Therefore, the goal of this combination is to make the treatment still more efficient and environmentally friendly and to explore the possibility of reusing the treated effluent for agricultural purposes.

After all the research, we can conclude that for the less organic matter content effluent (MBR) the hybrid process will not be optimal as it becomes more turbid after passing through the CW and to achieve a higher removal rate only an AOP would be needed. (70 % CW+AOP-80 % AOP). On the other hand, for the mixed water and IFAS, being much more turbid, with more organic matter, nitrites, more alkalinity, the hybrid process was optimal as it considerably reduces the concentrations of the MPs, eliminating some completely, suspended solids(80 % IFAS), BOD and nitrites in the pre-treatment, so the effluent arrives much less turbid and the photolysis of the AOPs is much more efficient than without the pre-treatment.

Therefore, it was concluded that the mixed water is the optimal water for the hybrid process as it has the highest removal percentages of MPs with 97.2 %.

Finally, a survey will be conducted to find out if people are willing to live with this recycled water and implement it in their lives.

Keywords: Contaminants of Emerging Concern, wastewater reuse, water scarcity, Wetlands Constructed and Advanced Oxidation Processes

# RESUMEN

El agua es un recurso vital para la vida en la Tierra, con un incalculable valor económico, social y medioambiental. Sin embargo, debido a la demanda cada vez mayor de agua y al continuo cambio climático, la escasez de agua se ha convertido en el principal reto al que nos enfrentamos en el siglo XXI. Ante este panorama crítico, se prevé que la reutilización del agua residual seguirá siendo necesaria para garantizar la cobertura de la demanda de agua en un futuro próximo.

El agua destinada a la agricultura representa aproximadamente el 70 % de la demanda total de agua dulce, y este porcentaje asciende al 90 % en algunos países en desarrollo. Por lo que, la reutilización de agua residual en la agricultura parece ser esencial para reducir el porcentaje de agua dulce destinado a este sector. No obstante, la calidad de esta agua residual recuperada debe cumplir algunos requisitos mínimos para garantizar un uso seguro como recurso alternativo para el riego de cultivos como la demanda bioquímica de oxígeno (DBO), la turbidez y los patógenos se definen como principales parámetros a controlar. No obstante, las aguas residuales también pueden contener micro contaminantes (MCs), ya que las estaciones depuradoras de aguas residuales no están diseñadas para eliminarlos. Además, estos no están completamente regulados.

Sin embargo, dado que la presencia de estas sustancias en el agua puede ser nociva para los ecosistemas y la salud humana, se prevé que pronto se incluirán nuevos criterios de calidad en las regulaciones de reutilización de agua relacionados con este tipo de contaminación.

Debido a este escenario, se necesitan tratamientos específicos para eliminar estos MCs y preservar el medio ambiente. Los Procesos de Oxidación Avanzada (POAs) son procesos químicos que implican la generación de especies transitorias, principalmente el radical hidroxilo (•OH), y han demostrado su eficiencia en la eliminación de los MCs. Sin embargo, son opciones costosas. Por otro lado, los humedales construidos son sistemas diseñados que recrean las condiciones y procesos que ocurren en la naturaleza, y han demostrado eficacia en la mejora de

la calidad del agua. Estos implican menores costos de implementación y operación, pero requieren más espacio, tiempo de tratamiento, pero son menos eficientes.

En algunos casos, no se han realizado estudios sobre la posible eficiencia de un proceso híbrido que combine AOP y humedales construidos (HCs). Para ello, en este estudio se investigará un proceso híbrido que combina un humedal construido con diferentes procesos de oxidación avanzada (foto-Fenton solar a pH neutro y UVC/H<sub>2</sub>O<sub>2</sub>) para tratar diversos tipos de efluentes (diferentes características fisicoquímicas) que contienen MCP de diferentes familias.

Para llevar a cabo la investigación, se construyeron 3 humedales a escala de laboratorio, uno por cada efluente residual que se estudiará (MBR, MEZCLA, IFAS). Con los efluentes resultantes de esta primera etapa (HCs) se realizarán los dos procesos de oxidación avanzada. Además, también se realizarán estos procesos sin el pretratamiento de los HCs para poder investigar cuál sería la combinación más eficiente dependiendo del agua residual a tratar. Por lo tanto, el objetivo final de esta combinación es hacer que el tratamiento siga siendo más eficiente y respetuoso con el medio ambiente y explorar la posibilidad de reutilizar los efluentes tratados para fines agrícolas.

Después de toda la investigación, podemos concluir en que para el efluente (MBR) el proceso híbrido no será óptimo al volverse más turbia después de pasar por el HC y para conseguir un mayor porcentaje de eliminación únicamente haría falta un AOP. (70 % HC+POA-80 % POA). En cambio, para el agua mezclada y IFAS, al ser mucho más turbia, con más materia orgánica, nitritos, más alcalinidad el proceso híbrido fue óptimo al reducir considerablemente las concentraciones de los MCs, eliminando algunos por completo, sólidos en suspensión (80 % IFAS), DBO y nitritos en el pretratamiento por lo que el efluente llega mucho menos turbio y la fotólisis de los POAs es mucho más eficiente que sin pretratamiento.

Por lo que se concluyó con que el agua mezclada es la óptima para realizar el proceso híbrido al tener los porcentajes de eliminación de MCs más elevados con un 97.2 %.

Finalmente, se realizará una encuesta para averiguar si las personas están dispuestas a vivir con esta agua reciclada e implementarla en sus vidas.

Palabras claves: Contaminantes Emergentes, reutilización de aguas residuales, escasez de agua, Humedales construidos y Procesos Avanzados de Oxidación.

# SUSTAINABLE DEVELOPMENT GOALS

El proyecto se centra en mejorar la calidad del agua de las salidas de las depuradoras aplicando un tratamiento terciario.

La necesidad principal que aborda el proyecto es la carencia de métodos eficientes y sostenibles para la eliminación de micro contaminantes en el agua. Estos compuestos representan una amenaza significativa para la salud humana y el medio ambiente y su eliminación eficaz es crucial para la sostenibilidad de los recursos hídricos.

El proyecto propone un enfoque innovador mediante la combinación de humedales construidos con procesos de oxidación avanzada. Esta estrategia no solo ha demostrado ser efectiva en la eliminación de micro contaminantes, sino que también puede implementarse con costos relativamente bajos y menor impacto ambiental.

Si el proyecto se expandiera a gran escala, podría tener un impacto positivo en la restauración y conservación de ecosistemas acuáticos al disminuir los MCs que llegan a los mares, ríos...Además, implementando el agua residual en nuestras vidas, se reduciría la escasez y se beneficiaría directamente a las comunidades que dependen de estos recursos para su subsistencia y actividades económicas, promoviendo un desarrollo sostenible a largo plazo.

El proyecto se alinea con varios Objetivos de Desarrollo Sostenible (ODS), principalmente:

ODS 6: Garantizar la disponibilidad y la gestión sostenible del agua y el saneamiento para todos.

Meta 6.3: mejorar la calidad del agua reduciendo la contaminación, eliminando el vertimiento y minimizando la emisión de productos químicos y materiales peligrosos, reduciendo a la mitad el porcentaje de aguas residuales sin tratar y aumentando considerablemente el reciclado y la reutilización sin riesgos a nivel mundial.

6.3.2 Proporción de masas de agua de buena calidad reduciendo la concentración de los MPs mediante el proceso híbrido. ODS 15: Proteger, restablecer y promover el uso sostenible de los ecosistemas terrestres, gestionar sosteniblemente los bosques, luchar contra la desertificación, detener e invertir la degradación de las tierras y detener la pérdida de biodiversidad

Meta 15.1: Asegurar la conservación, el restablecimiento y el uso sostenible de los ecosistemas terrestres y los ecosistemas interiores de agua dulce y sus servicios.

Indicador 15.1.1: Proporción de lugares importantes para la biodiversidad terrestre y del agua dulce incluidos en zonas protegidas, desglosada por tipo de ecosistema creando los humedales construidos a gran escala.

Esta reflexión crítica destaca cómo el proyecto aborda una necesidad urgente en términos ambientales y de salud pública, alineándose con los objetivos globales de desarrollo sostenible establecidos por la ONU.





# **1. INTRODUCTION**

Water is a vital resource for life on Earth, having incalculable economic, social, and environmental value. However, due to the ever-increasing demand for water followed by continued climate change, water scarcity has become the main challenge we face in the 21st century. Furthermore, according to predictions presented by the United Nations, the world's population, which currently stands at 7.7 billion, will eventually reach between 9.4 and 10.2 billion by 2050. This demographic increase will result in an increase in water demand of 20% to 30%.[1]

More than 2 billion people reside in countries facing conditions of constant water stress. Approximately 4 billion people experience severe physical water scarcity for at least one month per year. In addition, factors such as population growth, socio-economic development and changing consumption patterns are expected to increase water demand by 50-80% in the coming decades. In addition, accelerating climate change could worsen the situation, leading to a rapid decline in global water availability.[2]

Water stress, the ratio of water demand to renewable supply, is a measure of competition for local water resources. The smaller the gap between supply and demand, the more vulnerable a place is to water scarcity. That a country faces 'extreme water stress' means that it is using at least 80 % of its available supply, while 'high water stress' means that it is using 40 % of its supply. [3]

Therefore, we are expected to experience a major water crisis by 2040. (Figure 1)



#### Water Stress by Country: 2040

Figure 1: Ratio of withdrawals to supply it makes us see that if we don't do something about it, by 2040 we will run out of water. Source: [3]

In the face of this serious situation, wastewater reuse can undoubtedly be considered as a major sustainable development strategy to cope with the water scarcity crisis. However, to do so, it is essential that wastewater is adequately treated by removing all the harmful elements resulting from various human activities.

# **1.1. PRESENCE OF MICROPOLLUTANTS IN AQUATIC ENVIRONMENTS**

The presence of micropollutants (MPs) in aquatic environments, even in minimal concentrations, represents a major risk to human health and the environment. For this reason, wastewater treatment plants (WWTPs) require specific treatments to remove these MPS from water matrices, as they are not designed to completely remove these persistent compounds, especially when wastewater is reused. MPS are unknown or unrecognised pollutants whose presence in the environment is not new, but concern and control over their consequences (such as pharmaceuticals, insecticides, additives, fertilisers, etc.) [4] is new. Advanced oxidation processes, as a tertiary treatment, could be an excellent option for their elimination. [1-2]

# 1.2. ADVANCED OXIDATION PROCESSES (AOPS)

Advanced Oxidation Processes are an emerging method for the efficient mineralisation of MPs, mainly non-biodegradable constituents. The mineralisation of these emerging pollutants to H<sub>2</sub>O and CO<sub>2</sub> occurs due to the generation of oxidative species with higher oxidising power. Among the different radicals, •OH radicals stand out due to their high reactivity with a reduction potential of 2.8 V. Oxidation processes currently in use include chemical(Fenton, Persulfate), photolytic(UV,UV/H<sub>2</sub>O<sub>2</sub>,UV/persulfate), photocatalytic(Semiconductor photocatalyst, Metal doped photocatalyst, Non-Metal doped photocatalyst), sonochemical (Sono-Fenton, Sono-photocatalyst, Sono-persulfate), electrochemical (Electro-fenton) and ozone-based, being the mineralisation of emerging pollutants more efficient when several oxidising agents are combined. [5]

These processes have proven effective in the removal of a wide variety of these pollutants. However, it is important to note that these technologies require a high energy demand and entail significant costs for both implementation and maintenance.[5] In our experiments, we will use a process that is based on an oxidation process.

In our experiments we will use a chemical-photolytic (Solar-Photo Fenton) and a photolytic (UV/H<sub>2</sub>O<sub>2</sub>) process.

#### 1.2.1. Solar Photo-Fenton (SPF)

The Fenton process has been widely used for the oxidation of many organic compounds due to its high efficiency in generating hydroxyl radicals from the decomposition of H<sub>2</sub>O<sub>2</sub> at acidic pH by Fe salts. This process is optimal at pH=2.8 as iron does not precipitate. The problem is that, when it comes to large-scale production, it is not efficient to vary the pH. In the last decades, the use of iron chelators has been tested in order to be able to operate at neutral pH.

This is an attractive oxidation system because iron is abundant and non-toxic and  $H_2O_2$  is easy to handle and safe for the environment. The process can be enhanced by irradiating light with a wavelength between 300 and 650 nm, known as the photo-Fenton process.

This ultraviolet/visible light improves the efficiency of the process by producing more hydroxyl radicals and allowing regeneration of the catalyst as Fe (III) is reduced to Fe (II) by photo-reduction [6].

The reaction mechanisms of photo-Fenton with different iron complexes have not yet been clearly defined. However, the EDDS-Fe complex (is the most studied) is often extrapolated to understand further reactions in the photo-Fenton process at near neutral pH using other iron complexes.

There are several irons chelates such as EDDS, EDTA, DTPA, HEDTA and EDDHA, but in our case we will use EDTA. This chelate was chosen because it is used in agriculture and because it has a medium stability with iron, so it does not break the bond with iron immediately when hydroxyl radicals are formed or when light hits it, but it is not so strong as to decrease the kinetics of the •OH production.[7]

In the case of the photo-Fenton process using EDTA-Fe, it has been shown that there are additional mechanisms to produce hydroxyl radicals (•OH) besides the classical photo-Fenton reactions. [6]. I have not found the reactions with EDTA, so I will use the equations for EDDS, which is the most studied.

Photoexcitation of EDDS-Fe leads to the generation of an EDDS radical (EDDS•), expressed as •L in reaction (r1), as this organic compound decomposes when exposed to light.

Fe (III)-chelated complexes under irradiation can generate both Fe (II) and ligand free radicals (•L) via ligand-to-metal charge transfer (LMCT). The superoxide radical ( $O_2^{\bullet-}$ ) can be formed from the reaction between dissolved oxygen and •L. Meanwhile,  $O_2^{\bullet-}$  and its conjugate acid form can generate hydrogen peroxide ( $H_2O_2$ ) through reactions (r3) - (r7). Finally, •OH is generated by the Fenton reaction due to the available dissolved iron (r9).

However, pH is a crucial factor to consider. At neutral pH, reactions (r3), (r5), (r6), and (r7) occur more slowly than under acidic conditions, which affects the amount of H<sub>2</sub>O<sub>2</sub> formed and thus the amount of •OH available to react.

Furthermore, at pH values above 4, the concentration of dissolved iron and photoactive  $FeOH_{2^+}$  decreases, forming precipitated iron hydroxides, which affects reactions (r4), (r5), and (r8). This explains why the absorbance of the latter decreases as the process progresses. [7]

$$\begin{split} & \text{Fe (III)-L+ hu} \rightarrow [\text{Fe (III)-L}]^* \rightarrow \text{Fe (II) + L (r1)} \\ & \text{L+O}_2 \rightarrow \text{O}_{2^-} + \text{L}^{'}(r2) \\ & \text{O}_{2^-} + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} \text{ (pka=4.8 (r3)} \\ & \text{Fe (II) + O}_{2^-} + 2\text{H}_2\text{O} \rightarrow \text{Fe (III) + H}_2\text{O}_2 + 2\text{OH}^- (r4) \\ & \text{Fe (II) + HO}_{2^-} + \text{H}_2\text{O} \rightarrow \text{Fe (III) + H}_2\text{O}_2 + \text{OH}^- (r5) \\ & \text{O}_{2^-} + 2\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^- (r6) \\ & 2 \text{ HO}_{2^-} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 (r7) \\ & \text{Fe (II) + H}_2\text{O}_2 \rightarrow \text{Fe (III) + } \cdot \text{OH + OH}^- (r8) \\ & \text{H}_2\text{O}_2 + \text{hu} \rightarrow 2 \cdot \text{OH} (254\text{-}299 \text{ nm}) (r9) \end{split}$$

#### 1.2.2. UV-H<sub>2</sub>O (UVC)

The sun is the primary source of energy for life on Earth, providing both visible light for photosynthesis and ultraviolet (UV) radiation. This UV radiation is divided into UVA, UVB and UVC radiation according to wavelength, with significant differences in their penetrating power and biological effects.

- 1. UVA radiation: Wavelength 320-400 nm. Penetrates deep into the skin, causes photoaging and increases the risk of skin cancer.
- 2. UVB radiation: Wavelength 280-320 nm. Penetrates to the surface layer of the skin, is responsible for sunburn and can cause skin cancer.
- UVC radiation: Wavelength 200-280 nm. Completely absorbed by the ozone layer, it is extremely energetic and potentially dangerous to living organisms if it reaches the earth's surface.[8]

In our experiment, UVC radiation will be used due to the generation of 2 • OH with H<sub>2</sub>O<sub>2</sub>.[9]

UV light is generated from mercury lamps. These are low-pressure and emit nearmonochromatic UV light at a wavelength of 254 nm.

This advanced oxidation process is based on the photolysis of hydrogen peroxide. According to the following equation for each absorbed photon two hydroxyl radicals are produced. (r10) [10]

$$H_2O_2 + hu \rightarrow 2 \cdot OH (r10)$$

### **1.3. WATER QUALITY IMPACTS**

To define an effective water treatment strategy, it is essential to consider the quality of the water. When using AOPs, the presence of dissolved organic or inorganic compounds can compete for the hydroxyl radical due to their non-selective nature.

#### 1.3.1. Organic Matter Load

When we talk about carbon content in water, we often measure it as total organic carbon (TOC) or dissolved organic carbon (DOC). If this carbon comes from natural sources, it is called NOM (natural organic matter). However, if it comes from wastewater treatment plants, it is called EFOM (effluent organic matter). Although organic matter can interact with hydroxyl radicals, the diversity of organic materials in water makes it difficult to establish exact reaction rates. Still, some studies have given us an idea, suggesting that the reaction rate of dissolved organic matter (DOM) with •OH falls in the range of 10<sup>8</sup>-10<sup>9</sup> M<sup>-1</sup>·s<sup>-1</sup>. [11-12]

Because Dissolved Organic Matter (DOM) is generally more present than MPs, it tends to absorb hydroxyl radicals, reducing their effectiveness in removing MPs. In addition, organic matter absorbs a wide range of UV light, leading to competition between DOM, oxidants, micropollutants or catalysts for UV exposure. This competition ultimately reduces the generation of hydroxyl radicals, resulting in reduced efficiency of advanced oxidation processes (AOPs).

#### 1.3.2. Nitrates and Nitrites

These ions have a significant impact on Advanced Oxidation Processes (AOPs) that rely on UV light. Nitrates absorb light in the 230-240 nm range, while nitrites show their highest absorption peak between 300-310 nm. As with Dissolved Organic Matter (DOM), competition between these

ions and species involved in the production of •OH by UV light results in a decrease in the yield of AOPs. In addition, nitrite ions can react with •OH (r11) [13], which further reduces the efficiency of AOPs.

$$NO^- + \bullet OH \rightarrow NO^\bullet + HO^-$$
 (r11)

#### 1.3.3. Turbidity

Turbidity is the lack of transparency due to the presence of suspended particles. The more solid particles in suspension in the water, the dirtier it appears and the higher the turbidity value. Higher turbidity decreases the transmittance of the water and consequently reduces the penetration of light into the system. This results in less generation of hydroxyl radicals and therefore decreases the efficiency of the treatment. [14]

#### 1.3.4. Alkalinity

Bicarbonate (HC<sub>0</sub><sup>3-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) ions react with hydroxyl radicals to form carbonate radicals according to the following reactions: [15].

$$\begin{array}{l} HCO_3^- + \bullet OH \longrightarrow \bullet CO_3^- + H_2O \ (r12) \\ CO_3^{2-} + \bullet OH \longrightarrow HO^- + \bullet CO_3^- \ (r13) \end{array}$$

Although these two species have lower reaction rate constants compared to most MPs [15], the second-order reaction rate depends on the concentration of the compound. Since the concentration of bicarbonate and carbonate in wastewater influents or aquatic environments is usually much higher than that of recalcitrant compounds, hydroxyl radicals are more likely to be scavenged by these ions. Therefore, the efficiency of AOPs will decrease.

### 1.4. CONSTRUCTED WETLANDS (CWs)

In response to this, nature-based solutions for wastewater treatment, such as constructed wetlands (CW), have been explored because of their ability to remove MPs. Constructed wetlands are known to be environmentally friendly, cost-effective in terms of operation and maintenance, and simple to implement. CW is defined as an area of flat land that remains flooded or waterlogged for prolonged periods (2-4 days for horizontal flow CWs (HFCWs) and 1-2 days for vertical flow CWs (VFCWs)), with the presence of hydrophilic plants that act as water filters. CWs

reproduce processes where the set of several mechanisms such as biodegradation, photodegradation, sorption... play a crucial role for the removal of these MPs. [16].

The efficiency of CWs removal of MPs depends on different factors. These include the wetland configuration (surface and subsurface, horizontal and vertical) and the operating parameters (retention time, aerobic/anaerobic environment). [17].

In addition, they have proven to be effective in removing organic matter, suspended solids, nutrients and metals. However, it is important to note that CWs require a large land area, which can be a constraint in urban areas where space is limited and long retention times. Furthermore, relying solely on these solutions for effluent treatment may not meet minimum standards for water reuse, especially regarding the removal of emerging pollutants and bacterial inactivation.[1]

### 1.5. HYBRID SYSTEM

In this context, a hybrid CW-AOP system could be an effective solution to overcome the limitations of using them separately. The main advantages of combining them include reducing the required land area, lowering energy and maintenance costs, and facilitating water reuse by enhancing the removal of bacteria and MPs [18]

The most used hybrid system begins with HFCWs as the first step, followed by advanced oxidation processes (AOPs). The CW acts as a pre-treatment, removing organic matter and suspended solids before the water enters the AOP system, which then polishes the effluent to ensure the water can be reused in various sectors. [18]

However, there has been limited research in this area. Therefore, this study will focus on demonstrating whether this hybrid system is truly effective for three types of wastewaters: MBR (Membrane Bioreactor), MIX, and IFAS (Integrated Fixed Film Activated Sludge).

### 1.6. MPs SELECTION

This study aimed to investigate the potential of a hybrid system consisting of CW-SPF at neutral pH, ambient Temperature and a CW-UVC-H<sub>2</sub>O<sub>2</sub> for the removal of MPs with different effluents. For this purpose, the efficiency of the method was investigated by simultaneous removal of eight MPs. These 8 were chosen as they are the most common drugs and pesticides, so when

comparing results, it will be possible to see if the experiments have been successful. Additionally, it is necessary that they have different Kow values, different kinetics with the hydroxyl radical, and different wavelengths at which they are read, in order to perfectly distinguish them when analyzing the experimental results.

#### 1.6.1. Atenolol [ATNL]

ATNL is one of the most used drugs for treating widespread cardiovascular diseases today. It is a cardio selective beta-blocker used to treat heart failure, acute coronary syndrome, and hypertension. About 50 % of its oral dose is absorbed in the gastrointestinal tract, while the rest is excreted unchanged in the feces. Since ATNL is minimally metabolized in the human liver and is largely excreted unchanged through the kidneys, it often ends up in municipal effluents. ATNL's high water solubility, combined with its moderate resistance to biological and natural degradation, allows this drug to persist in the environment for some time. Due to its extensive use and discharge into wastewater, ATNL has been detected in surface waters across several European countries [19].

For this reason, it poses a risk to human health and ecological well-being.



Figure 2: ATNL Structural Formulae. Source: PubChem

#### 1.6.2. lopromide [IOPM]

IOPM is a low osmolarity non-ionic radiographic contrast agent for intravascular administration. It functions as a contrast agent by opacifying blood vessels in the flow path of the contrast agent, allowing radiographic visualization of internal structures until significant hemodilution occurs.

The amounts excreted unchanged in the urine represent 97 % of the dose in healthy adult subjects. Only 2 % of the dose is recovered in faeces. Therefore, it is often found in municipal effluents. For this reason, it also poses a risk to human health and ecological well-being.[20]



Figure 3: IOPM Structural Formulae. Source: PubChem

# 1.6.3. Acetamiprid [ACMP]

ACMP is a systemic and contact neonicotinoid insecticide that acts mainly by ingestion, affecting the central nervous system of insects, causing paralysis and death as a consequence. [21] ACMP has been shown to be one of the most toxic insecticides with negative effects on human health due to chronic exposure and negative consequences on aquatic species and other organisms such as bees. [22]



Figure 4: ACMP Structural Formulae. Source: PubChem

### 1.6.4. Primidone [PMDN]

PMDN is an anticonvulsant medicine used to control seizures [23]. About 40% of primidone is excreted unchanged in the urine, while the rest consists of unconjugated FEMA, and to a lesser extent, phenobarbital and its metabolites [24]. For this reason, it also poses a risk to human health and ecological well-being.



Figure 5: PMDN Structural Formulae. Source: PubChem

### 1.6.5. Carbamazepine [CBMZ]

CBZ belongs to a group of medicines called anti-epileptic drugs. It is used for the treatment of certain types of epilepsy. It is also used in the treatment of mania and in the prevention of manic-depressive (bipolar) disorders; in alcohol withdrawal syndrome, essential trigeminal neuralgia and essential glossopharyngeal neuralgia.[25] CBZ has been found to be toxic to organisms in water, such as bacteria, algae, invertebrates and fish [26].



Figure 6: CBZ Structural Formulae. Source: PubChem

#### 1.6.6. Atrazine [ATZ]

ATZ is an herbicide used to control weed growth in various crops. The role of this herbicide has spread globally due to its good performance in crop fields, preventing the growth of weeds that compete with crop plants for water and nutrients in the soil. Because of its toxicity, its use has been banned in countries such as the United States and Australia and in the European Union.

After application, atrazine is washed by rain into surface water bodies, such as lakes, rivers and seas; and also, into groundwater bodies, such as wells. The main problem is that

this herbicide takes many years to degrade when it is dissolved in water, and when it is found there it contaminates the water, reaching the drinking water we all drink.

Atrazine also mixes with the air, and when this happens it attaches itself to dust particles in which it can travel long distances. Because it is bound to these particles it does not degrade and when it rains it is washed into bodies of water.[27]



Figure 7: ATZ Structural Formulae. Source: PubChem

#### 1.6.7. Ibuprofen [IBP]

IBF is a drug used to treat fever, swelling, pain and redness by preventing the body from making substances that cause inflammation.[28] This star anti-inflammatory drug, which also reacts with other dilute, toxic agents, reduces survival, affects the endocrine and immune system and the stress response in the body.

This star anti-inflammatory of recent years, which also reacts with other dilute agents, also toxic, reduces survival, affects the endocrine and immune system and the stress response in an aquatic invertebrate. All this confirms the harmful effect of ibuprofen in the aquatic ecosystem, in

line with its effects in humans, decreasing the amount of testosterone, reducing male characters, sexual desire, sperm production and physical traits, which may lead to problems at puberty. [29]



Figure 8: IBF Structural Formulae. Source: PubChem

#### 1.6.8. DImetridazole [DMZ]

DMZ is an antimicrobial drug belonging to the nitroimidazole family, used on poultry farms to treat infections caused by bacteria and protozoa. However, high levels of exposure to DMZ in humans can cause genotoxicity, mutagenesis, peripheral neuropathy, encephalitis and seizures. Consequently, the European Union (EU), the United States (US), Canada and China have applied strict bans on DMZ. For this reason, it also poses a risk to human health and ecological wellbeing. [30]



Figure 9: DMZ Structural Formulae. Source: PubChem

# **2. OBJECTIVES**

Given the lack of experimental studies on the combination of constructed wetlands and advanced oxidation processes, the main objective of this work is to investigate the efficiency of the hybrid system (CW + AOP) in removing different types of micropollutants contained in three different wastewaters.

Thus, the following specific objectives were proposed:

- Exploring the efficiency of constructed wetlands to eliminate the micropollutants, DOC, total suspended solids and nitrites and nitrates.
- Examining the efficiency of UVC-H<sub>2</sub>O<sub>2</sub> and solar photo-Fenton using EDTA-Fe in micropollutant degradation.
- Studying the potential of the combination of the constructed wetlands and UVC-H<sub>2</sub>O<sub>2</sub> or solar photo-Fenton in the elimination of the micropollutants and establish the best option in terms of micropollutant removal.

Additionally, a survey will be conducted to determine whether people are willing to live with this recycled water and implement it in their lives.

# **3. HYPOTHESIS**

The expected results at the end of the experiments are as follows:

- The more turbid the water is, the worse the advanced oxidation processes will work, and the less MPs will be removed. Therefore, for mixed water and IFAS the hybrid process will be the most efficient.

- MBR wastewater is likely to be fouled, as it is quite clean, having passed through a membrane, so for MBR water it will be much more efficient to perform AOP only.

- The blended water will achieve the highest removal rate with the hybrid process due to the reduction of DOC, TSS, nitrite and nitrate contamination.

- As the cycles progress, less MPs may be removed as the system becomes saturated.

 In SPF, because it does not operate at a single wavelength like UVC, the effect of photolysis will be different.

 People will be fine with the future use of wastewater for irrigation in cities, but not for drinking water.

# 4. MATERIALS AND METHODS

# **4.1. MPS PROPERTIES**

Table 1 to table 8 shows the characteristics of the micropollutants. (Appendix I)

# 4.2. REAGENTS

In Table 1, all the reagents used throughout the process can be observed.

Table 1: Reagents

Name	Formula	Company	Purity (%)	Utility	Chemical Safety
Acetonitrile	CH₃CN	FischerChemical	99.8	HPLC analysis	Oxidant/Toxic
Orthophosphoric acid	H <sub>3</sub> PO4	Panraec AppliChem	85.0	HPLC analysis	Corrosive
Ammonium acetate	CH₃COOONH₄	Panraec AppliChem	99.0	Bisulphite preparation for Fe determination	Toxic
Ammonium metavanadate	H <sub>4</sub> NO <sub>3</sub> V	Sigma Aldrich	99.0	H <sub>2</sub> O <sub>2</sub> Determination	Toxic/ Health Hazard
Ascorbic Acid	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	Panraec AppliChem	91.0	Totally Fe Determination Reduce [Fe <sup>3+</sup> - >Fe <sup>2+</sup> )]	-
EDTA-FE	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>8</sub> Fe Na·3H <sub>2</sub> O	Phygenera	13.1	Solar Photo- Fenton	Irritant
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	Merck	30w/v	UV-H <sub>2</sub> O <sub>2</sub> /Solar Photo-Fenton	Flame/ corrosive
1,10- Phenantroline	$C_{12}H_8N_2$	Panreac AppliChem	99.0	Fe <sup>2+</sup> Determination	Corrosive/ Toxic

Liver Bovine catalase	$C_9H_{10}O_3$	Sigma Aldrich	-	Stop the reaction	-
Sodium Bisulphate	NaHSO₃∙	Panreac AppliChem	40	Stop the reaction	- Irritant

# **4.3. WATER MATRICES**

#### 4.3.1 Ultrapure water (UPW)

The water used for the dissolutions (MPs-Spectrophotometer -catalase-HPLC) is ultra-pure water (UPW). This water is purified in the laboratories of Milli-Q Millipore and is obtained by a purification system where the result is a high purity non-conductive water, with extremely low levels of impurities (neither dissolved cations nor anions).

According to ASTM (American Society for Testing and Materials), the maximum resistivity of high purity water is approximately 18.3 megohms.[31]

Table 2: Features UPW

Resistivity (MΩ·cm)	TOC (ppb)	Temperature (°C)	
16.7	2	26.1	

#### 4.3.2. Wastewater treatment plant matrices

The wastewater used in the introduction of the wetlands and experiments was obtained from the Gavà-Viladecans WWTP (Cami Pineda, 2, 08850 Barcelona).

Three types of water were collected:

#### 4.3.2.1. IFAS

In the IFAS system, plastic or biological supports are added to wastewater treatment tanks providing an additional surface for micro-organisms to attach to and grow on. This water is treated by an activated sludge process, where suspended biological microorganisms enrich the water by breaking down organic matter.[32]

Table 3: IFAS water characterization

Suspended solids DOC Co <sub>3</sub> <sup>2-</sup> Cl <sup>-</sup> SO <sub>4</sub> <sup>2-</sup> NO <sub>2</sub> <sup>-</sup> NO <sub>3</sub> <sup>-</sup> pH [mg/L]	L]
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### 4.3.2.2. MBR

In an MBR system, a semi-permeable membrane is used to separate suspended solids and micro-organisms from the treated water. It therefore allows the treated water to pass through the membrane retaining the solids. Suspended biological microorganisms are retained within the bioreactor system, which allows for high efficiency in the removal of organic matter and nutrients. [33]

Table 4: MBR water characterization

Suspended solids	DOC	Co3 <sup>2-</sup>	<b>CI</b>	<b>SO</b> <sub>4</sub> <sup>2-</sup>	NO2 <sup>-</sup>	NO3 <sup>-</sup>	
pH [mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	
7.8 1.4	10.0	312.0	481.8	156.5	1.2	21.9	

### 4.3.2.3. MIX

In addition to studying these two outlets separately, it was also decided to make a 50% IFAS-50% MBR mixture.

Table 5: Mix water characterization

Suspended solids DOC   pH [mg/L] [mg/L]   7.9 117.6 15.3	Co <sub>3</sub> <sup>2-</sup> [mg/L] 469.4	<b>Cl<sup>-</sup> [mg/L]</b> 469.4	<b>SO4<sup>2-</sup></b> [mg/L] 159.0	NO2 <sup>-</sup> [mg/L] 7.5	NO3 <sup>-</sup> [mg/L] 13.5	
--	--	---	--	-----------------------------------	------------------------------------	--
## 4.3.2.4. Comparison

Comparing the two waters theoretically and experimentally, we can see that the quality of the effluent is higher in the IFAS system due to the efficient separation of solids and microorganisms as the membrane is incorporated in the system.

We can see how the colour is very different: IFAS is brown, and the smell is unpleasant and intense, while MBR is transparent and the smell is much milder, although it does not smell like the water obtained at the Wetlands outlets.



Figure 10: Left: IFAS, Right MBR

## 4.4. ANALYTIC METHODOLOGIES

## 4.3.1 Evolution of the MPs concentration

High Performance Liquid Chromatography (HPLC Infinity Series, Agilent Technologies) with a C-18 column (250 x 4.6 mm internal diameter, 5  $\mu$ m particle size, Tecknokroma) was used to assess the concentration of target compounds. A constant injection volume of 100  $\mu$ L was used. The column temperature was maintained at 40 °C with a flow rate of 1 mL/min. The mobile phases consisted of two eluents: an aqueous phase with orthophosphoric acid (pH=3) (A) and an organic phase composed of acetonitrile (B). A gradient program was applied: starting with 5% B for 2 minutes, linearly increasing to 100% B from 2 to 28 minutes, returning to initial conditions at 28.5 minutes, and a final equilibration for 4.5 minutes before the next injection. Six wavelengths were utilized depending on the compound: 200 nm for atenolol, primidone, and ibuprofen; 214 nm for carbamazepine; 222 nm for atrazine; 240 nm for IOPM; 254 nm for acetamiprid; and 320 nm for dimetridazole. (Absorbance peaks were recorded as they appeared in the tables of microcontaminant properties [Appendix I].)

The concentration of MP was measured using HPLC. All 8 compounds could be analysed in the same sample, as they required the same working conditions despite some being read at the



same wavelength; they all had different retention times (RT).

For each reading time in the experiments, using the wavelength and RT, the Area [mAU\*S] is determined, which represents the concentration of MP.

Signal 1: DAD1 G, Sig=214, 4 Ref=off

Peak #	RetTime [min]	Ту	be	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.166	BV		0.0993	128. 18742	17.53711	0.6738
2	2.325	VB		0.0720	329. 20181	66. 18790	1.7304
3	3.207	BV		0.2694	9748. 59863	559. 28845	51.2411
4	3.359	VB		0.1943	6654.75830	537.96497	34.9791
5	3.898	BB		0.0822	5.22385	1.01256	0.0275
6	4.257	BB	R	0.0710	247.03444	50.56395	1.2985
7	4.621	VB	Е	0.0998	12.12484	1.81861	0.0637
8	8.848	BV		0.0728	10.22412	2.09827	0.0537
9	8.945	VB		0.0684	6.85581	1. 52769	0.0360

#### Figure 11: HPLC / Results

For the reading of the concentrations of each MPs, the sample was filtered with a 0.45 mm filter and placed in the HPLC pots.

#### 4.4.2. Determination of iron precipitation

Ferrous iron Fe (II) has been evaluated by complex formation using 1,10-phenanthroline. 1 mL of phenanthroline solution (1 g/L), 1 mL of acetate/acetate buffer solution (62.5 g of ammonium acetate is dissolved in 175 mL of acetic acid and made up to 250 mL in a volumetric flask with ultrapure water) with 4 ml of the sample solution at each selected time (UPW to make the blank). The complex is measured with a spectrophotometer (Hach Lange DR 6000) at 510 nm after reduction of the ferric iron to the ferrous form (Fe<sup>3+</sup> $\rightarrow$ Fe<sup>2+</sup>) with ascorbic acid acquiring an intense red colour as time progresses. We will leave it for 24 hours to make sure that it has been completely reduced.

 $Fe^{2+} + 3(1,10-Phenanthroline) \rightarrow Fe(1,10-phenanthroline)_{3^{2+}} (r14)$ 

In order to measure the total iron, at neutral pH, the samples are filtered with a 0.20 µm filter to ensure a good reading of this iron (chelated and non-chelated) by preventing the precipitate from passing through the filter.

#### 4.4.3. Determination of hydrogen peroxide consumption

For the determination of hydrogen peroxide, a spectrophotometric method was used during photodegradation reactions. The method is based on the reaction of H<sub>2</sub>O<sub>2</sub> with ammonium metavanadate in an acid medium (1.5 mL of ammonium metavanadate solution (5.14 g/L) was mixed with 1.5 ml of sample), forming the orange-coloured peroxovanadyl cation, with maximum absorbance at 450 nm, which was measured at this wavelength with a spectrophotometer (Hach Lange DR 6000).

In this way it will be possible to observe how the concentration of H<sub>2</sub>O<sub>2</sub>, varies as the experiment progresses.

$$VO_{3} + 4H^{+} + H_2O_2 \rightarrow 3H_2O + VO_2^{3+} (r15)$$

## 4.5. EXPERIMENTAL DEVICE

#### 4.5.1. Constructed Wetlands

In this study, 3 vertical Wetlands with recirculation were built.

The structure of the Wetland is a rectangular cube open at the top where the methacrylate sheets measure: Base (30-30 cm): Sides (30+60 cm). This material was used to avoid adsorption of the MPs on the plastic and to overestimate the removal. The wetland outlet was located at the bottom of the wetland together with an aquatic pump and PVC pipes to recirculate the flow. The material of these pipes, although less strong than for example Teflon, was chosen to prevent the formation of algae, as they are located with the sun shining on them and together with the water, which would add micro-organisms to the system, and this would not benefit us.





The interior consists of different layers of sands/rocks of different diameters. First 10 cm of a layer of boulder stones was filled, followed by a second layer of volcanic rock (5 cm layer), a third layer of sand gravel (5 cm layer) and finally a fourth cover consisting of roots and sand as a bedding substrate (30 cm layer). All these sands were cleaned over several cycles to remove all the dirt they had. (Figure 12).

A Carex Pendula was transplanted for each Wetland. This plant was used as it is easily found in the Iberian Peninsula. In a constructed wetland, plants play a key role in the adsorption of contaminants in several ways. Plant roots provide a surface for adsorption where contaminants can adhere. Contaminants present in the water can be absorbed by the roots and then transported upwards through the plant. Additionally, plant roots can develop a biofilm, which is a thin layer of microorganisms and organic matter, that can also adsorb water contaminants. The pebbles are placed at the bottom of the container to avoid obstructions. On the other hand, volcanic rock was used in the medium to increase the porosity of the substrate and thus promote the retention of pollutants and improve the development of biofilms. Gravel was placed on top to aid additional filtration, which is done by starting in the layers with less porosity. Sand was used as bedding substrate for the artificial wetland microcosms (Figure 12). The recirculating water oxygenates the entire medium and can lead to nitrification reactions or other reactions that require oxygen to remove micropollutants. In addition, recirculation also causes the water with the pollutants to pass through the different layers and biofilms and increase the percentage of elimination. Finally, everything was coated with silver foil to prevent algae growth.

#### 4.5.1.1. Acclimatization System

Prior to the introduction of the water to be tested, the wastewater from each wetland was cycled for 1 month without the introduction of the micropollutants. This was done so that all the micro-organisms would grow well, all the biofilms would be created, no losses would occur, the pumps would work well, and recirculation would occur properly before the experiment began, so that it could be observed that the system had acclimatised correctly, and a microcosm had formed.

#### 4.5.1.2. In of the Wetlands

Initially, stock dilutions of each 100 ppm micropollutant will be made (except for atrazine, which will be 20 ppm due to its solubility).

To make the dilution, it was added the required amount of each micropollutant weighed on an analytical balance and make up to the calculated volume. To aid dilution, we leave it for a whole day in a shaker with a magnetic core inside.

It was added 100 ppb of each micropollutant for each wetland.

We prepare the 3 dilutions that we will add to each wetland, which are made up of:

W1: Water MBR+ micropollutants (100 ppb of each one).

W2: Water 50% MBR+ 50% IFAS + micro contaminants (100 ppb of each).

W3: Water IFAS+ micro contaminants. (100 ppb of each)

This quantity of MPs was added because the concentrations at which these MPs are discharged from the scrubbers are 10 ppb. The problem is that at this concentration, they could not be observed in the HPLC, as it would be too small and would not detect them. No more than 100 ppb is added as otherwise it would be unrealistic as it would be too much higher than the actual 10 ppb.

Steps to follow:

Collect the water from the purifier and store it in the fridge.

- 5L of each water measured with a 1L measuring cylinder added to a bucket of 8 L total volume.
- 2. Add with a micropipette the corresponding aliquot of micropollutants.to obtain 100 ppb of each one.
- 3. Save 50 mL of the in solutions for later measuring the concentration of MPs.
- We gradually add the solutions to their respective wetlands until the 5 L of solution are used up without flooding them.
- 5. Turn on the pumps and check that the recirculation is working correctly.

## 4.5.1.3. Out of the Wetlands

Once the cycle has finished and the 3 days have passed, we empty all the wetlands.

Steps to follow:

- 1. We turn off the recirculation and empty the water from the wetlands.
- Note down the amount of water extracted, which is usually about 4.3 L, and add deionised water to the initial 5 L because, as the difference evaporates and evapotranspiration takes place, the concentration will have increased, and dilution is necessary.
- For cycles 1 and 8, we keep the 5 L of the dilutions in containers for later AOPs. In addition, we will also measure the concentration of micropollutants, DOC, nitrites, nitrates and Total Suspended Solids.
- For the other cycles, we keep 200 mL of the solutions in containers, since in this case the AOPs will not be carried out, to measure the DOC, Nitrites-Nitrates, suspended solids and phytotoxicity.

Once the cycles are finished, in order to continue trying to reduce the concentration of micropollutants in our water, we will use UVC-H<sub>2</sub>O<sub>2</sub> and Solar Photo-Fenton in the out of cycle 1 and in the out of cycle 8. Experiments with AOPs will also be conducted without passing through the wetlands to see their efficiency in removing micropollutants.

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## 4.5.2. Advanced oxidation processes

## 4.5.2.1. UV-H2O2 (UVC)

The first advanced oxidation process for the removal of micropollutants is presented. In figure 22 we can see the facilities to carry it out.



Figure 13: (1): Sample access (2): Reactor +magnetic stirrer inside them (3): Cooling plate+Agitator (4) Thermostatic bath (5): Thermostatic bath temperature controller, Setpoint=10.5 °C (6): Mercury monochromatic lamp (254 nm)

## Procedure:

- 1. Turn on refrigeration 30 minutes beforehand.
- 2. Wrap the lamp outside the reactor with silver foil before switching on the reactor. It has to be switched on 20 minutes before the start of the experiment.
- 3. Bring the water to room temperature (20-22 °C).
- 4. Place 2 L of wastewater in a 2 L flask and add the 2 mL of the contaminants (if the stock solution is 100 ppm). The atrazine being 20 ppm, add 10 mL and make up to the mark (in this way you will obtain the 100 ppb total concentration).

- If it comes from the pre-treatment, no micropollutants will be added.

- If it does not come from the pre-treatment, micropollutants shall be added.
- 5. Place the lamp inside the tank, close the reactor properly and cover it with aluminium foil.
- 6. Add the stirrer and switch on the stirring plate.
- 7. Take the sample at time 0 min

8. Add the peroxide (67  $\mu$ L of the stock solution (30% w/v) corresponding to 10 ppm of H<sub>2</sub>O<sub>2</sub> with the micropipette, switch on the lamp and start timing for 1 hour.

Sample collection:

- Time 0,2,5,7,10,15,15,20,30,45,60: Take 2 mL of sample with the syringe directly from the reactor and add it to the HPLC vial previously containing 23  $\mu$ L of thiosulphate (100g/L being 10 times molar greater than the peroxide to ensure that the peroxide is completely exhausted and thus stop the reaction) using a 0.45  $\mu$ m filter so that the HPLC machine can correctly obtain the results and store them in the refrigerator until they are analysed.

- Time 30,60 for determination of peroxide consumption.

Once the experiment is finished:

- Dry the lamp and leave it outside covered with aluminium.
- Empty the reactor.
- Recover the stirrer.
- Fill it twice with deionised water to clean it.
- Dispose of the Metha-vanadate and phenanthroline in the toxic product tanks.
- To clean the peroxide vials, pour citric acid (30% of the test tube) with water.

## 4.5.2.2. Photo Fenton Solar (SPF)

The second advanced oxidation process that has been carried out for the elimination of micropollutants is presented. Figure 23 shows the installations for this process.



Figure 14: (1): Cooling plate +Agitator + (2): Photoreactor glass with magnetic stirrer inside it (3): Sun test controller (4) Xenon Lamp (5): Thermostatic bath temperature controller, Setpoint=10.5 °C (6): Thermostatic bath

## Procedure:

- 1. Turn on the refrigeration 30 min before so that the plate is at 10.5 °C (Set point).
- 2. Temper the water to room temperature (20-22 °C).
- Place 0,2 L of wastewater in a 200 ml flask and add 0,2 mL of the contaminants (if the stock solution is 100 ppm). The atrazine being 20ppm, we will add 1ml (in this way we will obtain the 100-ppb total concentration).
  - If it comes from the pre-treatment, no micropollutants will be added.
  - If it does not come from the pre-treatment, the micropollutants will be added.
  - Dissolutions + iron is made up to 200 ml.
- Place the reactor in the centre of the cooling plate above the stirrer plate, both covered with black cardboard so that the black absorbs the light and so the rays fall directly on our solution.

- 5. Add 150 ml of the solution, measured with a measuring cylinder, to the reactor together with the stirrer and activate the stirring plate.
- 6. Take the sample at time 0.
- Turn on the SUNSET(1+START) at 765(W/m2) and 35°C, add the peroxide (25 μL) with the micropipette and start timing for the 2 hours.

Sample collection:

- Time 0,2,5,7,10,15,15,20,30,45,60,90,120: Take 2 mL of sample with the syringe directly from the reactor and add it to the HPLC vial previously containing 23  $\mu$ L of thiosulphate (100g/L) to stop the reaction using a 0.45  $\mu$ m filter so that the HPLC machine can obtain the results and store them in the fridge until they are analysed.

- Time 30,60,120 for determination of peroxide consumption.
- Time 0,30,60,120 for the determination of the iron precipitation.

At the end of the experiment:

- Switch off the SUNTEST CPS(STOP+0).
- Empty the reactor.
- Recover the stirrer.
- Fill it twice with deionised water to clean it.
- Dispose of the meta vanadate and phenanthroline in the toxic product tanks.
- To clean the peroxide vials, pour citric acid (30% of the test tube) with water.

## 4.5.3. Total Suspended Solids (TSS)

To determine the suspended solids, a filter (MF-Millipore 0.45 µm MCE membrane) was weighed using an analytical balance and placed in the device shown in Figure 15, which consists



of a vacuum pump, a porous membrane funnel, and a sample beaker. A known volume of the sample was passed through the filter, which was then placed in the oven for 24 hours, and finally, the weight difference was measured.

This was performed with the inputs and outputs of cycles 1 and 8.

Figure 15: Assembly of the determination of suspended solids.

## 4.5.4. Dissolved Organic Carbon

Samples from cycles 1, 2, 7 and 8 were filtered with 0.45 µm filters. Subsequently, Dissolved Organic Carbon (DOC) was determined following the Standard Methods 5310 B procedure, using a TOC-VCSN 5055 analyzer equipped with an ASI-V autosampler, both from Shimadzu (Japan). The analysis comprised three stages: first, the sample was acidified (HCI, 2 M) to remove inorganic carbon, followed by air bubbling; then, catalytic combustion of the sample was carried out at 680 °C; finally, CO2 was quantified after combustion.

The samples were filtered with 0.45 µm filters and taken to the geology department for analysis.

This was performed with the inputs and outputs of cycles 1,2,7 and 8.

#### 4.5.5. Ions Determination

The Separation Unit of the Scientific and Technological Services of the University of Barcelona carried out an ion determination analysis. Ion chromatography was used to measure the concentration of nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), chloride (Cl<sup>-</sup>) and sulphate (SO<sub>4</sub><sup>-</sup>) anions in water samples. This was carried out using a high-performance liquid chromatograph equipped with serial UV and conductivity detectors. The separation was performed with a 4.5 x 150 mm IC-PAK ANION column from Waters (USA). The mobile phase, composed mainly of borate buffer (B(OH)<sub>3</sub>) and acetonitrile (C<sub>2</sub>H<sub>3</sub>N), had a flow rate of 2 ml/min. 200  $\mu$ L were injected, and the UV detector was set to a wavelength of 214 nm.

#### 4.5.6. Alkalinity

The alkalinity of the wastewater samples was determined using an automatic titration method (pH Burette 24) together with a pH Basic 20 meter, both from CRISON (Spain). Also, hydrochloric acid (0.1 M) was used and an end point of pH 4.3 was set in the titration. This technique allows measuring the ability of water to neutralize acids. In wastewater, alkalinity is mainly attributed to bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) species.

#### 4.5.7. pH measurement

The pH reading was taken using the CRISON GLP 22 pH meter, which was properly calibrated each day with buffer solutions of pH 7.0 and pH 4.0.

# 5. RESSULTS AND DISCUSIONS

# 5.1. MPS REMOVAL EFFICIENCY AS A FUNCTION OF THE EFFLUENT USED.

#### 5.1.1 Constructed Wetlands (CWs)

The performance of CWs in the removal of MPs can be affected by biodegradation, plant sorption and by the effect of the n-octanol/water partition coefficient (log Kow).

The n-octanol-water partition coefficient (Kow) represents the ratio of the concentration in the n-octanol phase to that in the aqueous phase at equilibrium. It is a measure of the hydrophobicity, or affinity for lipids, of a substance dissolved in water. Octanol is considered a model solvent that mimics lipid tissues in organisms and humans, and organic carbon in soils and sediments. Therefore, octanol has been widely used as a suitable surrogate for the partitioning of chemicals from aqueous media to organic matrices [34]. Chemical compounds with high Kow values (Kow >1) tend to accumulate in the lipid portions of organisms and to concentrate in soils and sediments [34]. Therefore, they are easily adsorbed on soil, mineral surfaces and biofilms [35].

On the contrary, compounds with low values (Kow<1), tend to be distributed in water or air because of their good solubility and therefore, should not be adsorbed by microcosms.

The Dow represents the ratio between the concentration in the n-octanol phase of the ionic species. It is calculated from Kow and pKa.[34] Chemical compounds with low values (Dow < 0) show in general a very efficient removal efficiency (>80 %) and those with high values (Dow > 3) are also efficient (60-80 %), although somewhat lower.[36] In previous studies, various drugs have been investigated for their solubility in the n-octanol phase of the microcosm.

Previous studies investigated various drugs, with different log Kow and pKa values, and found no consistent relationship between clearance efficiencies and log Kow and pKa values. [36]

Figure 16 shows the range of all MPs removal results of the 3 different CWs during the 8 cycles by marking with an X the mean removal of each.





Figure 16: Removal of 8 micropollutants by microcosms planted with Carex Pendula constructed during 8 cycles with recirculation: W1(MBR), W2(MIX), W3(IFAS). Retention time= 3 days; [MPs]<sub>0</sub> = 100 ppb each.

Comparing our results (figure 16) with the articles [36-37-38], we can see that the elimination trend is the same. In all three cases, IBF, ATNL and IOPM have a removal rate of 90%.

For IBF, the main reason for its elimination is due to the fact that its Kow (3.97) is very high, so it will surely remain adsorbed in the different layers of the biofilm and roots of the plant.

What is unexpected is that both ATNL and IOPM, with such a low Kow (0.16-0.057), have such a high percentage of elimination. A study by Dettenmaier et al. (2009) suggests that compounds that are highly polar (log Kow<1: the most hydrophilic compounds) have the highest sorption potential by the plant. The finding of Dettenmaier et al. (2009) is in agreement with a recent study by Zhang et al. (2013a) who investigated caffeine sorption by *Scirpus validus* grown under hydroponic conditions. These authors demonstrated that caffeine, which is highly polar and water-soluble organic compound, was substantially absorbed by plant roots and then translocated to shoot tissues. [36]

The main reason why these two MPs have been virtually eliminated in each of the cycles is because of their Dow. As mentioned above, a Dow<0, generally shows a very efficient elimination (>80%). And this has been the case with the Dow of both being negative (log Dow [ATNL]=-2.14, log Dow [IOPM]=-0.44).

The three MPs with the highest removal rates are readily biodegradable pharmaceuticals, and previous studies have indicated that direct sorption of pharmaceuticals by plants is a surprisingly effective removal mechanism.

Both processes had CBZ in their studies as did ours. In all three cases, the removal rate is a maximum of 40 %. Having the intermediate log Dow of between 2 and 3 shows a poor overall removal. [37] Log Dow [CBZ]=2.77. Furthermore, in our study, PMD has very similar elimination percentages to CBZ as in [36]. The percentage of the mass of CBZ and PMD stored directly in plant tissues (22%) was significantly lower than the total mass elimination of carbamazepine (64%).

ACTM, being a very recalcitrant species, was the most difficult to eliminate in all studies. [38]

Finally, MPs with log Kow values ranging from 1 to 3 are lipophilic enough to cross the lipid bilayer of membranes, and yet water-soluble enough to travel to cellular fluids. So, the clearance rates of these MPs will be very similar and moderate (log Kow [ATZ]=2.64, log Kow [DMZ]=1.42, log Kow [CBZ]=2.45).

For all MPs, photolysis could also play a role (it is possible that they were degraded by solar irradiation as they were not covered by the top of the CW but we have no data on this).

Figure 17 shows the average of the MPs removal results of the 3 different CWs during the 8 cycles.



Figure 17: Removal of 8 micropollutants by microcosms planted with Carex Pendula constructed for 8 cycles with recirculation: W1(MBR), W2(MIX), W3(IFAS Retention time= 3 days; [MPs]0 = 100 ppb each.

The presence of more DOC can stimulate microbial activity, as many micro-organisms use organic matter as a source of energy and carbon. This can lead to increased biodegradation of pollutants in the system. [39]

For this reason, by varying the effluent, and having more and more organic matter, more and more microorganisms in the system, the percentage removal of MPs increases. In the case of IFAS, if there is an excess, the system could become saturated (plant/sand) and it is no longer totally eliminated. That is why the optimum is mixed water.

The removal rate of ATNL does not vary as the effluent varies, so its removal could be mainly due to plant adsorption.

A plausible explanation for this observation could be that micropollutants that are moderately hydrophilic (with log Dow between 2.5 and 3) tend not to bind significantly to organic matter [37]. So, for this reason, for ATZ (Kow=2.64), their removal is more associated with sorption processes than with biodegradation. [36]

Finally, in the case of IBF, as effluent turbidity increases, its percentage removal decreases. This could be because the pH is increasingly higher, and the n-octanol/water partition coefficient could differ from equilibrium.

Figure 18 shows the average Mps removal for each cycle of the 3 different CWs during the 8 cycles.



Figure 18: Removal of 8 micropollutants by microcosms planted with Carex Pendula constructed for 8 cycles with recirculation: W1(MBR), W2(MIX), W3(IFAS Retention time= 3 days; [MPs]0 = 100 ppb each.

The average percentage of PM removal, as the cycles go by, gradually decreases.

The reason why the percentages vary in cycle 6 (increasing considerably) is that the effluent was changed to a more turbid effluent (due to rain), with more suspended solids and organic matter.

Despite this, the mixture has higher average removal percentages except in cycle 6,7,8 where the incoming MBR is much more turbid than that of cycle 1 and in this case, it would perform the function of the cycle 1 mixture being the one with the highest removal percentage.

Pictures of CW results and growth percentages are in appendix IV.

It can be seen that all 3 plants have managed to grow throughout these months, the plants that have grown the most being those of W1 and W2. The W3 plant, having the IFAS effluent, has reduced its growth.

#### 5.1.2. Organic Matter, TSS ands NO<sub>2</sub><sup>-</sup> evolution

During the investigation, the removal efficiency of dissolved organic carbon, total suspended solids and nitrite (NO<sub>2</sub><sup>-</sup>) was measured in all CWs. As already explained in the introduction, these parameters negatively influence the efficiency of the AOPs. Dissolved organic matter is generally more abundant than micropollutants and therefore tends to react with hydroxyl radicals. Nitrite ion competes with the species involved in •OH formation by presenting a second order reaction rate with a maximum peak between 300-310 nm and total suspended solids cause turbidity in the water, which reduces the penetration of light into the solution. All this influences a decrease in •OH generation and a lower removal efficiency.

Figure 19 shows the range of all DOC removal results of the 3 different CWs during the 8 cycles by marking with an X the average removal of each.

## DOC



## Figure 19: Removal efficiency of dissolved organic matter in three constructed wetlands: W1(MBR), W2(MIX), W3(IFAS) during 8 cycles. Retention time = 3 days.

As can be seen in Fig. 18, DOC removal was always higher the more turbid the water. Among them, the system with IFAS had an average removal rate of 53 % compared to 26 % for MBR. It makes sense that the blended water has an average rate of 37 % being between the 2 waters.

In all three systems, there is a reduction in DOC as the CWs are recirculated, the removal of DOC can be attributed to the fact that the plants were able to sorb the organic matter to carry out their vital functions as the effluent is continuously circulated through the system. The most significant change is reflected in IFAS, which, starting with higher DOC, is more likely to be reduced as the effluent is more turbid than the other two (W1, W2). Also, the continuous contact time with the roots of the microcosms and the presence of more oxygen could favour oxygen removal.[36]

Figure 20 shows the range of all the TSS removal results of the 3 different CWs during the 8 cycles marking with an X the average removal of each.



Figure 20. Total suspended solids removal efficiency in three constructed wetlands (MBR, MIX, IFAS) for 8 cycles. Retention time = 3 days.

As can be seen in Fig. 4, TSS removal was always higher as the water is more turbid. Among them, the system with IFAS had an average removal rate of 85 % compared to 75 % for MIX. The MBR had very few suspended solids compared to the other effluents (MBR passes through a membrane) so the few that were present were not removed.

In both systems, there is a reduction in the TSS when the CWs are recirculated, the elimination of these may be because the larger ones have settled by gravity at the bottom of the CW, the smaller ones may have been filtered by passing through the different sands of different diameters, they may have biodegraded or been adsorbed by the plant. [37]

As the cycles progress, the percentage removal of TSS increases significantly to a percentage removal of 93.8 % (W2) and 98.2 %(W3): As the cycles progress, the system has acclimatised, and biofilms have formed thus increasing the percentage removal.

Figure 21 shows the range of all the results of NO<sub>2</sub><sup>-</sup> disappearance and NO<sub>3</sub><sup>-</sup> formation of the 3 different CW during the 8 cycles marking with an X the average removal of each one.









As the water has more DOC, more nitrate is produced because, there might be more nitrifying bacteria present in the system. Nitrification is an aerated biological process where ammonia is oxidised to nitrate. It is divided into two stages, the first stage is defined by the oxidation of NH<sub>4</sub><sup>+</sup> to nitrite (NO<sub>2</sub><sup>-</sup>) and the second stage is defined by the oxidation of (nitrite) NO<sub>2</sub><sup>-</sup> to (nitrate) NO<sub>3</sub><sup>-</sup>. [39] As it can be seen, nitrification is a biological process where ammonia is oxidised to nitrate.

Therefore, as can be seen in the graphs, during the stay in the CW, the MBR becomes "dirty" forming NO<sub>2</sub>-, which it did not have when it entered, and on the other hand IFAS and MIX consume the NO<sub>2</sub>- forming NO<sub>3</sub>- by nitrification.

As the CWs are recirculated, the nitrification process takes place, with a maximum concentration for W1 of 390 mg/L, for W2 of 225 mg/L and for W3 of 75 mg/L.

## 5.2. HYBRID SYSTEM(CW<sub>s</sub>+AOPS)

In this part of the study, the effectiveness of a Hybrid system (CW followed by SPF or UVC) is evaluated. As explained above, the first one aims to remove most of the MPs, together with suspended solids, dissolved organic matter and nitrogenous species that negatively affect the AOPs in the form of pretreatment. The second step (AOPs) aims to increase the quality of the treated water by trying to increase the removal rate as the turbidity of the foul water has been greatly reduced, so that more light can penetrate the solution and more •OH can be generated.

#### 5.2.1. Elimination of the 8 MPs only by using the AOPs.

## 5.2.1.1 SPF

To compare the efficiency of the hybrid system with the SPF, the micropollutants are injected into each effluent, where each represents different reaction kinetics with the •OH radical and photolysis. Both are controlling factors in the performance of the photochemical transformation processes. [41]

Photolysis is the decomposition by natural or artificial light of a chemical mixture composed of direct and indirect photolysis. Organic compounds absorb UV light in the direct photolysis process, while photosensitisers such as oxygen and hydroxyl radicals or peroxide perform the light decay in indirect photolysis. If organic compounds are sensitive to light, the main method of removal will be optical scattering. The strength and frequency of the light is based on the photochemical breakdown. The photolysis mechanism does not occur if the surface of the bioreactor is obscured as it cannot be incident. [42]

In this process, the rapid and high generation of hydroxyl radicals favours the rapid removal of contaminants with higher second order reaction rate constants (K<sub>OH-MP</sub> Table 6) as, these react more quickly and efficiently with the available radicals. [43]

Table 6: Kinetics with the hydroxyl radical of each MPs: [43].

Mps:	[ATNL]	[IOPM]	[ACMP]	[PMDN]	[CBZ]	[ATZ]	[IBF]	[DMZ]
К.он-мр [M <sup>-1</sup> ·s <sup>-1</sup> ]:	8·10 <sup>9</sup>	3.3·10 <sup>9</sup>	2.1·10 <sup>9</sup>	6.7·10 <sup>9</sup>	8.8·10 <sup>9</sup>	3·109	7.4·10 <sup>9</sup>	5.6·10 <sup>10</sup>

Figure 22 shows the degradation results achieved for each MPs with the SPF treatment. The percentage degradation is a function of C/C0 so 1 means 0 % removal and 0 is 100 % removal.

A)





Figure 22: Degradation results achieved for each PM with the SPF treatment at neutral pH with EDTA-Fe of cycle 1 for each effluent (MBR (a)-MIX(b)-IFAS(c)) in 120 min.

It is observed that, for any effluent, the MPs with the highest percentage of removal are DMZ and CBZ. Both are the ones with the highest hydroxyl radical kinetics, so as it is a second order reaction with the same concentration of MPs (100 ppb), increasing the kinetics increases the speed of the reaction and the percentage of elimination. In the same way, the lowest percentage of elimination is observed for ACMP and ATZ, as they have the lowest kinetics with the lowest hydroxyl radicals. [42]

As the water increases in turbidity, photolysis becomes less efficient as it is unable to affect the water matrix as it becomes increasingly opaque to the point of no longer occurring and each time the percentage of elimination decreases. [43]

For this reason, in the MBR effluent, the percentage of CBZ removal, despite having lower kinetics than DMZ. The removal rate is higher. As the turbidity of the effluent increases, the percentage of CBZ decreases and in both MBR and IFAS, as light is not incident, DMZ is removed more than CBZ.

This is also the case for PMDN. In the MBR effluent, it has a higher removal rate than ATNL despite having lower kinetics. As the turbidity of the effluent increases, the percentage of PMDN removal will decrease until practically nothing is removed as light is no longer able to penetrate.

Furthermore, as mentioned above, as the turbulence of the effluent increases, the DOC, suspended solids, nitrites/nitrates increase. Given the non-selective behaviour of the ·OH radicals, there is more and more competition for the hydroxyl radical and, therefore, the removal rate also decreases.

In addition, H<sub>2</sub>O<sub>2</sub> is consumed earlier and earlier. After 60 min, an absorbance of 0.208 was read in MBR and 0.032 and 0.029 in MIX and IFAS, respectively. In the case of iron, the percentage of iron precipitation is very regular for both MIX and IFAS due to the fact that it precipitates practically in the same way during the 120 min, being 50 %. For this reason, it can be seen in the figure above how they stabilise at 60 min. On the other hand, in the case of MBR, as the peroxide is present for a longer time and is exhausted at 120 min, the iron precipitates 65.44 %, thus increasing the number of hydroxyl radicals and improving the percentage of elimination of the MPs (Appendix 3).

Thus, with MBR, a removal rate of 100% is reached, clearly distinguishing the MPs where the kinetics are higher. In the mixture, up to 42 % removal is achieved and with IFAS up to 32 %.

Comparing DMZ times at a 30 % elimination rate, with MBR this elimination is reached after 20 min, with Mixture after approximately 60 min, and with IFAS after 120 min. 5.2.1.1 UVC

To compare the efficiency of the hybrid system with UVC, the micropollutants are injected into each effluent, where each represents different reaction kinetics with the -OH radical and photolysis.

In this case, near-monochromatic UV light is emitted at a wavelength of 254 nm. So, the MPs that are read closer to that wavelength, along with the higher  $K_{OH}$ -MPs. [44]

Figure 23 shows the degradation results achieved for each MPs with the UVC treatment. The percentage degradation is a function of C/C0 so 1 means 0 % removal and 0 is 100 % removal.

A)



B)



C)



Figure 23: Shows the degradation results achieved for each MPs with the UCV treatment at neutral pH of cycle 1 for each effluent (MBR(A)-MIX(B)-IFAS(C)) in 60 min.

Comparing our results (figure 8) with the article [10], we can observe that the removal trend is the same. In both cases, ATZ and IOPM are the 2 MPs with the highest percentage of removal. IOPM is the highest with 92 % at 60 min.

These MPs have in common that they are read at wavelengths close to that of the monochromatic lamp (254 nm), being read at a wavelength of 240 nm, 222 nm, respectively. In addition, they have the slowest reaction speed, so it makes sense that they are the ones that are eliminated the most.

ACMP, however, by reading at exactly 254 nm despite its very low reaction rate, competes with hydrogen peroxide for photons from the UV lamp, reducing the formation of hydroxyl radicals (·OH) necessary for its degradation and, during its degradation, intermediates may also form which also absorb at 254 nm, interfering with the measurement and giving the appearance that ACMP is not being removed effectively.

DMZ and CBZ, despite having the highest reaction rates, are not removed as much when read at a wavelength of 320 nm, 214 nm being a little far from the 254 nm at which the monochromatic lamp emits, respectively, so photolysis predominates in this advanced oxidation process.

Therefore, PMD ANT and IBF, which are read at 200 nm and are the furthest away from 254 nm, are the ones with the worst percentage of elimination.

Furthermore, IBF and CBZ also appeared in the article, with a removal percentage of 80% and 45 % respectively at 60 min. Above all, for IBF, photolysis is essential as it decreases considerably as the turbidity of the water increases.

In the case of IOPM, as photolysis is so dominant, its removal rate will not vary greatly as the effluent becomes increasingly turbid.

The  $\cdot$ OH generated during the UV/H<sub>2</sub>O<sub>2</sub> process can be inhibited by the presence of suspended solid DOC, Nitrites/Nitrates, as the water becomes more turbid by competing for the hydroxyl radical. However, despite this, the MPs with the highest percentage of removal are the ones with the highest percentage of removal, which reaffirms that photolysis is the most predominant.

Finally, most of the MPs are not completely degraded due to UV doses or insufficient retention times, and no removal has stabilised. At time 30 min, the peroxide for all three effluents is almost non-existent so that, for AOPs without the help of CWs, the amount of peroxide set could be increased, being economically optimal. This could be the reason why higher MPs removal rates are not achieved compared to those in the article [45].

Removal efficiency of MPs at 100 ppb by the hybrid system.

The last part of this work consists of the evaluation of the performance of the hybrid system in the removal of the 8 MPs studied with the same initial concentration for each of them.

## 5.3. HYBRID SYSTEM + COMPARED CYCLES

## 5.3.1. Cycle 1

Figure 24 compares all the removal rates for cycle 1.





Figure 24: Comparison of UFAs without Pretreatment (SPF/UV), CW and Hybrid Process (CW+SPF/CW+UVC) cycle 1.

As discussed in the previous sections, for SPF, the hybrid process, if the effluent is the MBR/IFAS, is much more efficient than using CW or SPF alone. On the other hand, for MBR effluent, performing an AOP directly is more efficient than CW alone or the hybrid process.

On the other hand, for UCV, the hybrid process, if the effluent is the mixture/IFAS, is much more efficient than using CW alone or UVC. In contrast, for MBR effluent, the difference between the hybrid process and UVC alone is not as great. In this case, as the MPs with the highest reaction rates are removed with CW (MPs with the lowest percentage of removal achieved with AOP), the following removal with UCV, despite being slightly dirtier, and gaining Solids, Nitrites, DOC, makes the total removal percentage a little higher than that of UCV alone. In the same way, for the UCV alone the percentage of elimination is 71 % and for the hybrid elimination process it is 74.4 %, so that, the percentage difference being so small, it will be better to use only the AOP.

In conclusion, the MIX water has been the one with the best elimination, so it has been the optimal effluent for this work, despite the great improvement in the quality of the IFAS effluent.

## 5.3.2. Cycle 8

Figure 25 compares all the removal rates for cycle 8.



Figure 25: Comparison of UFAs without Pretreatment (SPF/UV), CW and Hybrid Process (CW+SPF/CW+UVC) cycle 1.

Compared to cycle 1, in this case, as the effluent is changed and is much more turbid due to the effect of the rain, in cycle 8 for all effluents, the hybrid model will be the most efficient. Both the MIX and the IFAS have practically the same results, as the IFAS water is so important and is so opaque and with a large number of TSS, that the mixture was practically IFAS and the MBR part did not vary practically at all.

# 6. SURVEY

A survey was carried out (Appendix 3) to find out whether the population is aware of the current problems of water scarcity and whether they have an idea of the quality of the water coming out of the treatment plant.

Conceptually, the percentages of people who know how a sewage treatment plant works and what its effluent looks like, or who know what a micro-pollutant is, or what a micro-pollutant is, or what the effluent is.

Overall, of the 300 people who responded to this survey, 87.1% consider water conservation to be very important in our lives.

Two waters from two different WWTP outlets (IFAS/MBR with a photograph) were compared and asked which water they thought would be the water from the WWTP outlet. Only 38% knew that both were an effluent so after explaining that both are full of micro pollutants, and after they saw how dirty one of them is, 78.4% would be willing to pay more for the water if it would guarantee a higher quality and 93.2% would see the need for the government to invest funds to develop water reuse methods. So, in general, the population understands that the problem with scarcity is very important, but they are not aware that even though these effluents comply with the regulations, these should be much more stringent than they currently are. Initially, before I started the work, I did not know that the quality of the effluent was so low. Therefore, given the great importance of water, I would see it as essential that this knowledge be implemented in our basic and compulsory studies.

Furthermore, in order to see if the work on water reuse with the hybrid method makes sense and can be implemented in people's lives, certain questions were asked about reused water and these are the answers: Esta sería una fotografía de agua reutilizada(Ya sin microcontaminantes). ¿Beberías agua reutilizada? 279 respuestas





¿Verías bien que los parques, plantas, etc... de las ciudades se regaran con agua reutilizada? 279 respuestas





¿Irías a una piscina o porque acuático en que el agua es reutilizada? 279 respuestas



As can be seen, in general, people would be willing to use reused water. 90.7% would use this water for watering parks, plants... so this would be the way they would start using it. Furthermore, the negative percentages of the following questions are very small, so if we explain well how water is recovered and the properties it has, I don't see any problem in implementing reused water in our lives.
## 7. CONCLUSIONS

Both the CWs, the AOPs and the hybrid system have been useful in the elimination of MPs, reaching higher than expected elimination percentages.

On the one hand, removal in the CWs has been successful, practically eliminating ATNL, IOPM and IBPD in each cycle, with an average removal rate of 90 %. As the cycles progressed, more TSS, DOC and nitrites were eliminated, so that the percentage of elimination in cycle 1 was around 50 %, and in cycle 8 around 95 %. So, despite not removing more MPs throughout the cycles, the fact that the effluent was much less turbid and transparent meant that for the AOPs afterwards, photolysis could be produced more efficiently and the final results for the hybrid removal processes were up to 90 %.

In addition, the plants have grown, with the W2(MIX) having the highest growth rate of 64.33 %. CWs would be ready to continue with the removal of MPs.

On the other hand, the elimination in the AOPs, in the case of SPF, as it does not operate at a single wavelength like UVC (254 nm), the effect of photolysis has had a different impact. In SPF, the second-order reaction rate with hydroxyl radicals is more influential, with hydroxyl radicals having the highest removal rates [DMZ, CBZ], both with removal rates of 90 %.

On the other hand, in the UVC, a higher percentage of elimination is obtained for the MPs that are closer to 254 nm. [ATZ, IOPM] have 85 % removal rates. The percentages are not as high as expected as the peroxide is almost totally consumed at low times (30 min), reading an absorbance of 0.029 on average.

In both cases, as the water becomes more turbid, with more organic matter, TSS... the removal efficiency decreases considerably, consuming the peroxide at a faster rate.

However, in the hybrid process (CWs+AOPs), for CWs+SPF, if the effluent is MIX/ IFAS, it is much more efficient than using only CW or SPF. Reaching percentages of 90 % on average for the hybrid process (higher than 24.4 % for SPF and 63.5 % for CW). On the other hand, for the MBR effluent, carrying out an AOP directly is more efficient than the CW alone or the hybrid

process. The average percentage for the hybrid process is 82.4 % (higher than 24.4 % for the hybrid and 66 % for the hybrid process).

On the other hand, for the UCV, the hybrid process, if the effluent is the mixture/IFAS, is much more efficient than using only CW or UVC. It reaches very similar percentages around 85 %. On the other hand, for MBR effluent, the difference between the hybrid process and UVC alone is not so great, as CW removes the MPs with a lower percentage of UVC removal. For the UCV alone the removal rate is 71 % and for the hybrid removal process 74.4 %.

As mentioned above, when moving from cycle 1 to cycle 8, the CWs were leaving the effluent in better and better condition, so photolysis occurs more efficiently and the results for the hybrid processes for all 3 effluents in cycle 8 are 95 % for AOP.

Furthermore, people agree with the future use of wastewater for irrigation in cities with 91 % of votes, although they are not so sure when it comes to consuming it directly, these percentages being lower (70 %).

## 8. IMPROVEMENTS AND FUTURE PROPOSALS

To prevent algae from appearing, the toilets should have been better sealed with aluminium when they broke underneath during emptying.

In addition, to improve the percentages of elimination of micropollutants, we could add a layer that eliminates [those that have gone with them], leave the cycle recirculating for more days, eliminate recirculation, change the plants, increase the elimination time in some experiments in which the peroxide has not been consumed,

Moreover, for further research, the water could have been tested for the presence of *Eschericia coli* and Phytotoxicity and check whether this water could be used for agricultural purposes.

Finally, water collected from the wetlands could be used to irrigate radishes or tomatoes. This would make it possible to observe how the plants grow and to analyse the fruits, thus assessing the quality of the treated water and its impact on growth and food safety.

# 9. REFERENCES AND NOTES

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# **APPENDICES**

# **APPENDIX I: MPs PROPERTIES**

#### I.I. Atenolol [ATNL]

Table I: [ATNL] properties [I]

Propriety	Value
Molecular Formula:	$C_{14}H_{22}N_2O_3$
IUPAC Name:	2-[4-[2-hydroxy-3-(propan-2 ylamino)propoxy]phenyl]acetamide
Chemical Safety:	(!)
	Irritant Health Hazard
Molecular Weight (g/mol):	266.34
Density(g/cm <sup>3</sup> ):[II]	1.13
CAS Number.:	29122-68-7
Solubility (mg/mL):	13.30
pKa:	9.60
log kow:	0.16



Figure I: Absorption spectrum [ATNL] (0.1 ppm in UPW) Peak= 193 nm

#### I.II. lopromide [IOPM]

Table II: [IOPM] properties [III]

Propriety	Value
Molecular Formula:	C <sub>18</sub> H <sub>24</sub> I <sub>3</sub> N <sub>3</sub> O <sub>8</sub>
IUPAC Name:	1-N,3-N-bis(2,3-dihydroxypropyl)-2,4,6-triiodo-5-[(2-methoxyacetyl) amino]-3-N-methylbenzene-1,3-dicarboxamide
Categorization Type:	Low osmolar, non-ionic X-ray contrast agent for intravascular administration.
Chemical Safety:	
	Environmental Hazard
Molecular Weight (g/mol):	197.10
Density(g/cm <sup>3</sup> ):[V]	2.17
CAS Number.:	73334-07-3
EC Number:	277-385-9
Solubility (mg/mL):[V]	0.37
pKa:[VI]	11.09
log kow:	0.06



Figure II: Absorption spectrum [IOPM] (0.1 ppm in UPW). Peak=241 nm

### I.III. Acetamiprid [ACMP]

Table III: [ACMP] properties [VII]

Propriety	Value
Molecular Formula:	C <sub>10</sub> H <sub>11</sub> CIN <sub>4</sub>
IUPAC Name:	N-[(6-chloropyridin-3-yl) methyl]-N'-cyano-N-methylethanimidamide
Categorization Type:	Carboxamidine
Chemical Safety:	Irritant-Health/Environmental Hazard-Acute
Molecular Weight (g/mol):	222.67
Density(g/cm <sup>3</sup> ):	1.17
CAS Number.:	135410-20-7
EC Number:	603-921-1
Solubility (mg/mL):	2.95
pKa:	0.70
log kow:	0.80



## Figure III: Absorption spectrum [ACMP] (0.1 ppm in UPW). Peak=245 nm

#### I.IV Primidone [PMDN]

Table IV: [PMDN] properties [VIII]





#### I.V. Carbamazepine [CBZ]

Table V: [CBZ] properties [IX]

Propriety	Value	
Molecular Formula:	C15H12N2O	
IUPAC Name:	benzo[b][1] benzazepine-11-carboxamide	
Categorization Type:	Anticonvulsants	
Chemical Safety:	(!)	
	Irritant Health Hazard	
Molecular Weight (g/mol):	236.27	
Density(g/cm <sup>3</sup> ):[X]	1.27	
CAS Number.:	85756-57-6	
EC Number:	206-062-7	
Solubility (mg/mL):	0.15	
pKa:	13.90	
log kow:	2.45	



## Figure V: Absorption spectrum [CBZ] (0.1 ppm in UPW). Peak=210 nm

#### I.VI.Atrazine [ATZ]

Table VI: [ATZ] properties [XI]

Propriety	Value
Molecular Formula:	C <sub>8</sub> H <sub>14</sub> CIN <sub>2</sub>
IUPAC Name:	6-chloro-4-N-ethyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine
Categorization Type:	Herbicide that does not occur naturally
Chemical Safety:	
	Environmental/ Health Hazard
Molecular Weight (g/mol):	215.68
Density(g/cm <sup>3</sup> ):	1.20
CAS Number.:	1912-24-9
EC Number:	217-617-8
Solubility (mg/mL):	0.035
pKa:	1.6
log kow:	2.6



## Figure VI: Absorption spectrum [ATZ] (0.1 ppm in UPW). Peak=222 nm

#### I.VII. Ibuprofen [IBF]

Table 7: [IBF] properties [XII]

Propriety	Value	
Molecular Formula:	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	
IUPAC Name:	2-[4-(2-methylpropyl) phenyl] propanoic acid	
Categorization Type:	non-steroidal anti-inflammatory drug	
Chemical Safety:		
	Irritant Health Hazard	
Molecular Weight (g/mol):	206.28	
Density(g/cm <sup>3</sup> ): [XIII]	1.03	
CAS Number.:	15687-27-1	
EC Number:	239-784-6	
Solubility (mg/mL):	0.02	
рКа:	4.91	
log kow:	3.97	



Figure VII: Absorption spectrum [IBF] (0.1 ppm in UPW). Peak=193 nm

#### I.VIII. Dimetridazole [DMZ]

Table VIII: [DMZ] properties [IVX]

Propriety	Value	
Molecular Formula:	C5H7N3O2	
IUPAC Name:	1,2 -dimethyl-5-nitroimidazole	
Categorization Type:	Antiprotozoal drug	
Chemical Safety:	(!)	
	Irritant Health Hazard	
Molecular Weight (g/mol):	141.13	
Density(g/cm <sup>3</sup> ): [XV]	1.38	
CAS Number.:	551-92-8	
EC Number:	209-001-2	
Solubility (mg/mL):[XV]	9.68	

pKa:[XV]	2.81
log kow:[XV]	1.42



Figure VIII: Absorption spectrum [DMZ] (0.1 ppm in UPW). Peak=320 nm

# **APPENDIX II: ABSORBANCE TABLES**

#### II.I UVC-H<sub>2</sub>O<sub>2</sub>

Table IX: Absorbance of peroxide for the 3 effluents (IFAS-MIX-MBR) for 60 minutes.

With MPs (C1)	UVC-H2O2		
	Time(min)	30	60
	MBR	0.027	0.023
	MIX	0.055	0.029
	IFAS	0.038	0.029

IFAS	UVC-H2O2		
	Time(min)	30	60
	MPS AÑADIDOS (C1)	0.038	0.029
	MPS AÑADIDOS (C8)	0.000	0.000
	Cycle 1	-	0.048
	Cycle 8	-	0.013

МІХ	UVC-H <sub>2</sub> O <sub>2</sub>			
	Time(min)	30	60	
	MPS AÑADIDOS (C1)	0.055	0.029	
	MPS AÑADIDOS (C8)	0.000	0.000	
	Cycle 1	0.038	0.034	
	Cycle 8	0.045	0.029	

MBR	UVC-H <sub>2</sub> O <sub>2</sub>		
	Time(min)	30	60
	MPS AÑADIDOS (C1)	0.027	0,023
	MPS AÑADIDOS (C8)	0.063	0,076
	Cycle 1	0.032	0,019
	Cycle 8	0,027	0,023

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### II.I UVC-H<sub>2</sub>O<sub>2</sub>

Table X: Absorbance of iron and peroxide for the 3 effluents (IFAS-MIX-MBR) for 120 minutes.

	Solar photo-Fenton (H <sub>2</sub> O <sub>2</sub> )					Solar photo-Fenton (Iron)				
With MPs (C1)	Time(min)	30	60	120	0	30	60	120	Reduction %	
	MBR	0.324	0.208	0.016	0.787	0.642	0.497	0.272	65.44	
	MIX	0.055	0.029	0.004	0.962	0.879	0.603	0.481	50.00	
	IFAS	0.038	0.029	0.004	0.864	0.749	0.603	0.432	50.00	

	Solar photo-Fenton (H <sub>2</sub> O <sub>2</sub> )					Solar photo-Fenton (Iron)					
	Time(min)	30	60	120	0	30	60	120	Reduction %		
IEAS	MPS AÑADIDOS (C1)	0.055	0.029	0.004	0.962	0.879	0.603	0.481	50.00		
IFAS	MPS AÑADIDOS (C8)	0.000	0.000	0.000	0.864	0.749	0.603	0.432	50.00		
	Cycle 1	0.331	0.278	0.247	0.660	0.549	0.427	0.255	61.36		
	Cycle 8	0.293	0.248	0.187	0.574	0.406	0.286	0.143	75.09		

	Solar photo-Fenton (H <sub>2</sub> O <sub>2</sub> )				Solar photo-Fenton (Iron)					
	Time(min)	30	60	120	0	30	60	120	Reduction %	
MIX	MPS AÑADIDOS (C1)	0.055	0.029	0.004	0.962	0.879	0.603	0.481	50.00	
IVIIA	MPS AÑADIDOS (C8)	0.000	0.000	0.000	0.818	0.728	0.630	0.561	31.42	
	Cycle 1	0.347	0.300	0.244	0.688	0.515	0.342	0.138	79.94	
	Ciclo 8	0.351	0.399	0.308	0.473	0.398	0.255	0.103	78.22	

	Solar photo-Fenton (H <sub>2</sub> O <sub>2</sub> )					Solar photo-Fenton (Iron)					
	Time(min)	30	60	120	0	30	60	120	Reduction %		
MDD	MPS AÑADIDOS (C1)	0.324	0.208	0.016	0.787	0.642	0.497	0.272	65.44		
WIDK	MPS AÑADIDOS (C8)	0.208	0.205	0.204	0.559	0.618	0.564	0.521	6.80		
	Cycle 1	0.391	0.359	0.340	0.863	0.823	0.814	0.792	8.23		
	Cycle 8	0.254	0.182	0.118	0.840	0.650	0.372	0.178	78.81		

# **APPENDIX III: SURVEY**













48% 10,4% 41,6% Si, no me importaría Puede ser No, de ninguna manera

Esta sería una fotografía de agua reutilizada(Ya sin microcontaminantes). ¿Beberías agua reutilizada? 279 respuestas

¿Verías bien que los parques, plantas, etc... de las ciudades se regaran con agua reutilizada? 279 respuestas



¿Te ducharías con agua reutilizada? 279 respuestas





¿Comerías alimentos regados con agua reutilizada? 279 respuestas



¿Irías a una piscina o porque acuático en que el agua es reutilizada? 279 respuestas





Figure IV: Absorption spectrum [DMZ] (0.1 ppm in UPW). Peak=320 nm

# **APPENDIX IV:**



Figure V: This is how the CWs were at the end of the 8 cycles. (W1-W2)





Figure VI: W2(MBR A)Start B)Final) plant growth for 3 months and 8 cycles

A)

WC	Mo (g)	Mf (g)	Mass difference (g)	growth rate (%)
W1(MBR)	22.10	52.90	30.80	58.22
W2(MIX)	36.20	101.50	65.30	64.33
W3(IFA)	21.80	33.20	11.40	34.34

Table XI: Plant growth for each CW for 3 months and 8 cycles.