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Nature-based solutions as a pretreatment to enhance the removal of contaminant of emerging concern in wastewater

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El agua es la fuerza motriz de toda la naturaleza.

Leonardo da Vinci

En primer lugar, me gustaría expresar mi más sincero agradecimiento a mi tutora, la doctora Núria López. Su esfuerzo y dedicación han sido inspiradoras para realizar el trabajo. Gracias a ella también he aprendido la importancia de la investigación para que el mundo sea un lugar mejor. *Moltes gràcies per tot, ha estat un plaer, ens veiem per Menorca!*. Además, me gustaría agradecer al doctor Alberto Cruz por la ayuda en la primera fase del proyecto, así como a Ivan Díaz por ayudarme en la parte experimental. No me gustaría olvidarme de agradecer a Javier Sánchez formar parte del trabajo y hacer que las horas en el laboratorio fueran más amenas.

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CONTENTS

SUMMARY

The Sustainable Development Goal (SDG) number 6, established by the United Nations in 2015 as part of Agenda 2030, aims to ensure availability and sustainable management of water and sanitation for all. However, according to the United Nations' 2021 World Water Development Report, the current state of water is significantly far from achieving this goal. More than 2 billion people live in countries facing constant water stress, and approximately 4 billion suffer severe physical water scarcity for at least one month per year. Factors such as population growth, socio-economic development, and changes in consumption patterns are expected to increase water demand by 50% to 80% in the coming decades. Moreover, accelerated climate change could exacerbate this situation by rapidly reducing water availability globally.

In response to this scenario, the reuse of wastewater emerges as a crucial sustainable development strategy to address the scarcity crisis. However, it is essential that wastewater undergoes proper treatment to remove all harmful elements resulting from various human activities. Emerging microcontaminants such as pharmaceuticals, pesticides, personal care products, and steroid hormones are examples of substances that must be eliminated from water bodies, despite being detected at very low concentrations (from ng/L to µg/L). Conventional wastewater treatment systems were not initially designed to completely remove these persistent compounds, underscoring the need to implement additional technologies such as advanced oxidation processes, activated carbon adsorption, or membrane filtration to significantly enhance their removal.

Constructed Wetlands (CWs) are promising nature-based technologies for removing various types of microcontaminants due to their simplicity, low investment and operational costs. These wetlands are periodically flooded flat land areas with aquatic plants acting as natural filters. Through mechanisms like biodegradation, phytodegradation, photodegradation, rhizofiltration, and other processes, CWs can effectively eliminate heavy metals, nutrients, and organic matter.

However, they face challenges such as long retention times, large space requirements, and may not be suitable for certain compounds unaffected by biological or adsorption processes.

To improve the efficiency of the CWs and overcome these challenges, it is proposed to combine them with advanced oxidation processes. This can enhance treatment efficiency by reducing the load of organic matter and suspended solids before the oxidation stage. Additionally, the use of a natural waste product from the food industry in the CWs will be investigated due to its high adsorption capacity, and the effect of recirculation in these systems will be studied to optimize contaminant removal and nitrification-denitrification. The goal is to develop a more efficient and environmentally friendly treatment, also exploring the possibility of reusing the treated effluents for agricultural irrigation. By adding a layer of almond shell as a natural adsorbent, layers of 2 and 4 cm, greater removal was observed compared to the HC without this layer, with removal increasing by 70% for the 2 cm layer and 80% for the 4 cm layer. Therefore, the thickness of this layer influences the removal of microcontaminants. On the other hand, values such as DOC and TSS were also reduced by an average of 45% and 80% respectively. Nitrite levels decreased by almost 100%, and nitrate levels increased in all CWs due to the presence of oxygen. Finally, it was observed that the removal performance of the hybrid system (CW + AOP) increased compared to the processes separately, achieving an average removal of between 85-96%. In this case, the organic adsorbent layer is not as significant as in the separate CWs.

Keywords: Constructed wetlands, wastewater, microcontaminants, advanced oxidation processes, hybrid system, environment

RESUMEN

El Objetivo de Desarrollo Sostenible (ODS) número 6, establecido por las Naciones Unidas en 2015 como parte de la Agenda 2030, busca asegurar la disponibilidad y gestión sostenible del agua y el saneamiento para todos. Sin embargo, según el Informe Mundial sobre el Desarrollo del Agua de las Naciones Unidas de 2021, la situación actual del agua está considerablemente lejos de alcanzar este objetivo. Más de 2 mil millones de personas viven en países con estrés hídrico constante, y aproximadamente 4 mil millones sufren de escasez física severa de agua durante al menos un mes al año. Factores como el crecimiento poblacional, el desarrollo socioeconómico y los cambios en los patrones de consumo se anticipa que aumentarán la demanda de agua entre un 50% y un 80% en las próximas décadas. Además, el cambio climático acelerado podría agravar esta situación al reducir rápidamente la disponibilidad de agua a nivel mundial.

Ante este panorama, la reutilización de aguas residuales emerge como una estrategia de desarrollo sostenible crucial para abordar la crisis de escasez. Sin embargo, es fundamental que las aguas residuales sean tratadas adecuadamente para eliminar todos los elementos nocivos resultantes de diversas actividades humanas. Los microcontaminantes emergentes, como productos farmacéuticos, plaguicidas, productos de cuidado personal y hormonas esteroidales, son ejemplos de sustancias que deben ser eliminadas de los cuerpos de agua, a pesar de detectarse en concentraciones muy bajas (desde ng/L a µg/L). Los sistemas convencionales de tratamiento de aguas residuales no fueron inicialmente diseñados para eliminar completamente estos compuestos persistentes, lo que subraya la necesidad de implementar tecnologías adicionales, como procesos avanzados de oxidación, adsorción con carbón activado o filtración por membranas, para mejorar significativamente su eliminación.

Los Humedales Construidos (HCs) son tecnologías prometedoras basadas en la naturaleza para la eliminación de diversos tipos de microcontaminantes, gracias a su simplicidad, bajo costo de inversión y operación. Estos humedales son áreas de terreno plano inundadas periódicamente, con la presencia de plantas acuáticas que actúan como filtros naturales. A través

de mecanismos como la biodegradación, la fitodegradación, la fotodegradación, la rizofiltración y otros procesos, los HCs pueden eliminar metales pesados, nutrientes y materia orgánica de manera efectiva. Sin embargo, enfrentan desafíos como largos tiempos de retención y grandes requerimientos de espacio, y pueden no ser adecuados para ciertos compuestos que no se ven afectados por los procesos biológicos o de adsorción. Se han obtenido valores de eliminación de media del 65% empleando esta tecnología

Para mejorar la eficiencia de los HCs y superar estos desafíos, se propone combinarlos con procesos avanzados de oxidación. Esto puede mejorar la eficiencia del tratamiento al reducir la carga de materia orgánica y sólidos en suspensión antes de la etapa de oxidación. Además, se investigará el uso de un residuo natural de la industria alimentaria en los HCs, debido a su alta capacidad de adsorción, y se estudiará el efecto de la recirculación en estos sistemas para optimizar la eliminación de contaminantes y la nitrificación-desnitrificación. El objetivo final es desarrollar un tratamiento más eficiente y respetuoso con el medio ambiente, explorando también la posibilidad de reutilizar los efluentes tratados para riego agrícola. Mediante la adición de una capa de cáscara de almendra como adsorbente natural, capas de 2 y 4 cm, se ha observado una eliminación mayor que el HC que no disponía de esta capa, la eliminación aumento en 70% para la capa de 2 cm mientras que un 80% para la capa de 4 cm. Por lo tanto, el grosor de dicha capa tiene influencia en la eliminación de microcontaminantes. Por otra banda, valores como DOC, TSS también se vieron reducidos en una media del 45% y 80% respectivamente. En cuanto a los niveles de nitritos, disminuyeron casi al 100%, y los niveles de nitratos, aumentaron en todos los HCs por la presencia de oxígeno. Por último, se observó que el rendimiento de eliminación del sistema híbrido (HC + AOP) aumentó respecto los procesos por separado, obteniéndose una media de eliminación entre el 85-96%. En este caso la capa de absorbente orgánico no tiene tanta importancia como en los HCs por separado.

Palabras clave: Humedales construidos, agua residual, microcontaminantes, procesos de oxidación avanzada, sistema híbrido, medio ambiente

SUSTAINABLE DEVELOPMENT GOALS

Los Objetivos de Desarrollo Sostenible (ODS) de las Naciones Unidas proporcionan un marco global para abordar desafíos ambientales, económicos y sociales de nuestros tiempos. En particular, la búsqueda soluciones naturales para el tratamiento de aguas residuales y la eliminación microcontaminantes, como en este caso los humedales artificiales combinado con tratamientos de oxidación avanzados, contribuye con los siguientes ODS:

- **Agua limpia y saneamiento (ODS 6):** Los humedales artificiales ofrecen una solución eficaz y sostenible para la mejora de la calidad del agua al eliminar microcontaminantes como fármacos, cosméticos, químicos industriales y/o compuestos orgánicos persistentes.
- **Producción y consumo responsables (ODS 12):** La implementación de tecnologías como los humedales artificiales fomentan la práctica de tratamiento de aguas más sostenibles.
- **Acción por el clima (ODS 13):** Al reducir la cantidad de microcontaminantes del agua, los humedales construidos ayudan a mitigar el impacto medio ambiental ya que se consigue una mejor calidad en el agua y, de este modo, un apoyo a la biodiversidad.
- **Vida submarina (ODS 14):** La eliminación de los microcontaminantes promueven la salud de los ecosistemas acuáticos, protegiendo la vida biodiversidad marina.

1. INTRODUCTION

Water is an extremely significant resource on Earth, due to its properties, which make it essential for life as it sustains vital living activities such as nutrition, respiration, circulation, excretion, and reproduction. In addition, water serves as a natural habitat for numerous species of animals and plants, playing a fundamental role in creating life environments [1].

As shown in Figure 1, water distribution across the Earth's surface is highly disparate. Merely 3% of surface water is fresh, while the vast majority, 97%, is found in oceans. Within freshwater sources, 69% reside in glaciers, 30% are underground, and less than 1% may be uncovered in lakes, rivers, and swamps. Alternatively, when considering usable water for humans, only 1% of the Earth's water is available [2].

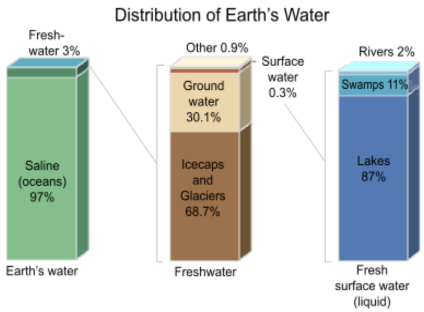

Figure 1. Water Distribution on Earth.
Source: Penn State University (United States) [2]

On the other hand, water also intervenes in economic, social, and industrial growth. It is estimated that each European inhabitant consumes an average of 144 L of water per day distributed between personal care, consumption, or cleaning. Industrial water consumption is also worth considering as it represents 18% of annual usage. However, the sector that consumes the most water, between 40-60%, is agriculture as there are highly demanded vegetables that require a lot of water to mature [3]. Figure 2 shows the distribution of water consumption in Europe.

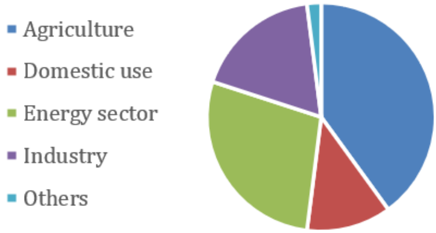

Figure 2. Water consumed in Europe.
Source: European Environment Agency [3]

1.1. NOWADAYS WATER PROBLEM

The Sustainable Development Goal (SDG) number 6, established by the United Nations in 2015 to fulfill the 2030 Agenda, aims to ensure full availability and sustainable management of water and sanitation for everyone. Unfortunately, according to the 2021 United Nations World Water Development Report, the current state of water is still far from the proposed goal. More than 2 billion people live in countries with constant water stress conditions, and around 4 billion people experience severe physical water scarcity for at least one month per year [4]. Additionally, factors such as population growth, socio-economic development, or changes in consumption patterns are expected to increase water demand by 50% to 80% in the coming decades. Moreover, accelerated climate change can exacerbate the situation, rapidly reducing water availability worldwide. Given the severity of this situation, it is crucial to identify effective solutions to confront water scarcity. One potential measure involves the reutilization of wastewater (WW) as a strategy to mitigate the demand for freshwater, or otherwise, as observed in Figure 3, by 2040 water stress by countries would increment severely [5].

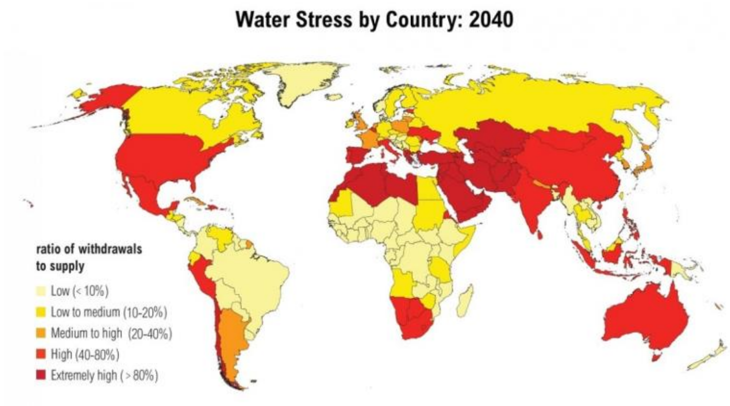

Figure 3. Water stress by Country: 2040.
Source: World Resources Institute [5]

1.2. WATER CONSUMPTION

Every year, Europeans consume billions of cubic meters of water for various needs such as agriculture, manufacturing, heating, cooling, tourism, and human consumption. Despite possessing many freshwater sources including lakes, rivers, or groundwater, there is significant water scarcity due to climate change, pollution, or overpopulation.

The regionalized water exploitation index (WEI+) measures the total water consumption as a percentage of the renewable freshwater resource in a specific area and period. This index quantifies how much water is extracted and returned to the environment in a period [6]. Economic activities in Europe consume an average of 243.000 hm^3 of water annually, according to the Water Exploitation Index. Although more than half of this consumed water is returned, it contains MPs.

Agriculture is the largest water consumer. Europe's utilized agricultural area (UAA) is nearly 175 million hectares, 40% of the total land area [7]. This represents around 40% of total annual water consumption. Despite efficiency improvements since the 1990s, agriculture will remain the major user in the upcoming years because of population growth and increasing water stress.

Energy generation also consumes a significant amount of water, about 28% of total annual consumption. This is mainly used as a refrigerant in industries such as nuclear and fossil fuel power plants.

The remaining water consumption is used in mining and manufacturing industries, about 18%, followed by domestic consumption, which represents about 12% [8].

1.3. WASTEWATER TREATMENT AND REUSE

The increasing volumes of wastewater, conducted by factors such as population growth, improved living standards, and economic development, present difficulties for global water management. Despite the perception of wastewater as a pollutant, it holds significant potential as a sustainable resource for water, energy, and nutrients. Currently, the annual global production of municipal wastewater reaches 380 m^3, expecting a 24% rise by 2030 and 51% by 2050. This situation enriches the necessity for developing strategies in wastewater management [9].

Although it seems impossible, it is necessary to change the perception of wastewater as a non-usable resource and set a strategy that emphasizes its potential benefits. Using advanced treatment technologies and practicing efficient reuse, it is possible to reduce the hydraulic stress experienced by society. Nowadays traditional wastewater treatment plants are not prepared to remove various inorganic and organic micropollutants. In front of this scenario, this water cannot be reused safely to decrease the freshwater demand. The reuse of wastewater from different human activities for secondary use, such as agriculture, reduces the demand for freshwater and helps address water scarcity issues. The demand for freshwater for agriculture represents almost 70% of total freshwater [10], reusing wastewater would drastically decrease water stress.

1.4. MICROPOLLUTANTS

In recent years, human activities such as industrial, agricultural, or farming have notably disrupted the natural balance of ecosystems. This disruption stems from the contamination of the environment with a range of toxic substances. Among the various environmental pollutants, organic, and inorganic compounds, alongside several anions such as chlorate, arsenate, and bromate, as well as micropollutants (MPs), raise significant concerns due to their presence in the environment at potentially harmful levels. Although MPs are found in low concentrations, between ng/L and µg/L, exposure to them can lead to mutagenicity or genotoxicity in living organisms. In 2012, approximately 143,000 compounds, between pharmaceutical and care products or pesticides, were identified in various European markets finding their way into aquatic systems over their lifecycle [11].

Most studies reveal that Wastewater Treatment Plants (WWTP) are the main source of MPs introduction in water bodies. MPs originating from soil are released into aquatic environments through leaching or runoff, potentially causing harm to aquatic organisms, they are accumulative and recalcitrant [12].

Micropollutants, also called contaminants of emerging concern (EC), have commanded awareness by scientists and environmental engineers due to WWTP is not capable of eliminating those MPs. Typically, these systems include primary (physical) and secondary (biological) treatments but often prove ineffectiveness in eliminating MPs due to their low concentrations and biological resilience [13]. Although some MPs are beginning to be regulated, the truth is that there is no clear record due to the enormous quantity of them. In this situation, new solutions are required to eliminate those EC from wastewater.

In the following section, the MPs employed in this study are described. Eight micropollutants commonly found in wastewater (detected from ng/L to µg/L) have been selected as potentially representative. The selection of micropollutants was made depending on their affinity with water (log K_{ow}), type of MPs, and retention time. MPs are divided into medicines (iopromide, dimetridazole, atenolol, primidone, carbamazepine, and ibuprofen), herbicide (atrazine) and insecticide (acetamiprid). All MPs, except carbamazepine, atrazine, and ibuprofen, present a low partition coefficient (log K_{ow} <1) which means a hydrophilic tendency. This characteristic is necessary so that MPs can be analysed by high performance liquid chromatography (HPLC).

1.4.1. Iopromide

Iopromide (IOP) is an iodinated contrast agent used to diagnose problems in the brain, heart, or blood vessels among other parts of the body (Figure 3). Although this compound may cause several adverse effects such as cardiac events or hypersensitivity, it is shown that only 0.7% of patients in a 2-year study experience adverse events [14]. Iopromide is soluble in water (0.36 mg/mL at 25 ^{o}C) and very hydrophilic (octanol-water partition coefficient, log K_{ow}= -2.35) [15].

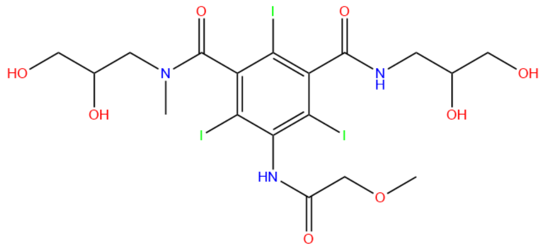

Figure 3. Structural formulate of Iopromide.
Source: ChemDraw

1.4.2. Dimetridazole

Dimetridazole (DMZ) is an antibiotic and antiprotozoal agent used primarily in veterinary medicine. It is commonly used to treat protozoan infections in animals, especially poultry and pigs, caused by organisms such as Trichomonas or Giardia. However, concerns about potential carcinogenicity and genotoxicity have restricted its use in food-producing animals in many countries. As a result, alternative medicines are often chosen to treat similar conditions in those animals [16]. Dimetridazole is a soluble compound (14 mg/mL at 25 ^{o}C) and hydrophilic (log K_{ow}= -1.23) [17]. Figure 4 shows its molecular structure.

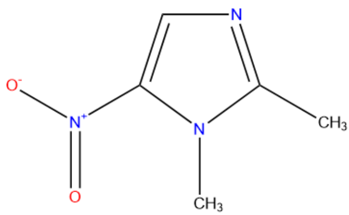

Figure 4. Structural formulate of dimetridazole.
Source: ChemDraw

1.4.3. Atenolol

Atenolol (ATL) belongs to a group of medicines called beta-blockers used to treat various cardiovascular conditions such as hypertension, chest pain, and certain heart rhythm disorders. Its actions include relaxing blood vessels and slowing heart rate, improving blood flow, and lowering blood pressure (Figure 5) [18]. It is soluble in water (13.3 mg/mL at 25 ^oC) and moderately hydrophilic (log K_{ow}= 0.16) [19].

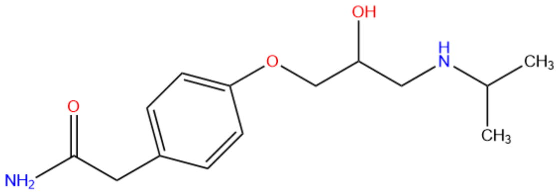

Figure 5. Structural formulate of Atenolol.
Source: ChemDraw

1.4.4. Primidone

Primidone (PRM) is used alone or in combination with other drugs to control certain types of seizures. It belongs to a class of drugs called anticonvulsants. Works by reducing abnormal electrical activity in the brain [20]. Figure 6 shows its structure. It is soluble in water (0.5 mg/mL at 22 ^oC) and hydrophilic (log K_{ow}= 0.91) [21].

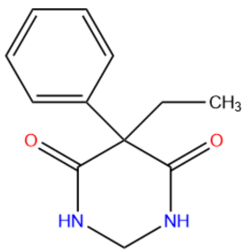

Figure 6. Structural formulate of primidone.
Source: ChemDraw

1.4.5. Carbamazepine

Carbamazepine (CBZ) is an anticonvulsant drug used to treat seizures and nerve pain such as epilepsy. It is also used to treat bipolar disorder (Figure 7) [22]. Carbamazepine is soluble in water (0.15 mg/mL at 25 °C) and presents high hydrophobicity (log K_{ow}= 2.45) [23].

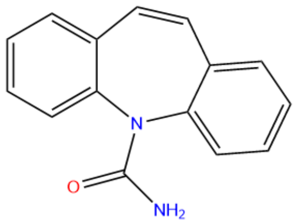

Figure 7. Structural formulate of carbamazepine.
Source: ChemDraw

1.4.6. Atrazine

Atrazine (ATZ) is a synthetic herbicide used in agriculture to inhibit the growth of plants by inhibiting the photosynthetic process (Figure 8). Once atrazine is absorbed into the soil, it can be taken up by plants or broken down within days or months. It can also enter rivers and groundwater and persist for a long time because it decomposes slowly in these environments [24]. This compound is soluble in water (0.033 mg/mL at 25 °C) and presents high hydrophobicity (log K_{ow}= 2.61) [25].

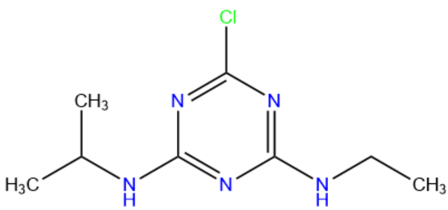

Figure 8. Structural formulate of atrazine.
Source: ChemDraw

1.4.7. Acetamiprid

Acetamiprid (ACMP) is an insecticide belonging to the neonicotinoid family (Figure 9). It is commonly used in agriculture to control a variety of pests affecting fruits, vegetables, and ornamental plants. Acetamiprid interferes with the transmission of nerve impulses in insects, eventually leading to paralysis and death. It is valued for its efficacy, relatively low toxicity to mammals, and the ability to be it in several ways, including sprays, soil, and seed applications [26]. It is soluble in water (4.24 mg/mL at 25 ^{o}C) and hydrophilic (log K_{ow}= 0.80) [27].

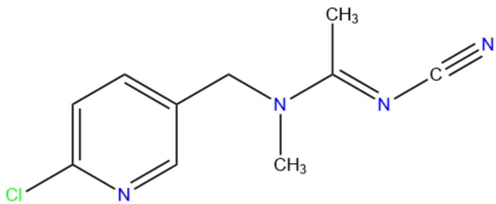

Figure 9. Structural formulate of acetamiprid. Source: ChemDraw

1.4.8. Ibuprofen

Ibuprofen (IBU) is a medication classified as a nonsteroidal anti-inflammatory drug. It is commonly used to relieve pain and reduce inflammation in various conditions such as arthritis, muscle pain, fever, headaches, etc. Ibuprofen inhibits the production of prostaglandins, chemicals in the body that cause inflammation, pain, and fever (Figure 10) [28]. Ibuprofen is soluble in water (0.025 mg/mL at 25 ^{o}C) and presents high hydrophobicity (log K_{ow}= 3.97) [29].

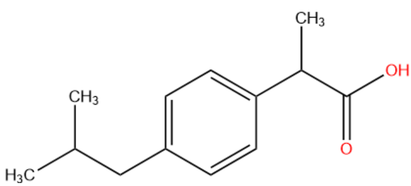

Figure 10. Structural formulate of ibuprofen. Source: ChemDraw

1.5. LEGAL FRAMEWORK OF WATER

Population growth and industrialization have caused constant pressure on water resources, deteriorating water quality for decades. This is a global concern due to the risk to human health and environmental ecosystems. As a result, the European Parliament has adopted measures to regulate urban wastewater conditions.

The first European directive on the treatment of urban wastewater is Directive 91/271/EEC, dated in 1991 (Modified in 1998 as Commission Directive 98/15/EC). This directive establishes the legal framework for the collection, treatment, and discharge of urban wastewater, as well as the discharge of biodegradable industrial wastewater from certain sectors, resulting in an improvement in the quality of water [30].

Nevertheless, over the years new concerns have emerged, especially regarding the presence of microcontaminants in water. European Commission has proposed a revision to that directive to implement a pathway to eliminate MPs. This new directive proposes the removal of MPs through quaternary treatment (Article 8) which is compulsory for plants with a load ≥ 150.000 h-e and those with a load of more than 10.000 h-e only if there is a risk of MPs accumulation in water bodies. This follows a progressive schedule, aiming for 100% treatment of discharges by 2045. It is required at least an 80% reduction of six specified substances listed in Annex I (including carbamazepine) [31, 32, 33].

1.6. WETLAND AND CONSTRUCTED WETLAND

A wetland is defined as a flat land area whose surface remains flooded for a considerable time with the presence of aquatic plants acting as water filters. They are transitional zones between aquatic and terrestrial ecosystems, characterized by unique soil conditions and plant life adapted to living in these conditions. Wetlands are known for their exceptional biological diversity as they host a vast array of animal, microbial, and plant species [34].

Constructed wetlands (CW) are promising technologies based on nature to treat wastewater. It typically consists of deep channels planted with several types of vegetation. These CW recreate processes in which the synergy of numerous mechanisms, whether physical, chemical, or biological (biodegradation, phytodegradation, photodegradation, rhizofiltration, phytovolatilization, phytoextraction, and sorption) make it possible the remove of micropollutants such as heavy metals, organic matter, or nutrients from WW. The principal natural mechanisms for removing contaminants from water in CWs are microbial degradation and absorption by plants [35, 36].

Constructed wetlands are often used as environmentally friendly alternatives to traditional wastewater treatment methods. Its low inversion cost, simplicity, and simple operation turn it into a useful method of wastewater treatment. However, they also present disadvantages such as long retention times and large space requirements. Additionally, the removal of micropollutants can also be difficult to control, as the performance of CW depends on many factors, including environmental conditions, such as temperature or pH, and the properties of individual contaminants [37]. In this sense, CW may not achieve adequate levels of removal for certain compounds that are not affected by sorption or biological processes, and therefore may not meet the requirements for water reuse.

1.6.1. NATURAL ADSORBENTS

Natural adsorbents have emerged as a promising alternative for the removal of MPs present in WW. Conventional wastewater treatment methods may not be efficient for the elimination of certain contaminants including heavy metals, organic compounds, nutrients, and pathogenic microorganisms. In this context, natural adsorbents have gained attention due to their capacity to adsorb a wide range of MPs and their cost-efficiency. Organic and inorganic materials commonly used as adsorbents, such as activated clay minerals, carbon, polymer material, or agricultural waste, possess different adsorption capacities for removing specific pollutants from wastewater [38].

Agricultural and forestry waste, including chestnut and almond shells, sawdust, or tree twigs are used as adsorbents for the removal of MPs from WW. These adsorbents composed of polysaccharides (pectin and cellulose) and polyphenol complexes (flavonoids, tannins, lignin, and terpenes), possess functional groups as hydroxyl (-OH) or carboxyl (-COOH), allowing them to interact with passing ions. This makes them effective in adsorbing ions via ion exchange [39].

Lignin is an organic and porous polymer found in the cell walls of plants. It is one of the primary components of wood, providing rigidity and strength to plant structures. In addition, it also helps plants to resist decomposition by microorganisms. This compound has gained significant interest in recent times as its effective adsorption capacity for heavy metals, and organic and inorganic compounds in water due to its functional groups (carboxylic and hydroxyl groups). This attention is owed to its abundance, low cost, and biodegradability [40].

In this research, almond shells were chosen as adsorbent material. This porous material with a high surface area can enhance the adsorption of MPs leading to their metabolism by microorganisms. In addition, as it is an agricultural waste, almond shells are a low-cost material that promotes waste management. Furthermore, no pretreatment is needed to enhance the adsorption capacity. On another hand, there is a potential risk of leaching organic compounds from the almond shells into treated water, new contaminants could be introduced.

1.7. ADVANCED OXIDATION PROCESS (AOP)

Advanced Oxidation Processes (AOPs) are new technologies known as sustainable solutions that may transform organic pollutants into non-toxic biodegradable products. AOPs take place under ambient temperature and pressure. These processes are based on the generation of hydroxyl radicals (·OH) among other oxidizing species such as chlorine (Cl·), hydroperoxyl (HO2·), ozonide anion (O3·) or sulphate (SO4·-) radicals [41]. The hydroxyl radical is a powerful, non-selective chemical oxidant. These reactions could lead to the mineralization of the organic compound into carbon dioxide (CO_2), water, and inorganic ions which are not pollutants [42].

AOPs are classified depending on the number of phases involved in the oxidation process, homogeneous or heterogeneous, and the generation of reactive species, photochemical, and chemical processes. The main disadvantage of AOPs lies in their high operating costs as it requires energy and chemical products. On the other hand, the efficiency of eliminating MPs from these processes is dependent on water quality; high levels of organic matter, solids, or nitrites may significantly reduce their effectiveness. That is why wetlands were previously used to lower the concentration of those substances.

In this study, solar photo-Fenton and UVC-H_2O_2 are chosen for wastewater treatment as they efficiently degrade a wide range of organic microcontaminants.

1.7.1. SOLAR PHOTO-FENTON

The photo-Fenton process is an advanced oxidation method typically used for wastewater treatment and purification. It takes advantage of the power of hydroxyl radicals (·OH) produced by the reaction of hydrogen peroxide (H_2O_2) with iron (Fe^{2+}) as a catalyst when irradiated with visible light (from 400-700 nm). This process is very effective in breaking down organic pollutants and eliminating microorganisms such as *Escherichia coli* or *Salmonella*. The reaction occurs under ambient temperature and pressure, and with acidic conditions, around a pH of 2.8. In these specified conditions, the catalyst (iron), does not precipitate. The following reactions take place in the Photo-Fenton process:

1- Decomposition of hydrogen peroxide with Fe (II):

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \text{-}OH + \cdot OH$ (Eq 1.1)

2- Decomposition of hydrogen peroxide into hydroxyl radical in the presence of UV radiation:

$H_2O_2 + h\nu \rightarrow 2HO\cdot$ (Eq. 1.2)

3- Generation of ·OH radical above Fe (II):

$Fe^{3+} + H_2O_2 + h\nu \rightarrow Fe^{2+} + \text{-}OH + \cdot OH$ (Eq 1.3)

$Fe(OH)_2 + h\nu \rightarrow Fe^{2+} + \cdot OH$ (Eq 1.4)

4- Generation of Fe(II)

$[Fe(RCO_2)]^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R$ (Eq. 1.5)

An important advantage of using the photo-Fenton process over conventional Fenton is to take advantage of visible light as an additional source of energy in the generation of hydroxyl radicals. This may be a limiting factor as it has low kinetics ($k = 3.1 \cdot 10^{-3}$ L mol^{-1} s^{-1}). The use of UV radiation allows a better efficiency, about 40 times faster, in the production of the radical, and, consequently, a faster oxidation of the organic compounds in water [43].

As mentioned above, photo-Fenton operates at a pH of around 2.8 so iron does not precipitate. However, the utilization of water at neutral pH highlights the necessity for a catalyst that maintains stability under those conditions. Fe-EDTA (iron complexed with ethylenediaminetetraacetic acid) would be the best choice. EDTA acts as a chelating agent that isolates the iron ions and releases them gradually during the process. This species prevents early iron precipitation optimizing the degradation [44].

1.7.2. UVC-H_2O_2

UVC-peroxide is an advanced oxidation process where UV radiation is used to produce highly reactive hydroxyl radicals ($\cdot OH$). A monochromatic lamp emitting light at a wavelength of 254 nm is employed so those radicals are formed when the light intercepts hydrogen peroxide molecules (H_2O_2). These hydroxyl radicals are oxidizing agents that degree organic compounds and disinfect wastewater [45]. UV-peroxide is commonly used in water treatment as it offers an environmentally friendly solution to treat wastewater without the need for additional chemicals. The reaction involved in UV-peroxide is the following:

1- Decomposition of hydrogen peroxide into hydroxyl radical in the presence of UV radiation:

$$H_2O_2 + h\nu \rightarrow 2HO\cdot \qquad \text{(Eq. 1.6)}$$

2. OBJECTIVES

The main objective of this project is to analyse the efficacy of a hybrid system comprising constructed wetlands and Advanced Oxidation Processes for the removal of distinct types of micropollutants, which present different physicochemical properties, from wastewater.

Concretely,

- To study the influence of adding almond shells as a natural adsorbent in constructed wetlands on wastewater treatment.
- To study the influence of the adsorbent depth on the quality of wastewater treated.
- To analyse the influence of the recirculation in constructed wetlands, since could affect the nitrification-denitrification process, and nitrites/nitrates could affect the efficiency of the subsequent oxidative treatment.
- To analyse whether dissolved organic carbon and total suspended solids could affect in the AOPs.
- To investigate which is the best combination in the dual treatment.
- To explore the possibility of reusing the treated effluents for agricultural purposes.

3. MATERIALS AND METHOD

3.1. WATER MATRIX

3.1.1. Wastewater matrix

The water utilized in this investigation comes from the secondary treatment Gavà-Viladecans wastewater treatment plant (WWTP). This plant is dedicated to treating wastewater generated by the populations of Gavà, Viladecans, and surrounding areas before it is discharged into the environment to comply with environmental legislation. The Gavà-Viladecans WWTP has two main treatment lines, one line with membrane bioreactor (MBR) and the other line with integrated fixed-film activated sludge (IFAS) [46]. As in this study, water samples from the IFAS line will also provide a vision of eliminating suspended solids and removing pathogens.

Table 1: IFAS water characteristics

Parameter	IFAS
pH	7.9
DOC [mg C/L]	20.6
Total suspended solids [mg/L]	146.9
Alkalinity: $CaCO_3$ [mg/L]	545
NO_3^- [mg/L]	5.17
NO_2^- [mg/L]	13.82
Cl^- [mg/L]	456.9

3.1.2. Ultrapure water matrix

The Mili-Q water purification system, developed by MiliporeSigma, is an advanced solution designed to produce ultrapure water, removing impurities and contaminants to low levels. Water is purified by passing through mixed bed ion exchange and organic cartridges. The water's purity is continuously monitored by measuring its conductivity, the higher resistance indicates fewer ions. According to International Organisation for Standardization (ISO) and American Society for Testing Materials (ASTM) International water is considered ultrapure when it has been purified to 18.2 MΩ·cm [47].

Table 2: Mili-Q water characteristics

Parameter	Mili-Q water
Resistivity [MΩ·cm]	18.2
Conductivity [µS/cm] at 25 °C	0.056
TOC [µg/L]	2
Chloride, max [µg/L]	1
Sodium, max [µg/L]	1
pH	5

3.2. REAGENTS

3.2.1. Micropollutants

3.2.1.1. Iopromide

Table 3: Iopromide properties [48]

Properties	Value
Molecular formula	$C_{18}H_{24}I_3N_3O_8$
Molecular weight (g/mol)	791.1
Molecular IUPAC name	1-N,3-N-bis(2,3-dihydroxypropyl)-2,4,6-triiodo-5-[(2-methoxyacetyl)amino]-3-N-methylbenzene-1,3-dicarboxamide
CAS number	73334-07-3
EC number	277-385-9
pKa	10.62
Melting point (°C)	840.90
Solubility (mg/mL)	0.36
log k_{ow}	-2.35
Seller	USP
Hazards identification	

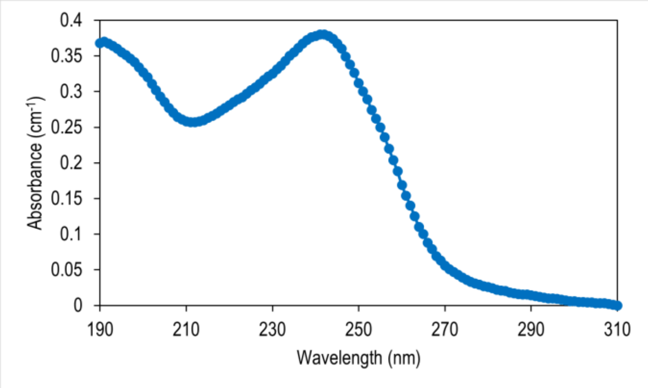

Figure 11. Iopromide absorption spectrum (1 ppm in Milli-Q water)

3.2.1.2. Dimetridazole

Table 4: Dimetridazole properties [49]

Properties	Value
Molecular formula	$C_5H_7N_3O_2$
Molecular weight (g/mol)	141.13
Molecular IUPAC name	1,2-dimethyl-5-nitroimidazole
CAS number	551-92-8
EC number	209-001-2
pKa	2.9
Melting point (°C)	167
Solubility (mg/mL)	14
log k_{ow}	-1.23
Seller	Sigma-Aldrich
Hazards identification	

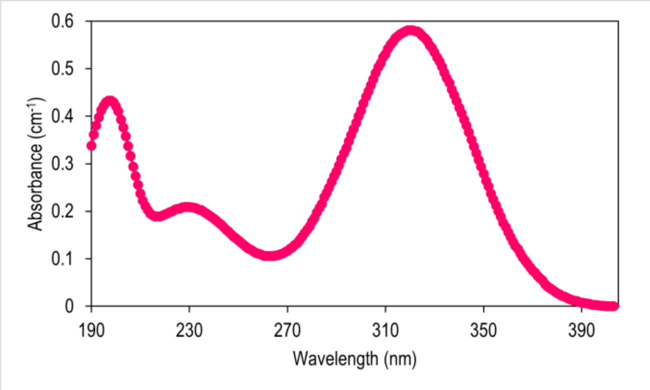

Figure 12. Dimetridazole absorption spectrum (1 ppm in Milli-Q water)

3.2.1.3. Atenolol

Table 5: Atenolol properties [50]

Properties	Value
Molecular formula	$C_{14}H_{22}N_2O_3$
Molecular weight (g/mol)	266.34
Molecular IUPAC name	2-[4-[2-hydroxy-3-(propan-2-ylamino)propoxy]phenyl]acetamine
CAS number	29122-68-7
EC number	262-544-7
pKa	9.60
Melting point (°C)	147-160
Solubility (mg/mL) at 25 °C	13.3
log k_{ow}	0.16
Seller	Sigma-Aldrich
Hazards identification	

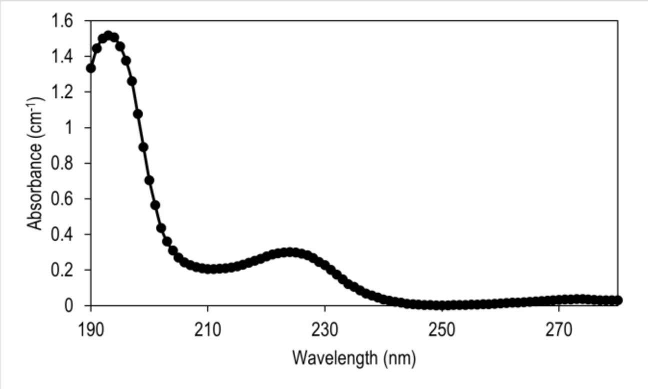

Figure 13. Atenolol absorption spectrum
(1 ppm in Milli-Q water)

3.2.1.4. Primidone

Table 6: Primidone properties [51]

Properties	Value
Molecular formula	$C_{12}H_{14}N_2O_2$
Molecular weight (g/mol)	218.25
Molecular IUPAC name	5-ethyl-5-phenyl-1,3-diazinane-4,6-dione
CAS number	125-33-7
EC number	204-737-0
pKa	12.3
Melting point (^{o}C)	281.5
Solubility (mg/mL) at 22 ^{o}C	0.5
log k_{ow}	0.91
Seller	Sigma-Aldrich
Hazards identification	

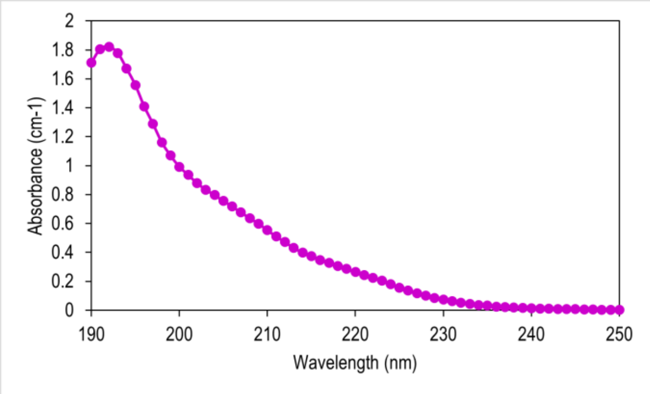

Figure 14. Primidone absorption spectrum (1 ppm in Milli-Q water)

3.2.1.5. Carbamazepine

Table 7: Carbamazepine properties [52]

Properties	Value
Molecular formula	$C_{15}H_{12}N_2O$
Molecular weight (g/mol)	236.27
Molecular IUPAC name	benzo[b][1]benzazepine-11-carboxamide
CAS number	298-46-4
EC number	206-062-7
pKa	13.9
Melting point (^{o}C)	189-192
Solubility (mg/mL) at 25 ^{o}C	0.15
log k_{ow}	2.45
Seller	Sigma-Aldrich
Hazards identification	

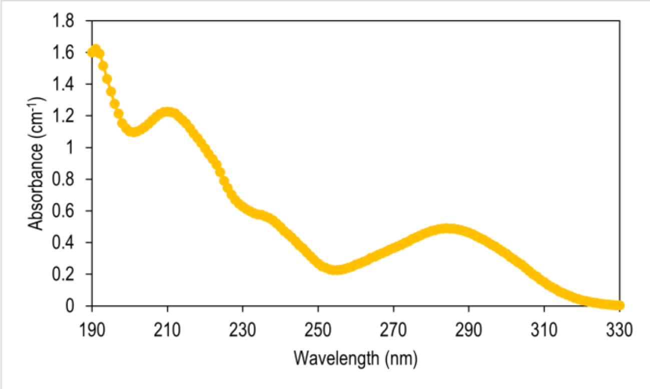

Figure 15. Carbamazepine absorption spectrum
(1 ppm in Milli-Q water)

3.2.1.6. Atrazine

Table 8: Atrazine properties [53]

Properties	Value
Molecular formula	$C_8H_{14}ClN_5$
Molecular weight (g/mol)	215.68
Molecular IUPAC name	6-chloro-4-*N*-ethyl-2-*N*-propan-2-yl-1,3,5-triazine-2,4-diamine
CAS number	1912-24-9
EC number	217-617-8
pKa	1.60
Melting point (°C)	173-177
Solubility (mg/mL) at 25 °C	0.033
log k_{ow}	2.61
Seller	Sigma-Aldrich
Hazards identification	

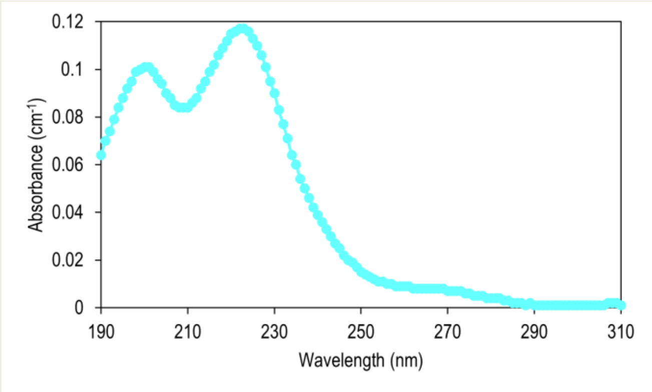

Figure 16. Atrazine absorption spectrum
(1 ppm in Milli-Q water)

3.2.1.7. Acetamiprid

Table 9: Acetamiprid properties [54]

Properties	Value
Molecular formula	$C_{10}H_{11}ClN_4$
Molecular weight (g/mol)	222.67
Molecular IUPAC name	*N*-[(6-chloropyridin-3-yl)methyl]-*N'*-cyano-*N*-methylathanimidamide
CAS number	160430-64-8
EC number	603-921-1
pKa	0.70
Melting point (°C)	98.9
Solubility (mg/mL) at 25 °C	4.24
log k_{ow}	0.80
Seller	Sigma-Aldrich
Hazards identification	

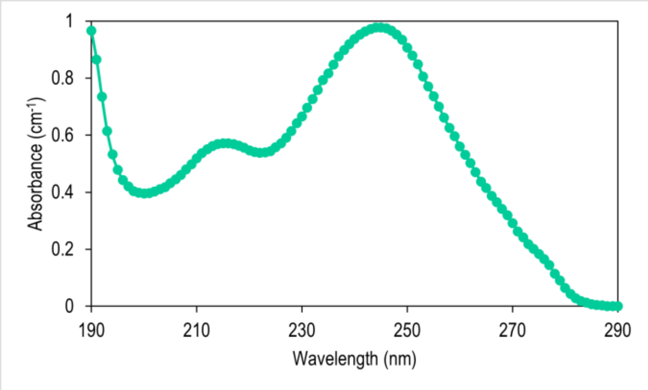

Figure 17. Acetamiprid absorption spectrum
(1 ppm in Milli-Q water)

3.2.1.8. Ibuprofen

Table 10: Ibuprofen properties [55]

Properties	Value
Molecular formula	$C_{13}H_{18}O_2$
Molecular weight (g/mol)	206.28
Molecular IUPAC name	2-[4-(2-methylpropyl)phenyl]propanoic acid
CAS number	15687-27-1
EC number	239-784-6
pKa	4.45-5.20
Melting point (°C)	75-77.5
Solubility (mg/mL) at 25 °C	0.025
log k_{ow}	3.97
Seller	Sigma-Aldrich
Hazards identification	

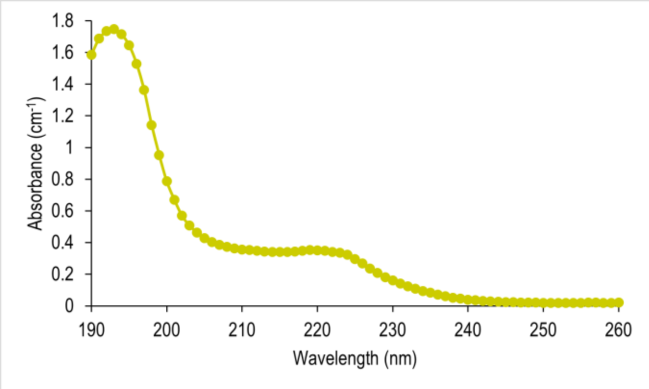

Figure 18. Ibuprofen absorption spectrum
(1 ppm in Milli-Q water)

Other chemical reagents are illustrated in Appendix I,

3.3. EXPERIMENTAL DEVICES

3.3.1. Constructed wetlands

In this study, 4 vertical wetlands were constructed at a lab-scale made by methacrylate plates (30*30*60 cm). The walls were covered with aluminium foil to protect them from solar light and avoid algae growth. The first CW, with a recirculation system, was filled by a layer of cobbles stones (10 cm), followed by a layer of volcanic rocks (5 cm), a third layer of fine gravel (5 cm), and a last layer of sand (30 cm). The second and third CW, also with a recirculation system, were filled with the same materials but, 5 cm starting from the top between the layer of sand, there is a layer of almond shells (2 and 4 cm respectively). Finally, the fourth CW was filled with the same materials as the first one but without a recirculation system. Aquatic plants were planted in each CW (Carex Pendula). Images of CW, rock layers, and plant can be found in appendix I.When wetlands were built, plants took one month to acclimate to their new environment with IFAS water (without MPs). After that period, each CW was filled with 5 L of IFAS water and 5 mL of each MPs (100 ppm) to reach a 100 ppb concentration.

3.3.2. UVC-H_2O_2

The UVC-H2O2 experiments were carried out using a cylindrical batch reactor (2.5 L of capacity) with a mercury lamp of 4 W in the 254 nm range (ultraviolet light). UV-C light is effective at disinfection because it damages the DNA and RNA of microorganisms. The reactor was covered by a cooling jacket connected to a thermostatic bath set at 20 ^{o}C. A layer of aluminum foil also covers the device so the light can be retained in the reactor and for security, as it may harm the eyes and skin. Figure 19 illustrates the experimental device.

Figure 19: UVC-H_2O_2 device

3.3.3. Solar photo-Fenton

The Solar photo-Fenton experiments were conducted using a bench-scale solar simulator (SUNTEST CPS +, Hereaus) with artificial sunlight supplied by a 1500-W xenon lamp in the 290-400 nm range. The irradiance was maintained at 500 W/m^2. A cylindrical Pyrex photoreactor (9.0 cm in diameter, 4.5 cm in height), with stirring of 350 rpm, was placed in a cooling plate connected to a thermostatic bath set at 10.5 ^{o}C, to keep the temperature at 20-22 ^{o}C during experimentation. Figure 20 shows the experimental device and Figure 21 shows the reactor and cooling plate.

Figure 20. Photo-Fenton device

Figure 21. Reactor and cooling plate

3.4. EXPERIMENTAL PROCEDURE

3.4.1. Solutions prepared

The wetlands were irrigated with 5 L of IFAS water containing micropollutants. The MPs solutions were prepared at a concentration of 100 ppm (except atrazine, which was prepared at 20 ppm because of its low solubility). Adding a known quantity of MPs to the water is necessary because their concentration in the matrix is so low that HPLC cannot detect them. For each solution, it was added the required quantity of MPs, previously weighed on an analytical balance, into a volumetric flask, and then filled to the mark. The table below illustrates the number of micropollutants required to achieve the 100 ppm solution.

3.4.2. Wetlands In/out

The experiments were conducted over 8 cycles of 3 days of retention time.

IN:

1- Take the IFAS water from the wastewater treatment plant.

2- Using a micropipette, add 5 mL of each MP to the 5 L of water to achieve a concentration of 100 ppb for each micropollutant.

3- Store 50 mL of the solution in a container to analyse dissolved organic carbon. Additionally, using a syringe transfer 1 mL of the water into HPLC vials, ensuring the water is pre-filtered with 0.45 µm filter to prevent saturation in the HPLC.

4- Carefully pour the 5 L of water into the wetlands to avoid flooding.

Out: After 3 days, wetlands were emptied following those steps:

1- Fully empty the wetlands.

2- Measure the amount of water extracted and add deionized water until reaching again the initial 5 litres. This adjustment is necessary due to water evapotranspiration and evaporation. It ensures that the levels of total organic carbon, micropollutants, and nitrites/nitrates remain unchanged.

3- For cycles 1 and 8, 5 L of the solutions were stored in containers to analyse in AOPs, and for the other cycles, only 200 mL were necessary. A syringe was used to transfer

1 mL of the water into HPLC vials (pre-filtered with 0.45 µm filter) for the MPs analysis. The water was kept for all cycles to measure dissolved organic carbon, nitrites/nitrates, and suspended solids.

3.4.3. Solar photo-Fenton

Solar photo-Fenton experiments were conducted over 120 minutes using Fe-EDTA as a catalyst due to its effectiveness at neutral pH. Samples were taken from the reactor at 0, 2, 5, 7, 10, 15, 20, 30, 45, 60, 90, 120 min. Each sample was then transferred into 1 mL HPLC vials for analysis in HPLC.

Preparation for Solar photo-Fenton was:

1- It was switched on the cooling plate 30 min before beginning the experiment and waited until the base was at 10.5 ^{o}C (set point).

2- Preparation of the solution: If the water came from the wastewater treatment station, the MPs were added as follows: For 0.2 L of IFAS water, it was added 0.2 mL of MPs (solution stock of 100 ppm). In the case of atrazine, 1 mL (solution stock of 20 ppm) was added to achieve a final concentration of 100 ppb for each MP. On the other hand, if the water was sourced from the wetlands, MPs were not added. Additionally, 7.5 µg of Fe-EDTA (5 ppm of Fe, 13.3% of iron is chelated) was added as a catalyst, by legal limits (0-5 ppm present in water) [56].

3- Twelve HPLC vials were tagged to add samples taken. To stop the reaction, 23 µL of thiosulphate (100 g/L) was added to each vial. The samples were filtered using a 0.45 mm filter.

4- When the experiment was about to start, 0.15 L of the solution was added to the reactor with 25 µL of H_2O_2 30% w/v (50 ppm of H_2O_2) to achieve a ratio 1:10 ($Fe:H_2O_2$)

5- At 30, 60, and 120 minutes, the consumption of H_2O_2 was determined by measuring absorbance of 1.5 mL solution + 1.5 mL metavanadate at 450 nm.

6- At 0, 30, 60, and 120 minutes, the precipitation of iron was measured by colorimetric method at 510 nm.

7- After 120 minutes, the experiment was over the light, agitation, and thermostatic bath were turned off.

3.4.4. UVC-H_2O_2

UVC-H_2O_2 experiments were conducted over 60 minutes. Samples were taken from the reactor at 0, 2, 5, 7, 10, 15, 20, 30, 45, 60 min. Each sample was then transferred into 1 mL HPLC vials for analysis in HPLC (pre-filtered with 0.45 µm filter).

Preparation for UVC-H_2O_2 was:

1- It was switched on the cooling system 30 min before beginning the experiment and waited until the base was at 22 °C (set point).

2- Preparation of the solution: If the water came from the wastewater treatment station, the MPs were added as follows: For 2 L of IFAS water, 2 mL of MPs (solution stock of 100 ppm). In the case of atrazine, 10 mL (solution stock of 20 ppm) was added to achieve a final concentration of 100 ppb for each MP. On the other hand, if the water was sourced from the wetlands, MPs were not added.

3- Twelve HPLC vials were tagged to add samples taken. To stop the reaction, 23 µL of thiosulphate (100 g/L) was added to each vial. The samples were filtered using a 0.45 mm filter.

4- When the experiment was about to start, 2 L of the solution was added to the reactor with 67 µL of H_2O_2 (10 ppm). The lamp and stirring were then switched on to begin the experiment.

5- At 30, 44, and 60 minutes, the consumption of H_2O_2 was determined by measuring absorbance (1.5 mL solution + 1.5 mL metavanadate).

6- After 60 minutes, the experiment was over, and the light, agitation, and thermostatic bath were turned off.

3.5. ANALYTICAL METHODS

3.5.1. High Performance Liquid Chromatography

The evolution of MP concentration from the experiments samples was measured by High Performance Liquid Chromatography (HPLC) analysis (Agilent Technologies Infinity Series system and a C-18 column (250 x 4.6 mm i.d; 5 µm, Tecknokroma)). The injection volume was consistently maintained at 100 µL. The column temperature was set to 40 ºC, and the flow rate was held at 1 mL/min. The mobile phases consisted of an aqueous solution with orthophosphoric acid (pH=3) and an organic solution of acetonitrile. The gradient elution program started with 5% B for 2 minutes, increased linearly to 100% B from 2 to 28 minutes, reverted to initial conditions at 28.5 minutes, followed by a 4.5-minute equilibration period before the next injection. Table II in appendix shows the characterization of the solutions. Detection wavelengths were selected based on the compound: 200 nm for atenolol, primidone, and ibuprofen; 214 nm for carbamazepine; 222 nm for atrazine; 240 nm for iopromide; 254 nm for acetamiprid; and 320 nm for dimetridazole.

3.5.2. pH and conductivity measurement

The pH was measured using a sensION™+ MM 374 multi-meter, which had been previously calibrated with buffer solutions at pH 4.00, 7.00, and 10.00. Conductivity was also measured with the same instrument, which is calibrated daily with 1413 μS/cm standard.

3.5.3. Iron precipitation determination

Ferrous iron (Fe^{2+}) was determined by the complexation with 1,10-phenanthroline according to standardized procedure (ISO 6332) [57]. 4 mL of the sample, previously filtered with a 0.20 μm PVDF filter to ensure accurate reading of the soluble iron, were mixed with 1 mL of phenanthroline solution (1g/L) and 1 mL of acetic/acetate buffer solution (62.5 g of ammonium acetate (CH_3COONH_4) dissolved in 175 mL of acetic acid and flushed to 250 mL with ultrapure water). The resulting complex, formed by the reduction of ferric iron to ferrous iron form by ascorbic acid, (equation 3.1) took a reddish colour. This was measured by spectrophotometer (Hach Lange DR 6000) at a wavelength of 510 nm. Since iron is chelated with EDTA at near neutral pH, it is not possible to differentiate between ferrous or ferric forms, so only total iron can be measured.

$$Fe2+ + 3(1,10\text{-phenantroline}) \rightarrow Fe(1,10\text{-phenantroline})_3^{2+} \qquad (\text{Eq. } 3.1)$$

3.5.4. Hydrogen peroxide consumption

To monitor the progress of the reaction in AOPs, the concentration of hydrogen peroxide was determined using metavanadate colorimetric method [58]. Specifically, 1.5 mL of ammonium metavanadate solution (5.14 g/L) in acidic medium was mixed with 1.5 mL of the sample. The resulting solution, which turned yellowish when peroxovanidium cations were formed (equation

3.2), was analysed by spectrophotometer (Hach Lange DR 6000) at a wavelength of 450 nm. Finally, the hydrogen peroxide concentration was determined by using a calibration curve that correlates absorbance with hydrogen peroxide concentration.

$$VO_3^- + 4H^+ + H_2O_2 \rightarrow 3H_2O + VO_2^{3+} \quad \text{(Eq. 3.2)}$$

3.5.5. Ions determination

The Separation Unit of the Scientific and Technological Services of the University of Barcelona conducted Ions determination analysis. Ionic chromatography was used to measure the concentration of nitrite (NO_2^-), nitrate (NO_3^-), chloride (Cl^-) and sulphate (SO_4^-) anions in water samples. This was achieved using a high-performance liquid chromatograph equipped with both conductivity and UV detectors in series. Separation was performed with a 4.6 x 150 mm IC-PAK ANION column from Waters (USA). The mobile phase, consisting mainly of borate buffer ($B(OH)_3$) and acetonitrile (C_2H_3N), flowed at 2 mL/min. An injection of 200 µL was used, with the UV detector at a wavelength of 214 nm.

3.5.6. Dissolved organic carbon

The total organic carbon content was quantified following the Standard Methods 5310 B procedure [59] and employing a 5055 TOC-VCSN analyser equipped with an ASI-V autosampler, both by Shimadzu (Japan). The following steps took place for the analysis: The sample was filtered using a 0.45 µm filter. Then, the inorganic carbon is removed by sample acidification (HCl, 2M), followed by air bubbling. After that, at 680 ^oC, the catalytic combustion of the sample took place. Finally, CO_2 was quantified after combustion.

3.5.7. Alkalinity

The alkalinity of wastewater samples was measured through an automatic titration method (pH Burette 24) and a Basic 20 pH meter, both by CRISON (Spain). Hydrochloric acid (0.1 M) was used, with a fixed end point at pH 4.3. This technique measures the water's capacity to neutralize acids. In wastewater, the alkalinity is mainly associated with bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) species.

3.5.8. Total suspended solids

The quantity of particulate matter (total suspended solids) floating in wastewater was determined by gravimetric analysis. The setup, illustrated in Figure 22 consisted of a Kitasato flask connected to a vacuum pump with a filter (filter MF-Millipore 0.45 µm MCE membrane) placed on top. A measured volume of sample was passed through the pre-weighed filter. As observed in Figure 23 the large particles were retained by the filter. The filter was then dried in an oven (105 ºC) for 24 hours to eliminate any moisture content and then placed in a desiccator for 1 hour. Finally, the filter was weighted again to calculate the total suspended solids concentration in the samples, expressed in terms of mg of solids per liter.

Figure 22. Total suspended solids experimental

Figure 23. Solids retained in the filter

4. RESULTS AND DISCUSSION

The main objective of this project is to the efficiency in removing eight micropollutants typically found in wastewater by a dual system composed of constructed wetlands and advanced oxidation processes. In addition, the presence of a natural adsorbent (almond shell) and its height influence this process. On another hand, to analyse the influence of nitrification/denitrification, with a CW without recirculation, total suspended solids, and dissolved organic carbon in AOPs. Finally, to discuss whether this water could be used in agriculture.

4.1. REMOVAL EFFICIENCY IN CONSTRUCTED WETLANDS

4.1.1. Micropollutants elimination

The effectiveness of constructed wetlands in removing micropollutants can be influenced by photosynthesis, evapotranspiration, and microorganism activity. CW's root zone, rhizosphere, is the active reaction zone. This is where physicochemical and biological processes are conducted by the interactions between plants, microorganisms, soil, and micropollutants which depend on different parameters such as temperature, pH, or ionic strength [60]. Another key aspect for the removal of MPs is hydrophobicity and hydrophilicity. Hydrophobic compounds (low log K_{ow}) are likely to be adsorbed on soil and biofilms, while hydrophilic compounds (high log K_{ow}) are removed through different mechanisms [61].

Figure 24 illustrates the average micropollutant elimination result of the three constructed wetlands over cycles 1-8 (3 days retention time). It can be observed that the CW with the highest MP elimination efficiency is W3, which contains a 4 cm layer of almond shell, achieving an average elimination rate between 63.3-79.4 %. In contrast, W2, which has a 2 cm layer of almond shell, shows a decreased efficiency compared to the third wetland, with an elimination rate between 45.1-69.5%. On the other hand, CW 1, without almond shell, shows the lowest elimination rate, ranging from 30.0 % to 61.0%. These results highlight the importance of the presence and quantity of a natural adsorbent, in this case, almond shell, to effectively enhance the global efficiency of MPs elimination.

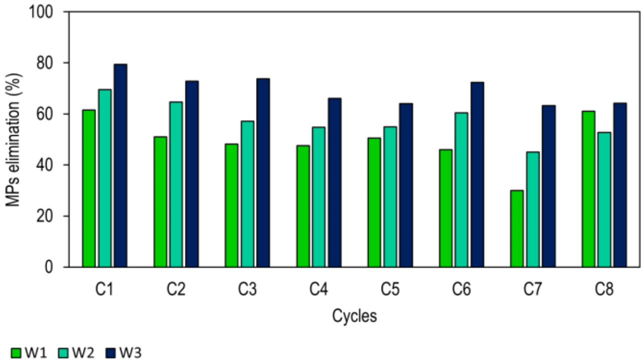

Figure 24. Global elimination of 8 MPs between all 8 cycles

Concerning the elimination of micropollutants in constructed wetlands during cycle 1, the elimination rates vary significantly between different types of micropollutants and wetlands. As observed in Figure 24, W3 exhibits the highest overall elimination capacity. However, the elimination efficiency is not uniform across all MPs due to the influence of several factors. Almond shells, used as an adsorbent in W2 and W3, contribute significantly to the enhanced elimination of MPs, especially in W3 which presents a deeper layer. The high surface area, porous structure, and natural adsorption capacity of almond shells facilitate the retention and degradation of MPs. Additionally, the pH of water, which is around 7.9, is crucial for adsorption processes, particularly for ionizable compounds with lower pka values. At this pH, ionizable compounds are more likely to interact with the adsorbent material, enhancing their removal. The octanol-water partition coefficient (log K_{ow}) is another crucial parameter in the elimination process. Compounds with a log K_{ow} greater than 1 tend to accumulate in biological organisms or sediments, indicating hydrophobicity and a higher propensity for adsorption to organic matter. The other way round, compounds with a low log K_{ow} value are more likely to remain dissolved in water, indicating hydrophilicity and a lower tendency for adsorption. This value helps predict the adsorption potential of MPs. Furthermore, solubility can also influence the elimination of MPs. Higher solubility increases the availability of MPs degradation, as microorganisms can more easily access and break down these compounds. Consequently, adsorbent materials can improve the removal of MPs. Finally, the action of plants and microorganisms is essential in this process.

Plants enhance the removal of MPs through various mechanisms such as root absorption, phytodegradation, or microbial metabolic processes present in the roots. A more accurate discussion of each MPs elimination will be provided in the following section (Figure 25).

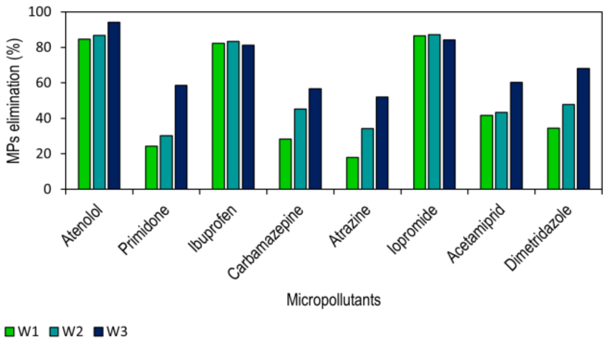

Figure 25. Elimination of 8 micropollutants by three types of constructed wetland for cycle 1

Atenolol: As a hydrophilic compound, with a low octanol-water partition coefficient (0.16), atenolol presents a significant elimination across all wetlands. The presence of an almond shell layer slightly increases the elimination rate respectively W1. In addition, its high solubility (13.30 mg/mL) provides the capacity for microorganisms to degrade it.

Primidone: Primidone is relatively hydrophilic (log K_{ow}= 0.91) and soluble (0.50 mg/mL). Its elimination in W1 is low at 24.21%, suggesting limited biodegradation and natural adsorption. Adding a 2 cm layer of almond shell in W2 slightly increases its elimination to 30.27 %. However, in W3 (4 cm layer), the elimination rate significantly increases to 58.51%. These results indicate that adsorption by almond shells is an important mechanism for eliminating this compound.

Ibuprofen: This compound is very hydrophobic (log K_{ow}= 3.97) and in IFAS water it is found ionized (pka= 4.45). In the three wetlands the elimination is high, 82.19% in W1, 83.19% in W2, and 81.32% in W3. These results indicate that ibuprofen elimination does not significantly depend on the almond shell layer. As reported by Janet Jan-Roblero and Juan A. Cruz-Maya [62], discovering a non-polluting pathway to eliminate ibuprofen is challenging as its chemical structure confers high resistance to biodegradation due to an aromatic ring. Furthermore, in recent decades, researchers have identified ibuprofen biodegrading bacteria such as the strain *Nocardia sp.,* which can be found in natural environments, although they can provide other more toxic compounds. This report suggests that a comparable microorganism may be responsible for breaking down ibuprofen in wetlands.

Carbamazepine: Carbamazepine is a low soluble (0.15 mg/mL) and hydrophobic (log K_{ow}= 2.45) compound. Its elimination rate in W1 is quite low at 28.38%, but it improves in W2 to 45.15%, and further increases in W3 to 56.72%. This suggests that almond shells provide additional adsorption. A study by the American University of Beirut [63] highlights the reasons behind carbamazepine's low elimination and how adsorbents can improve it. Carbamazepine is a non-ionizable compound due to its high pka value of 13.90, charged across all pH levels, and leading to poor electrostatic interaction with adsorbents. At low pH, the abundance of H^+ ions reduce hydrogen bonding between carbamazepine and the adsorbent, decreasing adsorption efficiency. At higher pH, fewer H^+ ions allow the amide group of carbamazepine to form hydrogen bonds with oxygen-containing functional groups of the adsorbent, enhancing adsorption. In IFAS water the pH is 7.9, which is favourable for enhancing elimination by the almond shell layer.

Atrazine: This compound is hydrophobic (log K_{ow}= 2.61) and ionized in IFAS water due to its low pka of 1.60. The elimination rate is low in W1 at just 17.87, improves to 34.32% in W2, and reaches 51.97% in W3. In its ionized form, it is likely to be adsorbed by almond shell. Studies, including one from Tongji University (China) [64], highlight the crucial role of bioaugmentation strategies in the degradation of atrazine in wetlands. This study may justify the higher removal in W3, as the deeper layer of almond shells promotes microbial activity, enhancing its removal.

Iopromide: As a hydrophobic compound with a low octanol-water partition coefficient (-2.35), iopromide's elimination rates are relatively consistent across all three wetlands: 86.49% in W1, 87.25% in W2 and 84.12% in W3. This trend shows that almond shell does not play a significant role in its elimination. Instead, microorganisms present in water, soil, and plant are likely responsible for its elimination.

Acetamiprid: Acetamiprid is a hydrophilic compound (log K_{ow}= 0.80) that in IFAS water is found ionized (pka= 0.70). Elimination in W1 and W2 are quite similar, at 41.56% and 43.39% respectively, but increase to 60.18% in W3. These results suggest that a deeper layer of almond shells is important for enhancing elimination via microbial degradation processes.

Dimetridazole: Dimetridazole is a hydrophilic compound (log K_{ow}= -1.23) found ionized in IFAS water (pka= 2.90). The elimination rate in W1 is low at 34.52%, increases to 47.85%, and reaches 68.18% in W3. This tendency suggests that a deeper layer in almond shell enhances elimination by microbial degradation and adsorption.

A supplementary graphic showing the elimination of MPs is available in Appendix I.

4.1.2. Nitrites/Nitrates, total suspended solids, and dissolved organic carbon evolution

4.1.2.1. Nitrites/Nitrates evolution

Nitrites (NO_2^-) and nitrates (NO_3^-) are species that impact AOPs due to their absorption in a large UV spectrum. Nitrites absorb at a maximum peak around 300-310 nm whereas nitrates absorb at 230-240 nm. The competition between these ions and the species involved in the production of hydroxyl radicals leads to reduced efficiency in AOPs when eliminating microcontaminants. Moreover, in solar photo-Fenton, nitrite ions can react with (·OH) following the following reaction Eq. 4.1 decreasing the process efficiency.

$$NO_2^- + \cdot OH \rightarrow NO^{\cdot}_2 + HO^- \qquad k_{\cdot OH,M} = 1.0 \times 10^{10}\ L\ mol^{-1}\ s^{-1} \qquad (Eq.\ 4.1)$$

While in UVC-H_2O_2 nitrates absorb UVC light, reducing the available light for the H_2O_2 photolysis which leads to a reduced production of hydroxyl radicals (reduction in UVC-H_2O_2 efficiency) [65].

The following graphics (Figures 26 and 27) represent nitrites and nitrates removal from IFAS water, W1, W2, W3, and W4 from cycles 1, 2, 7, and 8.

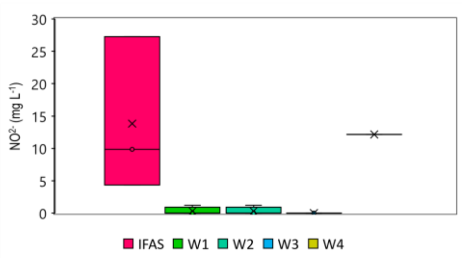

Figure 26. Nitrites concentration (mg L^{-1}) in IFAS water, W1, W2, W3 and W4 for cycles 1, 2, 7, and 8.

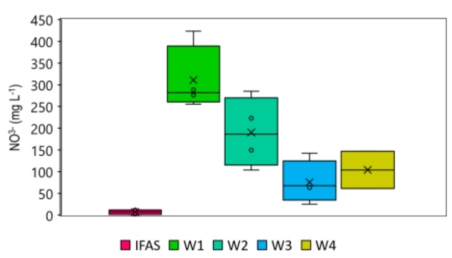

Figure 27. Nitrates concentration (mg L^{-1}) in IFAS water, W1, W2, W3 and W4 for cycles 1, 2, 7, and 8.

IFAS water presented an initial quantity on average of 13.82 mg NO_2^-/L and 5.17 mg NO_3^-/L. The values in Figures 26 and 27. vary because water samples were collected from the WWTS on three different days. Additionally, atmospheric conditions, such as rain, influenced the parameters.

Nitrites: The initial nitrite concentration in IFAS water averages 13.82 mg NO_2^-/L while in W1, W2, and W3, the average concentrations are nearly zero: 0.3 mg NO_2^-/L, 0.3 mg NO_2^-/L, and 0 mg NO_2^-/L respectively. This reduction lays that under aerobic conditions (oxygen presence due to recirculation), nitrifying bacteria can convert nitrites into nitrates through nitrification process (Eq. 4.2). The initial quantity of nitrites may have originated from the reaction of ammonium with oxygen (Eq. 4.3), although ammonium levels were not measured.

$$NO_2^- + \frac{1}{2} O_2 \rightarrow NO_3^- \qquad \text{(Eq. 4.2)}$$

$$NH_4^+ + O^2 \rightarrow NO_2^- + 2H^+ + H_2O \qquad \text{(Eq. 4.3)}$$

On the other hand, W4 presented a concentration of 12.15 mg NO_2^-/L which represents an increase compared to W1, its water source. Stagnant water conditions may result in decreased oxygen levels, creating anaerobic conditions where the nitrification process is not possible.

Nitrates: The initial nitrate concentration in IFAS water averages 5.17 mg NO_3^-/L. However, in the four CWs, the nitrate concentrations significantly increased on average: 310.65 mg NO_3^-/L in W1, 190.26 mg NO_3^-/L in W2, 75.50 mg NO_3^-/L in W3, and 103.90 mg NO_3^-/L in W4. As previously commented, the rise in nitrate levels is primarily due to the presence of oxygen dissolved in water, facilitated by recirculation. On the other hand, the presence of the almond shells in W2 and W3 may create anoxic areas where the bacteria reduce nitrates into molecular nitrogen (N_2). W4, without recirculation system, presents a concentration of 103.90 mg NO_3^-/L which means less oxygen was available to reduce nitrite.

4.1.2.2. Total suspended solids evolution

Total suspended solids (TSS) are non-settleable solid particles suspended in water which can give a vision on water quality levels: high levels of TSS indicate poor water quality [66].

Removing total suspended solids in wetlands is crucial for enhancing the efficiency of subsequent Advanced Oxidation Processes, as it can minimize interferences between reactive species and microcontaminants targeted for elimination.

IFAS water before constructed wetlands treatment contained an average of 146.9 mg TSS/L. Figure 28 shows TSS elimination in W1, W2, W3, and W4 during cycles 1 and 8.

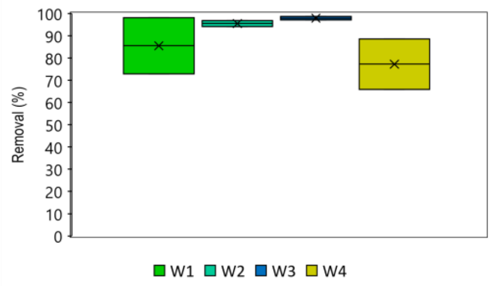

Figure 28. TSS removal in W1, W2, W3 and W4 for cycles 1 and 8

W1: In this wetland, without almond shells layer but incorporating recirculation, the average removal rate stands at 85.33%. The highest reduction occurred during cycle 8 at 96.87%, while the lowest was in cycle 1 at 72.94%. These results suggest that the recirculation system without almond shells layer positively influences the reduction on TSS.

W2: This wetland contains a 2 cm almond shells layer and recirculation. Its average removal rate is 95.55%, higher than previous wetland. Both cycles present an almost complete elimination, with 94.23% in cycle 1 and 96.87% in cycle 8.

W3: In this wetland, a 4 cm almond shells layer is incorporated with recirculation. This scenario achieves the highest TSS elimination, with an average of 97.94%. Cycle 1 shows a 97.15% elimination rate, and cycle 8 shows 98.73%.

W4: This wetland, whose water comes from W1, has no almond shells layer and lacks recirculation. It presents additional but lower TSS elimination, on average, 77.26%. In cycle 1, 65.90% is eliminated, while in cycle 8, 88.61% is removed.

Substrate materials are an important factor in the elimination of TSS. Materials such as sand, gravel or rocks present in CW act as excellent filters. In particular, the increased removal rates seen in W2 and W3 compared to W1 can be attributed to the presence of the almond shells layer which act as an extra filter due to its surface and porosity.

On the other hand, recirculation is another significant factor in TSS removal. As previously mentioned, the lower elimination on W4, compared to the other three CW, highlights the importance of recirculation. Recirculating water increases the possibility for the solids to be captured and settled in the substrate and vegetation. Additionally, biological activity is positively benefited from recirculation as it enhances nutrients distribution, improving the effectiveness of the filtration.

4.1.2.3. Dissolved organic carbon evolution

Dissolved organic carbon (DOC) measures the levels of organic carbon present in a sample. A lower DOC concentration suggests a reduction in organic matter, indicating that constructed wetlands effectively removed a significant part of the organic matter from the wastewater. Consequently, this reduction means the effluent is cleaner and sustainable for water reuse.

Eliminating as much organic matter in wetlands as possible is crucial because it enhances the efficiency of the following advanced oxidation process. The less organic matter to oxidize, the more effectively AOPs can degrade microcontaminants, which is the main objective.

IFAS water before constructed wetlands treatment contained an average of 20.6 mg DOC/L. According to Regulation (EU) 2020/741 it is not established specific requirements regarding limiting DOC permitted in agriculture. The regulation focuses on other parameters of water quality such as microbiological, chemical, and physical aspects [67].

The following graphic (Figure 29) illustrates the DOC elimination across four CW (W1, W2, W3 and W4) for cycles 1,2,7, and 8.

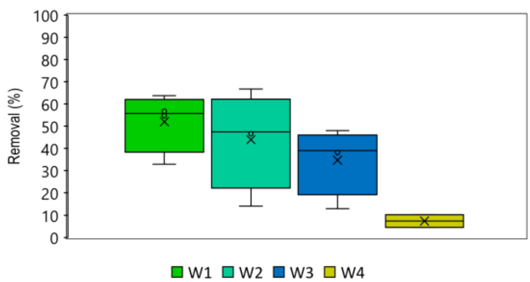

Figure 29. DOC removal in W1, W2, W3 and W4 for cycles 1,2,7, and 8

W1: In this wetland, without almond shells layer but incorporating recirculation, the average removal rate stands at 52.06%. The highest reduction occurred during cycle 2 at 62.80%, while the lowest was in cycle 1 at 32.94%. These results suggest that the recirculation system without almond shells layer positively influences the reduction on DOC.

W2: This wetland contains a 2 cm almond shells layer and recirculation. Its average removal rate is 43.98%, slightly lower than the previous scenario. In this CW it can be observed that the maximum removal is seen in cycle 7 at 66.76%, whereas the lowest was in cycle 1, at 14.12%.

W3: In this wetland, a 4 cm almond shells layer is incorporated with recirculation. The DOC removal rate is significantly lower than both W1 and W2, with a median around 34.77%. In this case, the maximum elimination rate lays in cycle 7, at 48.11%, while the lowest in cycle 1, at 12.94%. This may be due to the leaching process of the almond shells layer, an organic material that can release additional organic matter.

W4: This wetland, whose water comes from W1, has no almond shells layer and lacks recirculation. It shows a minimal additional average elimination at 7.38%. The highest extra elimination was during cycle 7 at 10.24%, and the lowest in cycle 2, at 4.52%.

Recirculation is a key factor when removing DOC in water because it enhances the contact between the water and microorganisms in charge of breaking down DOC. In addition, it ensures the flow of nutrients and oxygen for microbial communities responsible for Dissolved Organic Carbon. As it can be observed in the article: *Nature-based solution as an efficient wastewater pretreatment to enhance micropollutants abatement by solar photo-Fenton at natural pH* [68], there were conducted experiments in two operational modes, with and without recirculation, experiments carried out with recirculation obtained a 50-55% of DOC elimination whereas the ones without elimination obtained between 35 and 36% of elimination. It follows the tendency of less elimination.

The depth on the almond shell layer observed across W2 and W3 can also influence in the DOC removal. The highest DOC removal was performed in W1, whereas the addition of a 2 cm almond shells layer in W2 partially decreases removal efficiency. Comparing the results of W3 to W2, an increased quantity of organic layer worsened DOC elimination. This fact can lead to anaerobic condition due to a reduction in water flow caused by the depth of the almond shells. This can inhibit the activity of aerobic microorganisms responsible for the elimination of organic carbon dissolved. Additionally, the accumulation of organic matter in this natural filter may result in their decomposition increasing DOC levels.

4.2. REMOVAL EFFICIENCY IN HYBRID SYSTEM (CW + AOP)

The second order kinetics constant for reaction of hydroxyl radicals with micropollutants ($k_{\cdot OH}$) are essential to understand the degradation of contaminants in wastewater treatment. Hydroxyl radicals are highly reactive and present affinity for a wide range of inorganic and organic compounds. Therefore, the degradability of MPs can be predicted from its kinetic constant along with other physicochemical properties [69]. The following table (Table 11) represents kinetics constant of each 8 MPs.

Table 11: kinetics constant of each 8 MPs

MP	IOP	DMZ	ATL	PRM	CBZ	ATZ	ACMP	IBU
$k_{\cdot OH}$ [$M^{-1}s^{-1}$]	$3.3*10^9$	$5.6*10^{10}$	10^{10}	$6.7*10^9$	$8.8*10^9$	$3*10^9$	$2.1*10^9$	$6.67*10^9$

The results of AOPs will be discussed in cycle 1 because, as observed in Figure 24 the removal efficiency remained practically stable throughout the 8 cycles.

4.2.1. UVC-H_2O_2

UVC-H_2O_2 experiments were conducted initially by analysing IFAS water, containing 100 ppb of each 8 microcontaminants, to compare the results with the pretreated samples and discuss if the elimination rate improved. Then, water samples from W1, W2, W3, and W4 from cycle 1 were analysed, with W4 water coming from W1 in cycle 2. The removal results are represented in the following graphics (Figures 30-34).

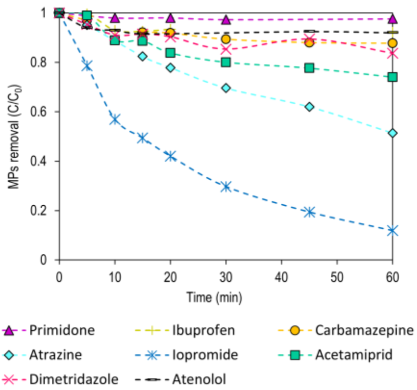

Figure 30. MPs removal by UVC-H_2O_2 for IFAS water

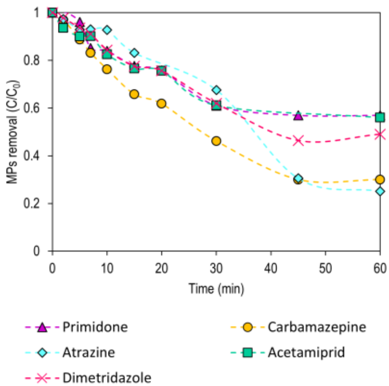

Figure 31. MPs removal by UVC-H_2O_2 for W1

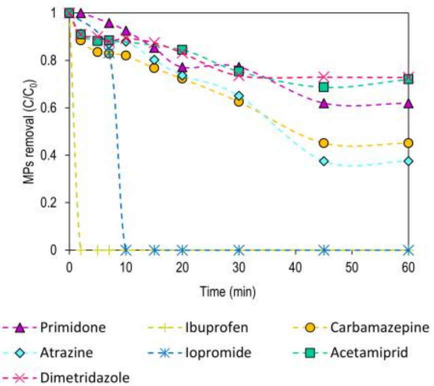

Figure 32. MPs removal by UVC-H_2O_2 for W2

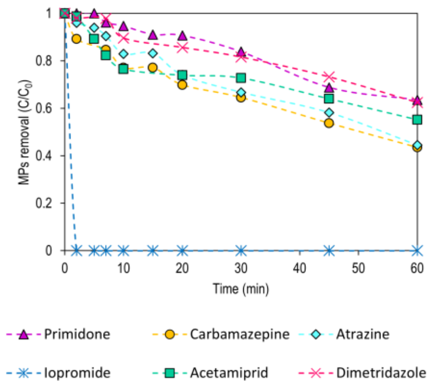

Figure 33. MPs removal by UVC-H_2O_2 for W3

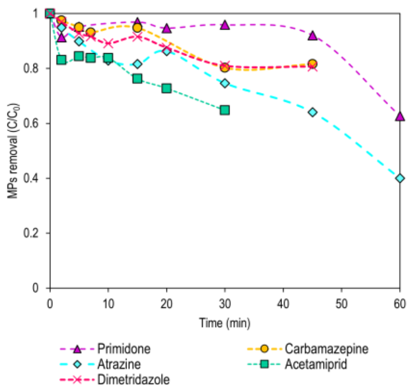

Figure 34. MPs removal by UVC-H_2O_2 for W4

IFAS water: This water, which has not been pretreated by CW, presents the lowest removal efficiency observed. None of the eight MPs have achieved complete degradation in 60 minutes. In fact, none of them even reached 50% degradation. However, iopromide stands out with an elimination of approximately 88%. This is due to its strong absorption peak at around 245 nm, closely matching the wavelength of the UVC lamp at 254 nm, making it susceptible to photolysis. Despite this, the presence of interferences such as TSS (146.9 mg TTS/L), DOC (20.6 mg DOC/L), nitrites (13.82 mg NO_2^-/L), and nitrates (5.17 mg NO_3^-/L) in the water matrix, the hydroxyl radicals were not able to effectively degrade MPs. Instead, another organic matter was oxidised.

W1: The pretreatment in CW was able to eliminate atenolol, ibuprofen, and iopromide. However, complete elimination of MPs in this experiment was not achieved, removal values ranged between 40-75%. The elevated nitrate levels in water (310.65 mg NO_3^-/L) could absorb a significant amount of UVC light, which reduces light availability for hydrogen peroxide photolysis. In addition, the concentration of MPs is lower, and the kinetics may be affected compared to IFAS water. The high elimination of atrazine and carbamazepine is attributed to their high 2nd order kinetics, with $k_{\cdot OH}$ values of 10^{10} M^{-1} s^{-1} and $8.8*10^9$ M^{-1} s^{-1}, respectively. At the same concentration, their reactivity with ·OH is higher which results in more elimination. On the other hand, primidone and acetamiprid have lower $k_{\cdot OH}$ values of $6.7*10^9$ M^{-1} s-1 and, $2.1*10^9$ M^{-1} s^{-1}, respectively, resulting in slower reaction progress and, less elimination. While the water is cleaner due to DOC reduction, the level is still high. Finally, alkalinity may be another factor, as it can react with ·OH, competing with MPs.

W2: Atenolol was fully degraded before the UVC-H_2O_2 process. In the first 10 minutes of the experiment, ibuprofen and iopromide were eliminated due to pretreatment, which reduced their concentrations by 94.67% and 91.37%, respectively. Photolysis could also degrade Iopromide as its peak absorption is approximately 245 nm. On the other hand, other MPs were eliminated in the range of 27-63%. This lower reduction is attributed to the initial concentration of each MP, with elimination in CW between 44.12-59.84%. Despite its high $k_{\cdot OH}$ value of $5.6*10^{10}$ M^{-1} s^{-1}, dimetridazole's elimination is low due to its low initial concentration. The hydroxyl radicals encountered difficulty reacting with MPs. Similar to W1, kinetics played a crucial role in the MPs elimination. Carbamazepine and atrazine still had the highest elimination rates, while acetamiprid and primidone continued to have lower elimination rates.

W3: In this case, atenolol and ibuprofen were degraded by CW. As in the previous case, iopromide was degraded in the first few minutes due to its infimal low concentration (11.60% of the initial amount) and its susceptibility to photolysis (245 nm absorption peak). However, the degradation of the other MPs ranged between 38-56%. This reduced elimination efficiency may be caused by the previous CW elimination, which had already eliminated between 63.81 and 83.69% of these MPs. However, the importance of kinetics also influenced this process, following the same trend as in previous cases.

W4: Atenolol, ibuprofen, and iopromide were eliminated in CW. The elimination rate in this experiment ranged from 20 to 60%. In this water, the concentrations of nitrites and nitrates were relatively high, at 12.15 mg NO_2^-/L and 103.40 mg NO_3^-/L, respectively. These species can react with ·OH, competing with MPs and decreasing the elimination efficiency. On the other hand, atrazine's high elimination rate is due to its kinetics, higher than the other MPs. In addition, the higher quantities of TSS (33.40 mg TTS/L) and DOC (12.45 mg DOC/L) could also impact the elimination.

4.2.2. Solar Photo-Fenton

Solar photo-Fenton experiments were also conducted. Firstly, the analysis of IFAS water, containing 100 ppb of each 8 microcontaminant, to compare the results with the pretreated samples and discuss if the elimination rate improved. Then, water samples from W1, W2, W3, and W4 from cycle 1 were analysed, with W4 water coming from W1 in cycle 2. The removal results are represented in the following graphics (Figures 35-39).

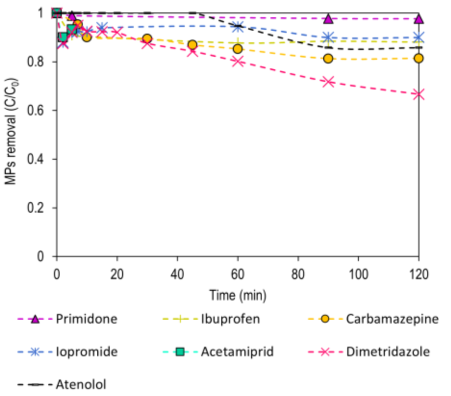

Figure 35. MPs removal by SPF for IFAS water

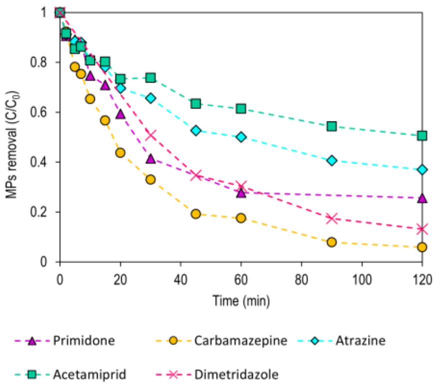

Figure 36. MPs removal by SPF for W1

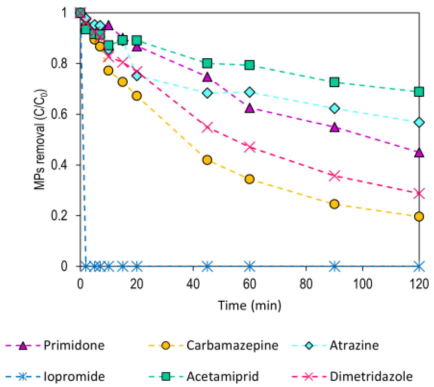

Figure 37. MPs removal by SPF for W2

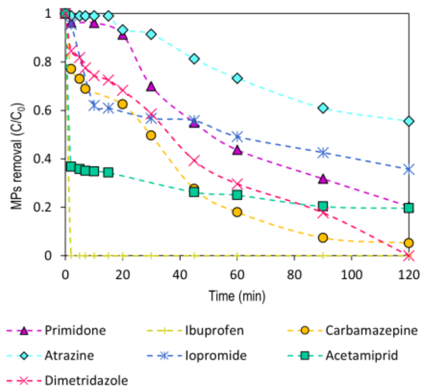

Figure 38. MPs removal by SPF for W3

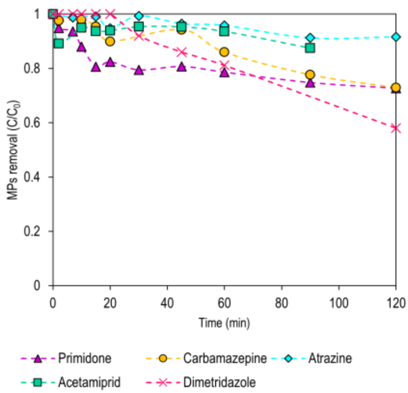

Figure 39. MPs removal by SPF for W4

IFAS water: This water, which has not been pretreated by CW, presents the lowest removal efficiency observed. None of the eight MPs have achieved complete degradation in 120 minutes. Any MPs have been eliminated by more than 30%. Dimetridazole is the most degraded compound (30%) due to photolysis (maximum absorbance at 320 nm) and its high kinetic rate ($k_{\cdot OH}$=5.6*10^{10}). More elimination has not been achieved due to high levels of TSS, DOC, nitrites, and nitrates.

W1: Atenolol, ibuprofen, and iopromide were not present due to their previous elimination in CW. In this CW the levels of DOC, TSS, and nitrites were lower than in the untreated water, this is reflected in elimination efficiency, which increased between 49-94%.

W2: In this sample, ibuprofen and atenolol were eliminated previously. In this experiment, iopromide was eliminated in the first minutes due to its initial low concentration (less than 9%). On the other hand, the other MPs elimination rate ranges 30-80%.

W3: All eight MPs were present in this sample. In this process, total efficiency increased considerably. Contaminants such as ibuprofen, dimetridazole, and carbamazepine were almost fully removed in 120 minutes. The elimination of the other MPs ranged between 44% to 80% because of the reduction in DOC, and TSS but especially in nitrates (75.05 mg NO_3^-/L) which are the main hydroxyl radicals' competitors.

W4: This sample, whose water came from W1 (cycle 2), was missing iopromide, atenolol, and ibuprofen. In this case, all parameters worsened, especially in nitrates and nitrites which incremented: 103.40 NO_3^-/L and 12.15 NO_2^-/L. This increment meant a reduction in the ·OH production and competitivity between those species and MPs. Their elimination rate, which reached an average between 9-41%, is far away from other CW elimination.

4.2.3. AOPs comparison

As can be seen in Figures 40 and 41 the hybrid system combining constructed wetlands and advanced oxidation processes demonstrated effective micropollutant removal. The degradation efficiency of MP was higher in the UVC-H_2O_2 system compared to SFP, with removal rates of 26.60% and 14.35% respectively. The difference is attributed to the increased generation of hydroxyl radicals under UVC light, which effectively degrades and oxidise microcontaminants. In addition, some compounds are sensitive to photolysis, which increases the average elimination rate. Regarding CWs, as previously commented, the presence of almond shells layer contributes to eliminating MPs from water, with the highest removal efficiency observed in W3 (79.49%), followed by W2 (69.54%) and W1 (61.61%).

Furthermore, the hybrid system, CW + SPF and CW + UVC-H_2O_2 reach higher elimination rates compared to individual systems. In the CW + SFP hybrid system, the highest removal is observed in W3 water, reaching 93.01% elimination, while W1 and W2 had removal rates of 90.19% and 86.59% respectively. On the other hand, in the CW + UVC-H_2O_2 hybrid system, the highest removal rate is also observed in W3 at 90.91%, followed by W2 at 86.19% and W1 at 84.50%. According to those results, removal efficiency is practically equal in both hybrid systems, regardless of the CW configuration. An additional organic layer, almond shells, is worth consideration for CW systems because the elimination is higher. However, in a hybrid system without the layer, the achieved elimination efficiencies are still highly acceptable.

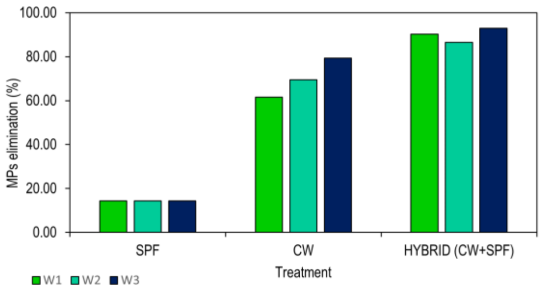

Figure 40. Hybrid system: CW + SPF

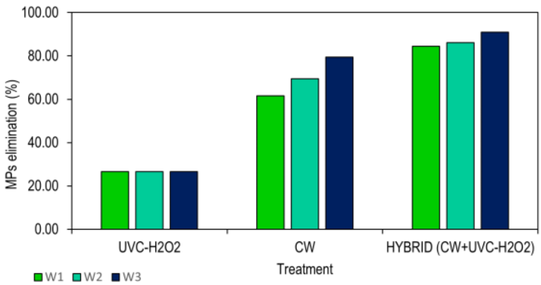

Figure 41. Hybrid system: CW + UVC-H_2O_2

5. CONCLUSIONS

Both hybrid processes, CW + SPF and CW + UVC-H_2O_2 would be efficient solutions to eliminate ATL, PRM, IBU, CBZ, ATZ, IOP, ACMP, and DMZ from IFAS water and the treated effluents could be reused for agricultural purposes.

Constructed wetlands have demonstrated high efficiency in eliminating MPs from water, on average 86.59% and 90.19%, with a retention time of 3 days. The addition of an almond shells layer as natural adsorbent further increased elimination efficiency, particularly for recalcitrant and hydrophilic compounds such as ACMP, PRM, ATL, DMZ, and CBZ. Moreover, the depth of the almond shells layer was a key factor in absorption as the deeper it was the more MPs were eliminated due to factors such as increased adsorption surface area, enhanced filtration from its porous, and heightened macrobial activity.

CW not only eliminated MPs but also affected nitrites, nitrates, TSS, and DOC levels. IFAS water initially had on average high levels of nitrites (13.82 mg NO_2^-/L), which decreased to nearly zero in W1, W2, and W3 due to the nitrification process in aerobic conditions. On the other hand, nitrate levels increased from an initial concentration of 5.17 mg NO_3^-/L due to the presence of oxygen. However, deeper almond shells layers created anoxic zones, resulting in lower nitrate concentrations. TSS levels drastically decreased in CW, especially those with the organic layer, which acted as an additional filter. Finally, DOC levels also decreased by 35-50%, though W2 and W3 had slightly higher DOC levels due to leaching from the almond shells layer.

As demonstrated in W4, recirculation is another key factor. Nitrite levels were higher (12.15 mg NO_2^-/L) compared to the other three CW due to anaerobic conditions. Nitrate levels were moderate (103.90 mg NO_3^-/L) as less oxygen was available to reduce nitrite into molecular nitrogen. Additionally, DOC and TSS removal were also lower because of stagnation conditions.

The efficiency of AOPs, on average elimination by 14.35% and 26.60%, depended on several factors. DOC compete for hydroxyl radicals and absorbs UV light, reducing the total energy available for hydroxyl radicals generation. TSS scatter light and provide surfaces for reaction. Nitrites also compete for hydroxyl radicals while nitrates absorb UV light. The high levels of those components reduce contaminant removal efficiency by competing for hydroxyl radicals, absorbing UV light, and affecting the generation of hydroxyl radicals necessary for contaminant oxidation. A key factor remained on 2nd order kinetics, where the MPs with higher $k_{\cdot OH}$ values, such as in ATZ or CBZ, had higher elimination rates. Photodegradation was also significant, MPs, such as DMZ or IOP, presented absorption peaks, at 320 nm (affected by SPF light) and 245 nm (affected by UVC-H_2O_2).

Finally, the efficiency of both hybrid systems was higher than CW and AOPs experiments separately, achieving efficiencies around 85-93%. Moreover, the organic layer, regardless of its depth or presence, did not notably enhance the overall treatment efficacy. Consequently, there appears to be no significant distinction between both hybrid systems in their capacity to effectively remove MPs from WW.

6. FUTURE WORK

It is important to recognize that this research project has been conducted on lab-scale. To validate the effectiveness of the hybrid system it would be interesting to perform studies on a larger scale, using different materials and dimensions. To confirm water reuse in agriculture, conducting additional tests, such as phytotoxicity or E. colli testing would be useful. Furthermore, evaluating the removal of other microcontaminants with different physicochemical properties would be essential to provide the efficiency of the system's performance.

Moreover, the effectiveness of another organic layer could be tested as there may be more efficient organic materials to eliminate micropollutants.

Finally, an economic analysis should be conducted to assess feasibility of the hybrid CW and AOPs system. The analysis would help to determine the cost-effectiveness and potential benefits of implementing the system on a larger scale.

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ACRONYMS

IOP: Iopromide

DMZ: Dimetridazole

ATL: Atenolol

PRM: Primidone

CBZ: Carbamazepine

ATZ: Atrazine

ACMP: Acetamiprid

IBU: Ibuprofen

WWTS: Wastewater Treatment Station

WEI+: Water exploitation index

EC: Emerging concern

MP: Micropollutant

WW: Wastewater

UAA: Utilized agricultural area

UN WWDR: United Nations World Water Development Report

SDG: Sustainable Development Goal

HPLC: High performance liquid chromatography

CW: Constructed wetland

AOP: Advanced oxidation process

·OH: Hydroxyl radical

SPF: Solar photo-Fenton

UVC: Ultraviolet

UVC-H_2O_2: Ultraviolet and hydrogen peroxide

EDTA: Ethylenediaminetetraacetic acid

H_2O_2: Hydrogen peroxide

K_{ow}: Octanol-water partition coefficient

TSS: Total suspended solids

DOC: Dissolved organic carbon

NO_2^-: Nitrite ion

NO_3^-: Nitrate ion

W1: Constructed wetland without almond shells layer and with recirculation system

W2: Constructed wetland with 2 cm almond shells layer and with recirculation system

W3: Constructed wetland with 4 cm almond shells layer and with recirculation system

W4: Constructed wetland without almond shells layer and without recirculation system

APPENDIX 1: GRAPHICS AND IMAGES

Figure I: Plant *Carex Pendula* in constructed wetland

Sand ø= 0.5-1 mm

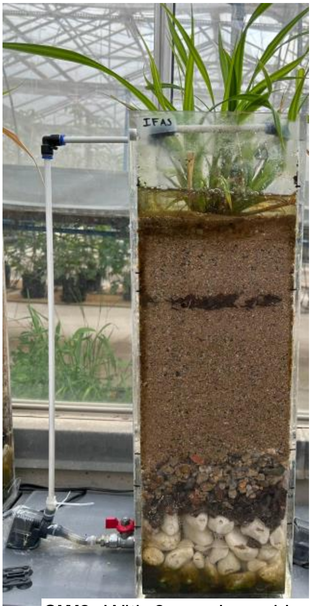
Volcanic rock ø= 20-50 mm

Fine gravel ø= 10-20 mm

Cobble stones ø= 50-80 mm

Figure II: Rock layers diameter

CW1: Without almond layer



CW2: With 2 cm almond layer

CW3: With 4 cm almond layer

CW4: Without recirculation system

Figure III: Constructed Wetlands

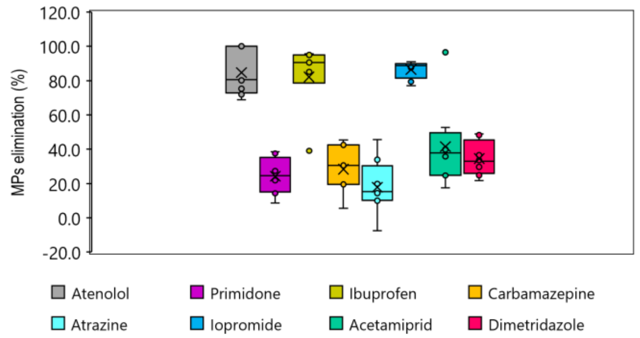


Figure IV. Elimination of 8 micropollutants by three types of constructed wetland for cycle 1

Table I: Other chemical reagents

Name	Formula	Company	Purity (%)	Used in/for
Fe-EDTA	$C_{10}H_{12}N_2O_8FeNa \cdot 3H_2O$	Pyhgenera	7	SPF
Metavanadate	H_4NO_3V	Sigma Aldrich	99	H_2O_2 determination
Phenanthroline	$C_{12}H_8N_2$	Panreac Química	99	Fe^{2+} determination
Acetic acid	CH3COOH	Panreac Química	95	Fe^{2+} determination
Hydrogen peroxide	H_2O_2	Merck	30 w/w	SPF and UVC-H_2O_2
Ascorbic acid	$C_6H_8O_6$	Panreac Química	91	Total Fe determination
Sodium thiosulfate	$Na_2S_2O_3$	Panreac Química	90	Stop reaction with H_2O_2
Acetonitrile	CH_3CN	Fischer Chemical	99.80	HPLC analysis
Orthophosphoric acid	H3PO4	Panreac Química	85	HPLC analysis

Table II: HPLC Mix Method Characterization

MP	Detection [nm]	RT [min]	Column	Pressure [bar]	Mobile phase	Flow-rate [mL/min]
IOP	240	8.9 + 9.1	Mediterranea SEA 18 (250x4.6 nm) 5 µm particle size	110	80% H2O with H3PO4, pH= 3 20% acetonitrile	1
DMZ	320	11.7				
ATL	200	7.45				
PRM	200	12.95				
CBZ	214	17.85				
ATZ	222	20.69				
ACMP	254	15.17				
IBU	200	24.4				

Table III: Micropollutants solutions

Contaminant	Concentration (mg/L)	Molar mass (mg/mol)	Salt mass (mg/mol)	Flask volume (mL)	Added mass (mg)
Iopromide	100	791.10	802.33	250	25.36
Dimetridazole	100	141.13	141.13	50	5.00
Atenolol	100	266.37	271.80	250	25.51
Primidone	100	218.25	218.25	100	10.00
Carbamazepine	100	236.27	236.27	100	10.00
Atrazine	100	215.68	215.68	100	2.00
Acetamiprid	100	222.67	222.67	100	10
Ibuprofen	100	206.29	228.29	200	22.13