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Removal of organic contaminants by constructed wetlands and solar-based oxidation processes

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SUSTAINABLE DEVELOPMENT GOALS

In the 1992 Rio de Janeiro summit, Agenda 21 was developed, which established the Millennium Development Goals (MDGs). In 2015, it was realized that these goals were not being met and the 2030 Agenda was developed where 17 sustainability development goals (SDGs) were defined, which are a set of global goals that ensure fair and sustainable health at all levels for both the biosphere and humanity. The SDGs are shown in the figure below.

The goal that this work fulfils is Goal 6, clean water and sanitation. This goal is divided into different sub-sections and the most similar is 6.3 which states: By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally. In this work we try to find an ecofriendly solution for the elimination of micropollutants present in wastewater.

SUMMARY

Micropollutants (MPs), substances that exist in very small traces in water, have been attracting the attention of the scientific community because of their frequent occurrence in the aquatic environment even after passing through conventional water and wastewater treatment systems. A large number of sources thus contribute to the introduction of MPs into the environment. Waste water treatment plants (WWTP) are also considered the major source of MPs entrance in the aquatic environment. Thus, appropriate treatment processes capable of removing MPs and other relevant pollutants need to be adopted in order to preserve the environment. So that, a hybrid process constructed wetland (CW) and advanced oxidation process (AOP) has been investigated in this study. The performance of MPs removal from constructed wetlands was investigated using two different aquatic plants (*Phragmites australis* and *Cyperus haspan*) and two modes of operation (with or without recirculation). The results revealed that no significant differences were observed between plants. However, an enhancement of the MPs elimination was achieved in the CW with recirculation (about 80 % of some MPs) compared to the CW without recirculation (about 50 % of MPs elimination). Additionally, it was studied the potential of CWs as a pretreatment of photo-Fenton in order to improve the process' efficiency on MPs degradation. The results disclosed that total removal of MPs were achieved in less than 30 min in the matrices pretreated with recirculated CW while less than 80% of MPs removal was obtained in 120 min without pretreatment.

Keywords: Constructed wetlands, micropollutants, photo-Fenton,iron complexes, hybrid system

CONTENTS

1. INTRODUCTION

1.1. Current situation of water

Water is an essential resource for the development of life. The 71 % of the Earth's mass is aquatic. However, only 3.5 % corresponds to fresh water, and only less than one-third of that percentage is available for our use, since 69 % of this belongs to frozen glaciers or in another way unavailable for using [1]. Due to the increasing world population there is a higher demand for freshwater compared to the available resources, this phenomenon is called water stress.

There are currently more than 2 billion people living with a water demand in excess of what they have available, water stress, and this continues to increase year after year. By 2030 these 2 billion people will become almost half of the people living in the world, and this is and will become more problematic as by 2050 over 5 billion people will suffer a full month of water scarcity, and this will continue to increase as the population continues to grow. All this will lead to a 20-30% increase in water demand related to domestic uses in that year (Figure 1) [2-5].
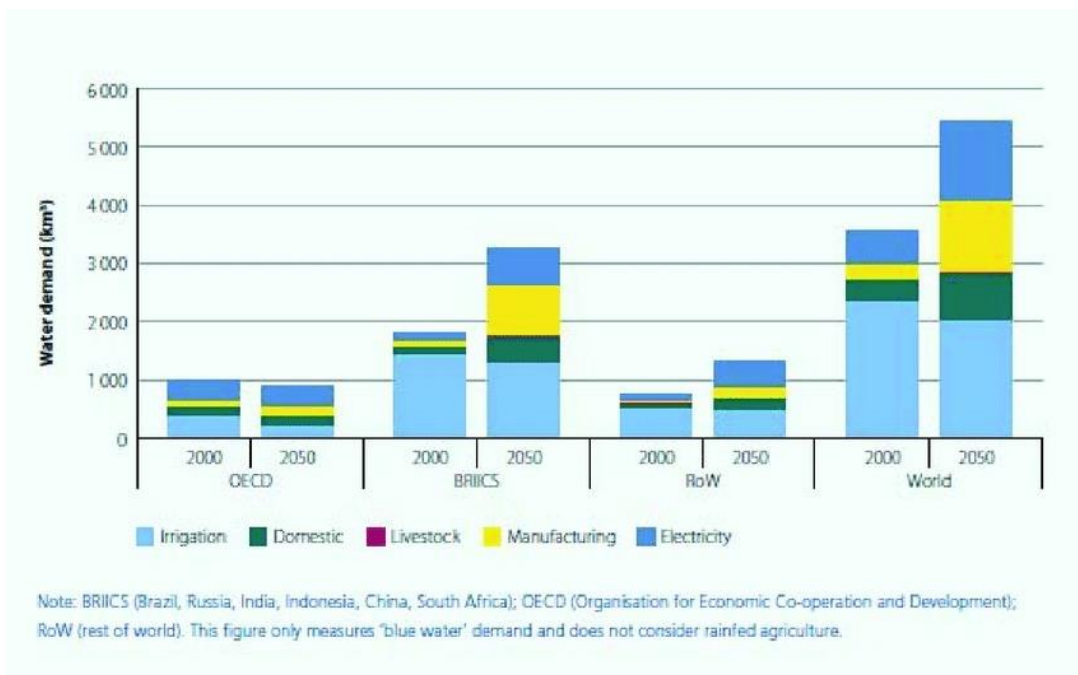
Figure 1 Predictions by 2050 of global water withdrawals based on data of 2000. The projections are divided by sector and for different groups of regions in the world.

For this reason, it is important to preserve both the quantity and quality of water resources. In front of this critical scenario, a possible partial solution to face water scarcity is to reuse water.

1.2. Wastewater treatment and reuse

The world's population is growing and with it the challenges of removing pollutants from wastewater. Urban and industrial wastewater contains pathogens, organic compounds, metals and other hazardous pollutants. If these waters are not properly treated and are discharged into

the aquatic environment, ecosystems and human health are endangered [6]. Wastewater reuse is a reliable new resource, which also competes against water scarcity and reduces the time of discharge of pollutants [7].

Globally, it is estimated that 80 % of untreated industrial and municipal wastewater is released into the environment causing water pollution [2,8].

However, large differences are observed between countries. On average, 27 % of total wastewater is untreated in high-income countries. Even so, the percentage increases in upper-middle-income countries and lower-middle-income countries, which present a value of 66 and 72%, respectively [2,8].

However, wastewater reuse is a process that is not being implemented due to the obstacles it presents. The main obstacles are the lack of legislation, financing, and technological and cultural barriers, as there are countries that do not welcome the reuse of wastewater for agriculture.

Nevertheless, WWTPs could eliminate the compounds that are present in relatively high concentration, but instead there are recalcitrant contaminants that are not eliminated and are harmful to humans and the environment. This fact is due to the conventional WWTPs (physicochemical and biological treatments) are not designed to treat these substances, since these organic compounds are characterized by their recalcitrant character and found at low concentrations (ng/L to µg/L) in the effluents [9]. These compounds are called micropollutants (MPs).

Although water reuse has many advantages, little implementation has been conducted due to its high capital cost. In addition, there is a global need to develop appropriate legislation and regulation for governments to implement to adopt the system as a future water supply.

1.3.   Micropollutants in water resources

Micropollutants are compounds of anthropogenic origin which do not have a specific regulation. As aforementioned, these compounds are present in the WWTP at very low concentrations and they are characterized by their recalcitrant and bioacumulative properties.

Micropollutants include a wide variety of products of diverse origin and chemical nature, derived both from personal use and from various industries. Microcontaminants can be classified in a several categories such as brominated flame retardants, polar pesticides, pharmaceuticals and illicit drugs, among others.

The occurrence of MPs in aquatic environments even at trace concentrations could pose risks to human health and the environment [9]. Thus, they must be removed before reuse in other activities. In front of this scenario, specific treatments are required to remove these MPs and preserve the environment.

Although there are some of these pollutants that are starting to be regulated, but it is a very difficult because there are so many types of chemicals.

1.3.1. Micropollutants used in constructed wetlands

Different studies have shown that the main micropollutants present in wastewater are herbicides, pharmaceuticals, hygiene products and hormones [10-12]. Therefore, a solution containing 20 MPs of different classes that can be representative of real wastewater has been used to study the performance of constructed wetlands in removing organic compounds. More information about these MPs can be found in Annex I. Moreover, these MPs have been selected for their different Log K_{OW}, since the CWs remove a part by adsorption and thus know their influence.

1.3.2. Specific micropollutants used in photo-Fenton

Acetamiprid

Acetamiprid (ACMP) is a neonicotinoid insecticide currently used to control insect plagues. It is slightly soluble in water (4.25 mg/L) and hydrophobic (log K_{OW} of 0.8) [13-15]. Due to chronic exposure to this compound, there have been cases of negative effects on human health [16,17,18]. Therefore, acetamiprid has been included as a neonicotinoid under vigilance in the European directive 2018/840/EU repealed by directive 2008/105/CE [19]. In aquatic systems, the highest value that has been detected is 380ng/L [20-26].
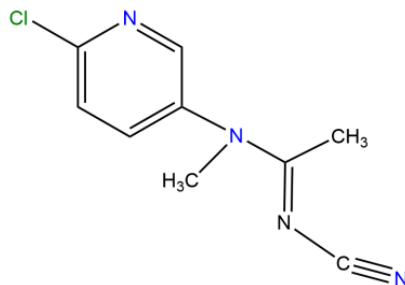
Figure 2 Structural formulate of Acetamiprid Source:ChemDraw

Sulfamethoxazole

Sulfamethoxazole (SMX) is a sulfonamide antibiotic widely used in humans and animals. This antibiotic is used to treat infections caused by bacteria [27] SMX inhibits the conversion of p-aminobenzoic acid to dihydropteroate, inhibiting the production of nucleic acids. [28-30] SXM is slightly soluble in water (610mg/L) and hydrophobic (log K_{OW} of 0.89) [31]. It is the antibiotic most frequently detected in aquatic environments and its presence was reported in many effluents of WWTPs worldwide [32-39]
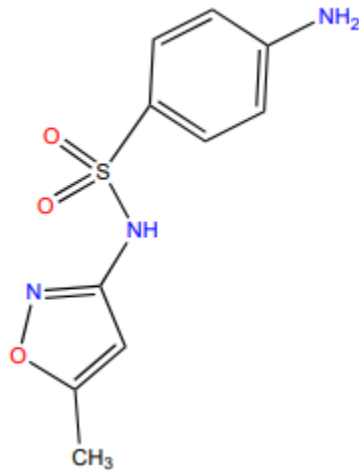
Figure 3 Structural formulate of Sulfamethoxazole Source:ChemDraw.

Metronidazole

Metronidazole (MET) is an antibiotic used for treatment of bacterial infections. It enters bacterial cell walls, disrupts DNA and inhibits DNA synthesis in certain microorganisms [40]. MET is soluble in water (11000mg/L) and presents low hydrophobicity (log K_{OW} of -0.02) [41].
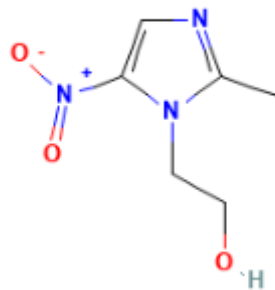
Figure 4 Structural formulate of Metronidazole Source:ChemDraw

1.4.   General legal framework of water

The presence of micropollutants in the environment is a problem that endangers human health and aquatic ecosystems. For this reason, water quality policies are being developed.

Directive 2000/60/EC also the Water Framework Directive, has as its objectives the conservation, protection and improvement of the quality of the environment, and the prudent and rational use of natural resources [42].

This directive establishes the European Environmental Quality Standards (EQS), which set the maximum concentration of each substance in aquatic systems.

This directive lists the main pollutants (Annex VIII) and priority pollutants (Annex X, added by decision 2445/2001/EC and amended by Directive 2008/105/EC and 2013/39/EU). Decision 2445/2001/EC, published in 2001, approves a list with 33 priority substances (PS) monitored at EU level. In the amendment by Directive 2008/105/EC the EQS values for 33 PS and 8 additional pollutants are published [43]. In amendment 2013/39/EU the PS are extended to 45, with more restrictive EQS for PS [44].

Another European regulation is Regulation (EU) 2020/741 on minimum requirements for water reuse, which aims to establish harmonised parameters to ensure the safe reuse of water for agricultural irrigation, with the objective of promoting this practice and helping to cope with droughts and water stress. [45]

1.5.   Advanced Oxidation Processes

The increasing presence of MPs in the water resources has triggered the development of new technologies for the removal of MPs. For that fact, technologies capable to remove these MPs are required to preserve the environment. These substances which are hardly removed in conventional WWTPs can be depredated by implementing a tertiary treatment based on advanced oxidation processes.

Advanced Oxidation Processes (AOPs) are chemical processes that produce deep changes in the chemical structure of a contaminant, involving the generation and use of transient species, mainly hydroxyl radical (·OH). Those processes can be divided into those that need light as part of process to generate ·OH, photochemical processes, and those that do not, non-photochemical processes [46].

Among different AOPs, photo-Fenton process has demonstrated its efficiency in the removal of different type of MPs [47].

Photo-Fenton

The photo-Fenton process is a combination of Fenton reagents (H_2O_2 and Fe^{+2}) including UV-visible radiation ($\lambda < 600$ nm) which produces additional hydroxyl radicals compared to the dark Fenton process. On the one hand by photoreduction of Iron (III) to Iron (II) ions and on the other hand, by photolysis of hydrogen peroxide at wavelengths below 310 nm. [48]

$$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^- + OH^{\cdot} \qquad [49]$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + HO_2^{\cdot} + H^+ \qquad [50]$$

$$Fe(OH)^{+2} + hv \rightarrow Fe^{+2} + OH^{\cdot} \qquad [51]$$

$$H_2O_2 + hv \rightarrow 2\ OH^{\cdot} \qquad [48]$$
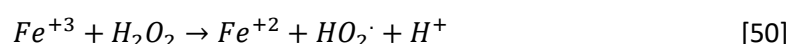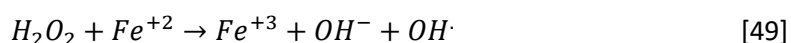
The photo-Fenton reactions are carried out in an acidic medium (pH 2.8) as this is their optimum medium. But to treat wastewater, which is normally at a pH around 7, this is a drawback because of the initial acidification and subsequent neutralization of the effluent which is required, which

entail large operational costs. To overcome these problems, iron complexes can be used to avoid iron precipitation at neutral pH [52]. Iron (II) complexes react with hydrogen peroxide and is oxidized to iron (III) complexes, generating hydroxyl radicals during the process. Chelated iron (III) when combined with solar radiation is reduced to iron (II) complexes. In this study DTPA has been used as chelating agent. This chemical is an organic compound typically used as a fertilizer in agriculture [53].

1.6. Constructed wetlands

A wetland consists of a flat land area that remains in flooded or waterlogged soil conditions for considerable periods of time. Hydrophilic plants act as water filters, storing and releasing water. Constructed wetlands (CWs) recreate natural wetland conditions and processes. CWs are controlled environments that aim to create mechanisms for the removal pollutants and organic matter, NO_3^- and NO_2^- from wastewater through simultaneous chemical, physical and biological processes. CWs are easy to maintain and low cost system that achieve good effluent quality. With the construction of wetlands an ecosystem is crated where flora and fauna can live. CWs are easy to adapt to the environment and are popularly well regarded as being ecofriendly. On the contrary, they have the disadvantage that the biological process that occurs depends on various factors, such as environmental conditions and the proprieties of the pollutant. Other disadvantage is that it takes time and a lot of space to realise. CWs need a minimum amount of water to survive [54].

In CWS are physical-chemical processes such as filtration, sedimentation, adsorption, volatilisation, phytoaccumulation and microbial activity, which are used to remove organic matter, suspended solids, nutrients and some metals such as iron, lead or cadmium from wastewater. There are different configurations of CWs depending on the hydrology of the system; the growth form of the plants and the direction of water movement.

CW are divided in two depending on the direction of the flow: Vertical Flow CW (VFCW) and Horizontal Flow CW (HFCW). In vertical CWs the feed is intermittent and distributed over the surface, these CWs allow a small oxygen supply to the plant roots. Horizontal CWs need more hydraulic retention times than vertical CWs. Horizontal CWs operate under anaerobic conditions, so the effluent has a low concentration of dissolved oxygen, which can lead to odours [55,56].

2. OBJECTIVES

Given the lack of the experimental studies on the potential synergy between constructed wetlands and solar-based oxidation processes, the main objective of this work is to see the potential of CWs for the removal of micropollutants from wastewater.

Concretely,

- To compare the efficiency of CW in the elimination of different MPs using different types of aquatic plants.

- To compare the efficiency of CW in the systems with recirculation and without recirculation.
- Testing the efficiency of the hybrid system composed by constructed wetlands and the solar-based oxidation processes.

3. MATERIALS AND METHODS

3.1. Wastewater effluent

The investigation presented in this work was performed using one secondary wastewater effluent from Gavà- Viladecans wastewater treatment plant. This WWTP has two treatments, one line with membrane bioreactor (MBR) technologic and one line with an integrated fixed-film activated sludge (IFAS) system. The latter is the one from which the samples are taken from. The main physicochemical parameters of the wastewater are shown in Table 1.

Table 1 Main physicochemical parameters of the secondary effluent

Parameter	IFAS
pH	7.6
UV 254nm(cm^{-1})	0.3
Alkalinity (mg $CaCO_3$/L)	414.4
Total suspended solids(mg/L)	38.0
DOC (mg C/L)	25.0
Cl^- (mg/L)	344.2
NO_3^- (mg/L)	<0.4
NO_2^- (mg/L)	<0.4
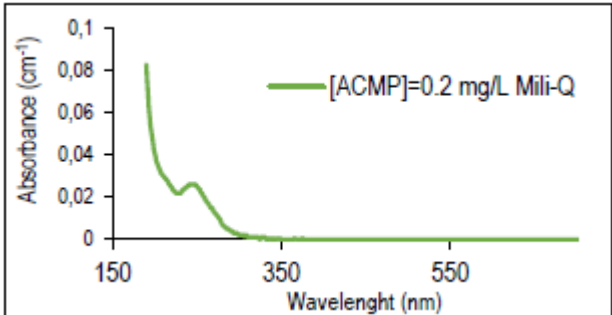
3.2. Chemicals and reagents

3.2.1. Model micropollutants

In the following section the properties of each studied pollutant are described.

Acetamiprid

Table 2 ACMP properties [13]

Propriety	Value
Molecular formula	$C_{10}H_{11}ClN_4$
Type	Pesticide
Molecular weight (g/mole)	222.67
Solubility (mg/mL)	0.425
Log K_{OW}	0.80
Company	Sigma Aldrich
Absorption spectrum (0.2 mg/L in Milli-Q water)	

Sulfamethoxazole

Table 3 SMX properties [31]

Propriety	Value
Molecular formula	$C_{10}H_{11}N_3O_3S$
Type	Antibiotic
Molecular weight (g/mole)	253.28
Solubility (mg/mL)	0.459
Log K_{OW}	0.89
Company	Sigma Aldrich

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

Metronidazole

Table 4 MET properties [40]

Propriety	Value
Molecular formula	$C_9H_9N_3O_3$
Type	Antibiotic
Molecular weight (g/mole)	171.15
Solubility (mg/mL)	0.0257
Log K_{OW}	-0.02
Company	Sigma Aldrich
Absorption spectrum (0.2 mg/L Milli-Q water)	

3.2.2. Other chemicals

The following table illustrates others reagents used during experiments.

Table 5 Information about reagents

Name	Formula	Company	Purity (%)	Used in or for
Acetronitrile	CH_3CN	Fisher Chemical	99.9	HPLC analysis
Acetic acid glacial	CH_3COOH	Panreac Quimica	95.0	Bisulphite preparation for Fe determination
Ammonium acetate	$CH_3COOONH_4$	Panreac Quimica	99.0	Bisulphite preparation for Fe determination
Ammonium metavanadate	H_4NO_3V	Sigma Aldrich	99.0	H_2O_2 determination
Ascorbic acid	$C_6H_8O_6$	Panreac Quimica	91.0	Totally Fe determination
DTPA-Fe	$C_{14}H_{18}N_3O_{10}FeNa_2$	Pyhgenera	7.0	Photo-Fenton
Hydrochloric acid	HCl	Panreac Quimica	37.0	Alkalinity
Hydrogen peroxide	H_2O_2	Merck	30.0 w/w	Photo-Fenton
Liver bovine catalase	$C_9H_{10}O_3$	Sigma Aldrich	-	Stop the reaction
Methanol	CH_3OH	Panreac Quimica	99.9	SPE
Orthophosphoric acid	H_3PO_4	Panreac Quimica	85.0	HPLC analysis
1,10-phenanthroline	$C_{12}H_8N_2$	Panreac Quimica	99.0	Fe^{+2} determination

3.3. Experimental Devices

3.3.1. Constructed wetlands

In this study, four CW were assembled at lab-scale in vertical CW with or without recirculation. Each one was filled with 1.5 L of spiked (1 µg/L of each MP, see annex I) secondary wastewater from the WWTP located in Barcelona (Spain). Each microcosm was made using polypropylene container (H=22.5 cm; D= 9.5 cm) filled with first layer of cobbles (2 cm), a second layer of volcanic rocks (2 cm), a third layer of fine gravel (2 cm) and, finally, a layer of sand (10 cm). Two aquatic plants were studied (*Phragmites australis* and *Cyperus haspan*). The experiments were carried out during 8 cycles of 3 days of retention time each one.

To counteract evaporation, milli-Q water is added to the 1.5 L when the water is removed from the CWs.

Figure 5 Constructed wetlands.

3.3.2. Solar light simulator

The photo-Fenton experiments were performed in a bench-scale solar simulator (SUNTEST CPS+, Heraeus, see Figure 6) with artificial sunlight provided by a 1500-W Xenon lamp (290-400 nm) with infrared and UV-C cut off-filters. The irradiance was set at 500 W/m^2.

A cylindrical Pyrex glass photoreactor (D=9.0 cm and H=4.5 cm) was used under constant stirring of 350rpm. The photoreactor was placed over a refrigerant plate, which was connected to a thermostatic bath at 15°C, to maintain the temperature of the solution constant during the experiments (20-25°C).
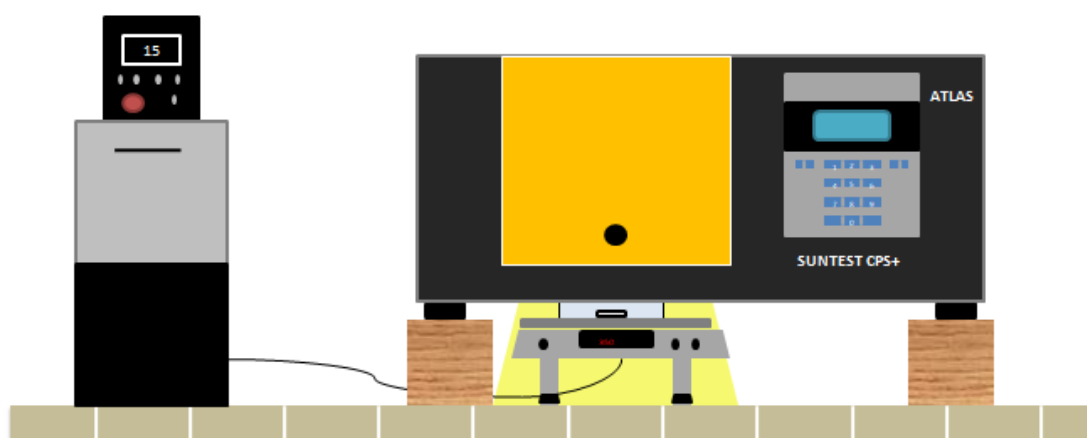

Figure 6 Solar simulator scheme.

3.4. Analyses

3.4.1. pH and conductivity measurement

The pH was measured in a sensION^{TM}+ MM 374multi-meter calibrated each day with pH 4.00, 7.00 and 10.00 buffers. Conductivity measured by using the same instrument and a conductivity probe, periodically calibrated with a 1413 μS/cm standard.

3.4.2. Alkalinity

The alkalinity of wastewater samples was measured through potentiometric titration using a sensION^{TM}+ MM 374 pH meter. Hydrochloric acid (0.1 M) was used and pH 4.3 as endpoint was fixed in the titration. This technique consists of adding 0.1 mL of hydrochloric acid and watching the pH change until the set end point is reached.

3.4.3. Solid phase extraction (SPE)

The solid phase extraction (SPE) consisted of three parts.

The first part, the conditioning, where The OASIS HLB 6cc (200 mg) extraction cartridges were used to pass 10 mL of methanol and 10 mL of milli-Q water. In each bottle 100 mL of sample was prepared with 12.5 μL of standard.

The second part, the extraction, where the cartridges were connected to the bottles as shown in Figure 7. The valves were opened, and the vacuum pump (V10 IBX series) was turned on (3 to 4 drops fell inside the cartridge). When the bottle was empty, 5 mL of milli-Q water was passed through.
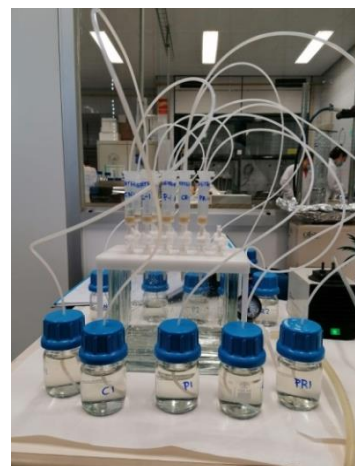
Figure 7 Assembly of SPE

Finally, the elution, where 9 mL of methanol was run through the cartridges until dry. The liquid was collected in test tubes that were introduced into the evaporator (Turbo vap LV) and then 0.5 mL of a mixture containing 95 % water and 5 % methanol was added. They were agitated 30 seconds with the vortex, then 30 seconds in the ultrasound and to finish 30 seconds more in the vortex and with the resulting liquid with a pasture pipette it was passed to a HPLC vial.

3.4.4. Ions determination

These analyses were subcontracted to the Separation Unit of the Scientific and Technological Services of the University of Barcelona. In brief, the concentration of relevant anions (i.e., nitrite, nitrate, chloride and bromide) in wastewater samples was determined by ionic chromatography through a high-performance liquid chromatograph coupled to conductivity and UV detectors connected in series. A 4.6x150 mm IC-PAK ANION column by Waters (USA) was used for separation. The mobile-phase (mainly mixtures of borate buffer and acetonitrile) flow-rate was set at 2 mL/min, the injection volume was 200 μL and the detection wavelength (in the case of UV detector) was 214 nm.

3.4.5. Dissolved organic carbon (DOC)

The quantification of dissolved organic carbon content was performed following the Standard Methods 5310B procedure [57] and employing a 5055 TOC-VCSN analyzer equipped with an ASI-V autosampler, both by Shimadzu (Japan).

3.4.6. Solids determination

For solids determination, a filter (filter MF-Millipore 0.45 µm MCE membrane) was weighed with the balance (COBOS PRECISION) and placed in the device shown in Figure 8, consisting of a vacuum pump, a porous membrane funnel and a sample beaker. A known volume of the sample to be determined was passed through and the filter was placed for 2 hours in the oven and then 1 hour in the desiccator, and finally weighed.

Figure 8 Assembly of solid determination

3.4.7. Ultraviolet absorbance

The ultraviolet absorbance was evaluated through a spectrophotometer DR6000 UV-Vis by Hach (USA). Absorbance shall be taken at a wavelength range of 190 nm and 700 nm.

3.4.8. Dissolved iron determination

Ferrous iron was determined by complexation with 1,10-phenanthroline according to ISO 6332 [58]. 1 mL of phentanthroline (1 g/L) and 1 mL of acetic/acetate buffer solution was mixed with 4 mL of the sample which was filtered with a 0.20 µm PVDF filter to ensure good reading of soluble iron (chelated and non-chelated). Some ascorbic acid was added to evaluate the total iron concentration. It was left for a few hours to precipitate all the iron. The sample presented a reddish colour and with a spectrophotometer (Hach Lange DR 6000) at 510 nm the absorbance was measured. Total iron was measured because when performing the experiments with chelated iron at circumneutral pH, it is not possible to differentiate between ferric and ferrous forms.

3.4.9. Hydrogen peroxide concentration

The concentration of hydrogen peroxide was determined by the metavenadate colorimetric method [59]. 1.5 mL of ammonium metavenadate (5.14 g/L) in acid medium was mixed with 1.5 mL of the sample. The solution presents an orange colour which was measured by spectrophotometer (Hach Lange DR 6000) at 450 nm. The concentration was determined from the calibration curve between absorbance and H_2O_2 concentration.

3.4.10. Model micropollutants

Ultra Performance Liquid Chromatography (UPLC)

The concentration of MPs used in the experiments used in constructed wetlands was followed using Ultra Performance Liquid Chromatography (UPLC-H class) triple quadrupole mass spectrometry Xevo TQ-S MS Detector. The analytical method is displayed in Annex II.

High Performance Liquid Chromatography (HPLC)

The evolution of micropollutants concentration used in the photo-Fenton experiments was measured by High Performance Liquid Chromatography (HPLC) analysis (Infinity 1260 HPLC equipped with a Diode Array Detector, all provided by Agilent Technologies (USA)). Depending on the micropollutant to be analysed, conditions may vary. The conditions of each micropollutant are shown in Table 6.

Table 6 Method characterization

	Detection (nm)	Column	Pressure (bar)	Mobile phase	Flow-rate (mL/min)
ACMP	250	Mediterranea SEA 18 (250x4.6 mm and 5 µm particle size) Teknokroma	110	80 % H_2O (with H_3PO_4 pH=3) 20 % acetonitrile	1
SMX	270				
MET	220				

3.5. Experimental procedure

With the sample extracted from the CWs, after 3 days, the photo-Fenton process was performed. A solution containing 50 mg/L H_2O_2, 10ppm of Fe chelated with DTPA, 0.2 mg/L of each MP (ACMP, SMX and MET) was prepared. This solution was added into the cylindrical reactor (150 mL) and the solar simulator was started. Samples were taken at different times during the experiment (0, 0.5, 2.5, 5, 5, 10, 15, 15, 20, 30, 45, 60, 90 and 120 minutes). Each sample was filtered by 0.45 µm filters (FILTER-LAB PVDF) and the reaction was stopped with a catalase solution (concentration of 200 mg/L, 10 µL in 5 mL of sample). Finally, the samples were kept for further analysis.

4. RESULTS AND DISCUSSION

Eight cycles of three days each have been carried out. In each cycle, samples were taken from the IN, from the *Cypersus haspan* with recirculation (CR) and without recirculation (C) and from the *Phragmites australis* with recirculation (PR) and without recirculation (P).

On the one hand, the aim of this investigation is to study whether the constructed wetlands are able to remove 20 typical pollutants, found in secondary effluents of wastewater, which present different physicochemical properties. On the other hand, it is intended to see if the water quality at the CWs outlet is sufficient to be treated with the photo-Fenton process.

4.1.   Constructed wetland system

4.1.1. Micropollutants evolution

The removal of 20 MPs (1 µg/L of each one was spiked in the wastewater effluent) in constructed wetlands with (PR or CR) or without recirculation (P or C) and using *P. australis* and *C. haspan* is displayed in Figure 9. The values correspond to cycle 1 and cycle 8 to investigate the influence on the exposure time.
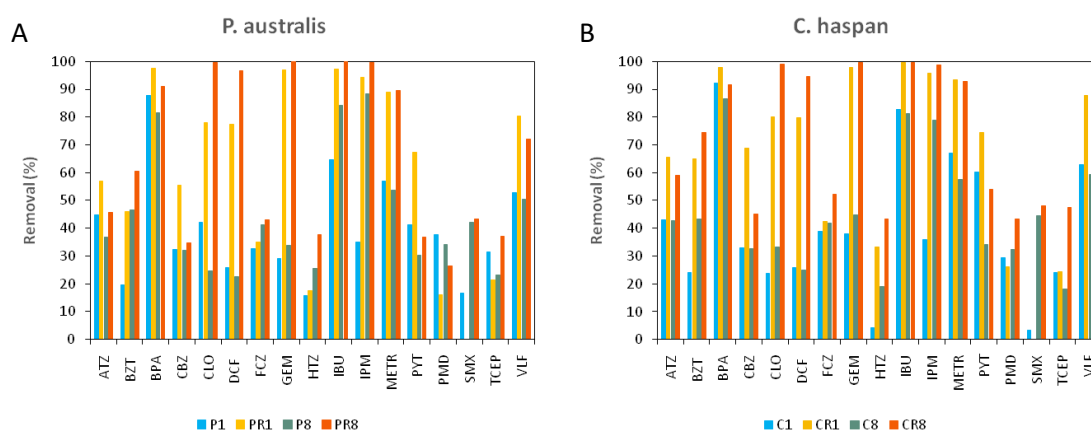

Figure 9 Removal of MPs at cycle 1 and cycle 8 in a) *P. australis* **(with recirculation and non-recirculation) b)** *C. haspan* **(with recirculation and non-recirculation).**

As can be observed in Figure 9, in the case of *P. australis* the trend is quite similar between cycle 1 and cycle 8. If we look at the system without recirculation (P1 and P8) in most cases the elimination of compounds in cycle 8 is higher than in cycle 1, this may be due to the fact that over time the plants form a biofilm that increases filtration, biodegradation and adsorption. The average degradation value for P1 is 39.18 % and that of P8 is 44.21 %. The difference between the two cycles is not very high but it can be seen that in cycle 8 the average elimination of the pollutants is quite higher. Equal than systems without recirculation, in the systems with recirculation the elimination of cycle 8 is also higher than cycle1. The average value of pollutant degradation is 60.27 % for PR1 and 65.45 % for PR8. So, it can be seen that ratio between P1-P8 and PR1-PR8 is maintained, therefore the passage of time affects the system with recirculation the same as the system without recirculation. With all the results, it is observed that the best system is the one with recirculation, since it obtains higher elimination values.

In the case of *C. haspan*, the trend between cycles is also quite similar than the behaviour of CW with *P. australis*. Observing the values obtained in the system without recirculation (C1 and C8) it is appreciated that cycle 8 has a higher degradation than cycle 1, the average degradation values being 45.62 % and 40.48 %, respectively. Looking at the systems with recirculation (CR1 and CR8) we can see that cycle 8 has a higher degradation than the first cycle. With an average removal value of 66.44 % for CR1 and 71.85 % for CR8 it can be observed that the best removal of compounds is performed by the system with recirculation and after the 8 cycles.

Regarding the comparison between plants, *C. haspan* has a higher degradation than *P. australis*, so if we have to choose a system as the best for the elimination of pollutants, it would be the *C. haspan* system with recirculation, this may be due to the fact that *C. haspan* has longer roots and therefore adsorbs more through them. Figure 10 displays the removal rates of different MPs in the CW with *C. haspan* and with or without recirculation for cycle 1 and 8. From the data presented in Figure 8 it has been seen that the CW with *C. haspan* presents higher removal rates than *P. australis*. For that reason, in Figure 10 is only shows the values of one of them. Additionally, the value of log K_{OW} was added to the Figure in order to investigate the potential influence of log K_{OW} in the removal of MPs.
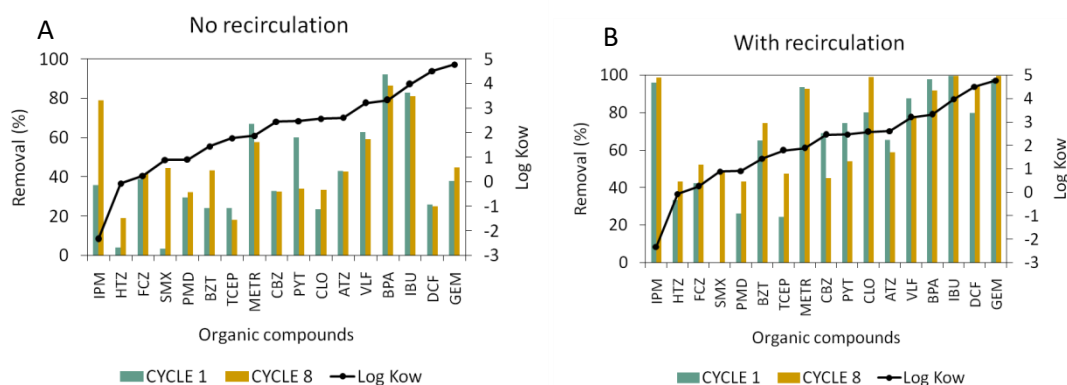

Figure 10 Removal of MPs with log K_{OW} a) Without recirculation; b) With recirculation.

As can be observed in Figure 10, the system without recirculation does not have a removal trend similar to log K_{OW}, instead the system with recirculation which presents a trend between the removal of the compounds and the log K_{OW} of each pollutant. Observing Figure 10 we can see that for a low Log K_{OW} as in the case of Hydrochlorothiazide, the percentage of elimination in cycle 1 without recirculation is 4.21 %, while the system with recirculation obtains 33.42 % of elimination. The same happens in the case of cycle 8 with an elimination rate of 19.06 % without recirculation and 43.40 % with recirculation. On the other hand, for a high log K_{OW}, as in the case of Gemfibrozil, the elimination rate in cycle 1 without recirculation is 38.05 %, while the system with recirculation obtains 44.78 % elimination. The same happens in the case of cycle 8 with an elimination rate of 97.74 % without recirculation and 99.55 % with recirculation.

Therefore, we can assume that the more times the sample passes through the CWs, the more it resembles its log K_{OW}. This may be due to the fact that as it has been previously mentioned, when passing more times through the system the roots can adsorb more of the components and therefore the K_{OW} log looks more similar. A low log K_{OW} means that the compound is polar and it is more difficult for it to adsorb, therefore the elimination of these compounds is lower. The

tendency is not exact because there are other factors, such as biodegradation or adsorption, which make it different for each compound and that is why there are these differences between compounds.

Then, CW is a potential treatment for the removal of PM of different types, although consideration should be given to the presence of compounds that are highly polar as their removal will be lower.

4.1.2. Organic matter evolution

The absorbance at 254 nm

The absorbance at 254 nm is the wavelength on aromatic compounds present maximum absorbance. And it is another indicator of the contamination in water effluents. So, a reduction of UV254 nm corresponds to an effluent less contaminated with organic matter. The results are shown in Figure 11.
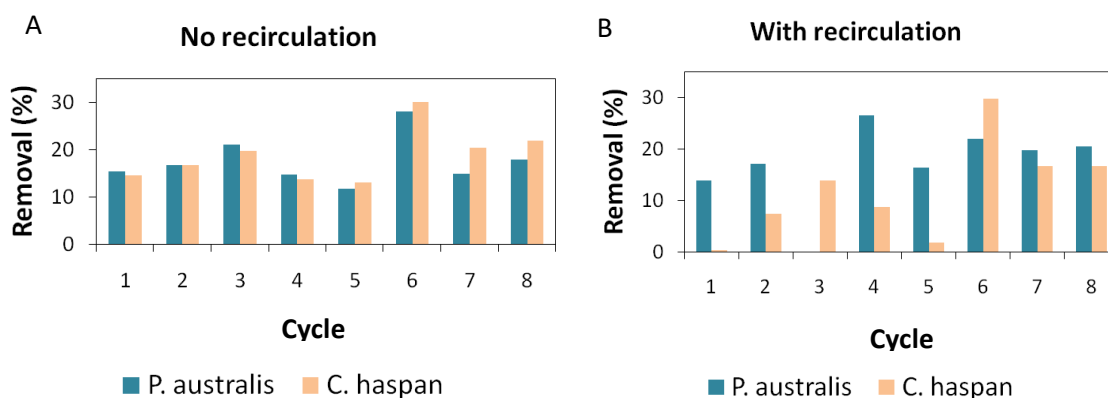

Figure 11 Reduction of absorbance at 254nm during 8 cycles in a) No recirculation; b) with recirculation

With the results obtained we can see that in non-recirculation mode the trend between the two types of plant is the same. In the Figure 11A it can be seen that in cycles 4 and 5 the percentage of removal decreases and increases in cycle 6, this is due to the fact that between cycles 5 and 6 there is a change of bottle where the sample water is stored. This change means that in cycles 4 and 5 the concentration of solids is higher than in the others and therefore the process does not remove the same percentage as in the other cycles. In the case of cycle 6, the removal of solids is higher with a higher amount of solids, so that even if there is a high concentration, the removal is equal or higher. Therefore, it is possible to have a sample with enough organic matter that the effluent will be similar, i.e. the system can remove organic matter without saturating.

The average trend of solids removal in both *C. haspan* and *P. australis* without recirculation is around 18 %. However, observing the Figure 11B we can see that, in this case, there are significant differences between the plants; *P. australis* achieves a higher removal percentage than the *C. haspan*. This means that the difference in absorbance at 254 nm elimination between them is 12 % in the case of *C. haspan* and 20 % in the case of *P. australis*. This may be due to the fact that *C. haspan* is a larger plant and if the sample is recirculated it may carry organic matter

and microorganisms from the plant and this affects the reduction in absorbance removal efficiency at 254 nm.

Therefore, the process that will work better will be the *P. autralis* with recirculation as it has a higher percentage of elimination.

Dissolved organic carbon (DOC)

The dissolved organic carbon (DOC) indicates the concentration of organic carbon in the sample. If the concentration is lower it means that there is less organic matter and therefore that the CWs remove a large part of the organic matter contained in the influent. A lower concentration of organic matter means that the effluent is cleaner and will therefore be an effluent that can be used for water reuse. The results are shown in Figure 12.
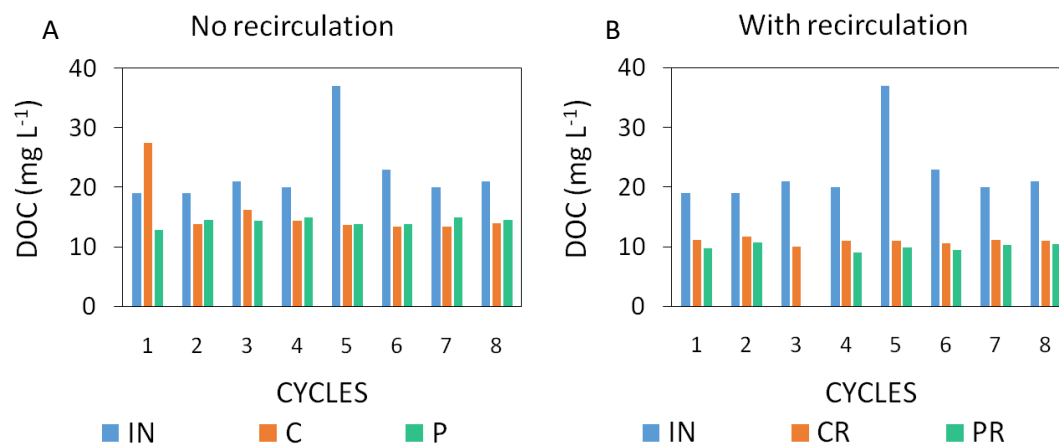

Figure 12 Concentration of DOC during 8 cycles a) without recirculation, b) with recirculation

As far as the DOC is concerned, in the systems without recirculation it is higher than in the systems with recirculation, this fact is due to when passing through the CWs the organic matter is more retained and could be more absorbed by the plants and the final sample has a lower concentration of DOC.

In the systems without recirculation and with recirculation, it could be seen that the IN are high, this is due to the fact that the organic matter contained in the sample has not passed through any CWs.

However, in the Figure 12A the CWs outputs of both *C. haspan* and *P. australis* are quite similar to each other. There is one case where the OUT of cycle 1 of *C. haspan* is higher than that of *P. australis* and IN, this may be caused by carryover of organic matter from the CWS. The IN of cycle 5 has the highest concentration reaching almost 40 mg/L, this is due to the fact that it was the bottom of the bottle where the samples were extracted and there is more organic matter and solids than in the others.

In the recirculation systems (Figure 12B), as mentioned before, the output concentration of CWs is lower and the trend is the same for all types of plants. The concentration is always slightly higher in *C. haspan*, but not significantly higher.

The systems with the best DOC are the systems with recirculation; therefore, CWs are able to remove organic matter.

IONs

Wastewater contains total nitrogen that must be removed both for water reuse and to return the water to water resources. The presence of nitrogen in nature can create eutrophication. Eutrophication is the over-enrichment of aquatic systems with nutrients leading to algal blooms and anoxic events. In the Figure13 nitrite has been evaluated [60].
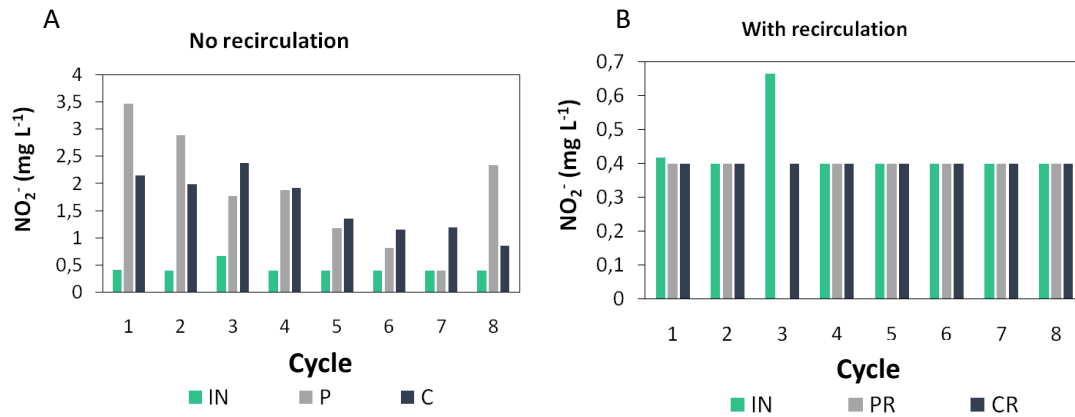
A
No recirculation

B
With recirculation

Figure 13 Concentration of Nitrate during 8 cycles in a) No recirculation; b) with recirculation.

Observing the Figure 13 it can be seen that the values of the concentrations between the experiments with recirculation and without recirculation are of different magnitude. In the case of CW without recirculation (Figure 13A) the concentration in IN is very low compared to the concentrations obtained in the experiments with the different types of plants, this is due to the fact that the concentration of nitrite (NO_2^-) in stagnant water will increase because there is no oxygen present in the experiment and the nitrification process will not occur. This increase may also be due to the influent containing ammonium, which has not been measured, and the ammonium reacting to nitrite. On the other hand, the denitrification process will occur because of the presence of organic matter and nitrate and the absence of oxygen.

In the case of experiments with recirculation (Figure 13B), the concentrations obtained are quite similar between the different cycles and between plants. The fact that the nitrite (NO_2^-) values are so low in these cases is due to the fact that in the recirculation processes the nitrification process is carried out by the presence of oxygen which will consume the nitrite (NO_2^-) to nitrate (NO_3^-), and for this reason the NO_2^- concentration will decrease. In Figure 13B the data of 0.4 does not mean that this is the value, but that it has not been detected and that is why we put 0.4, because it is the detection limit.

The total suspended solids

The total suspended solids give an idea of how much organic matter the CWs are capable of removing. A high organic matter removal will be good because the sample will have less organic matter and will be better for the subsequent performance of the photo-Fenton process.
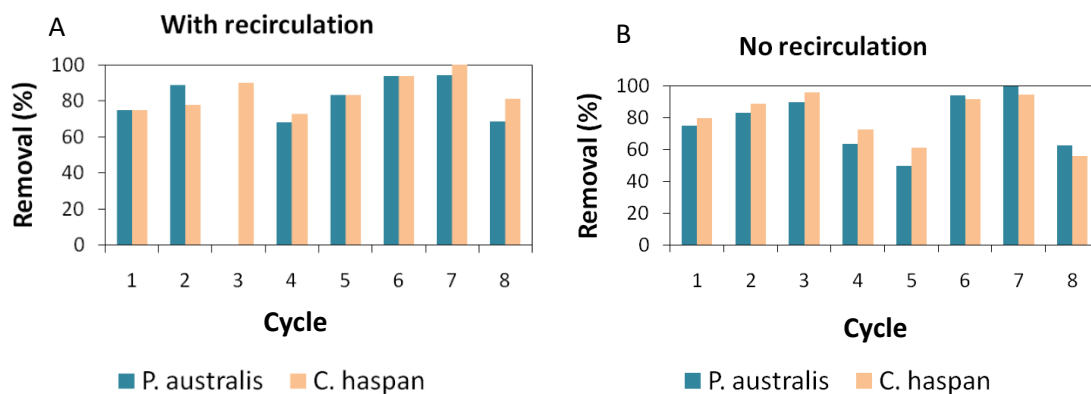

Figure 14 Reduction of total suspended solids 8 cycles in No recirculation and with recirculation

As can be observe in Figure 14 the trend between the two types of plants is the same. In the case of no recirculation, it can be see I that there is decay between cycles 4 and 5 but that it rises again in cycle 6. As mentioned in section 4.2.1. total organic matter, this is due to the change of bottle and therefore the concentration of solids in the inlet of cycles 4 and 5 is higher than in the other cases, so the system cannot assume this increase of solids in the same way. In the case of the recirculation experiments, the same thing happens, but the decrease is smaller.

Although there is not a big difference between the plant types, it can be observed that the percentage of elimination in the case of the *C. haspan* is slightly higher without recirculation than with recirculation, the percentages of elimination being 80 % and 84 %, respectively. In the case of *P. australis* the average removal rates are 77 % without recirculation and 82 % with recirculation.

Therefore, looking at the two Figures it can be observed that for total suspended solids removal the experiments with recirculation are better and *C. haspan* achieved the highest removals.

Then, with these results, the type of plant will not be a significant parameter for solids removal, at least comparing *C. haspan* and *P. australis.*

4.2. Photo-Fenton process

4.2.1. Micropollutants remove

Photo-Fenton experiments were carried out with three MPs at a higher concentration in order to better monitor the process. The MPs chosen are MET, SMX and ACMP. These three compounds have been chosen because they have different photolysis, are easy to analyse, have different kinetics with the hydroxyl radical and are easily observable in chromatograms. This process was done for each type of plant (*P. australis* and *C. haspan*) and each system (with recirculation and without recirculation) and cycle 1 was compared with cycle 8. In the following figures 15 and 16 the experimental points have been joined with lines to visualise the results more easily.

Figure 15 MPs degradation by Photo-Fenton at neutral pH over time for each system and plant type in the cycle 1 using DTPA-Fe at a) Metronidazole; b) Sulfamethoxazole c) Acetamiprid; [Fe] =10 mg/L [H_2O_2]=50 mg/L [MET]$_0$=[SMX]$_0$ =[ACMP]$_0$=0.2 mg/L. Irradiance =500 W/m^2.

The Figure 15A shows the removal curves MET. The degradation at IN, *P. australis* and *C. haspan* without recirculation shows a similar trend, reaching a 90 % of degradation at the end of the treatment (120 min). However, systems with recirculation reach total degradation in less time (at 30 min).

The Figure 15B shows the removal in percent per one of SMX. The experiment performed with IN (without pre-treatment in CW) present the worst removal, since total SMX degradation is achieved at 90 min. While, in that case, C and P, the two systems without recirculation, need 30 and 45 min, respectively to reach the completely elimination. The best performances on SMX removal are achieved by CR and PR, corresponding to experiments with recirculation. In both cases, the total SMX removal is observed in only 10 min. That fact represents that the treatment time is reduced by 9 times compared to experiments without pre-treatment. Therefore, again, it is observed that the best system would also be with recirculation without making a distinction by the type of plants.

The Figure 15C shows the removal in percent per one of ACMP. The experiment carried out with IN (without CW pretreatment) presents the worst removal, since the total degradation of ACMT is not achieved, at least in the 120 minutes that the experiment lasts. The same is true for C and P, the two systems without recirculation, which do not reach complete removal, remaining at a removal of approximately 0.7. The best ACMP removal performances are achieved with CR and PR, corresponding to experiments with recirculation. Total ACMP removal is observed in 20 minutes for CR and 45 minutes for PR. Therefore, again, it is observed that the best system would also be with recirculation, being the best results with *C. haspan*.

Comparing the three compounds, the one with the highest degradation is SMX followed by MET and finally, with a very low degradation is ACMP. These very different degradations are due to the different kinetics presented with the hydroxyl radical, the higher the kinetic constant, the higher the MP degradation. The MPs hydroxyl radical rate constant values are SMX of $5.5 \cdot 10^9$ L/mol·s, $1.98 \cdot 10^9$ L/mol·s for MET and $2.1 \cdot 10^9$ L/mol·s for ACMP. According to these data the MPs with the highest degradation would be SMX followed by ACMP and finally MET, but the results obtained show that MET degrades more than ACMP, this may be due to the differences between the photolysis of these compounds. As can be seen, the difference in MET between the different experiments is smaller than in the case of ACMP, which may be due to the different photolysis of the two compounds. The degradation by photolysis is 77.30 %, 15.00 % and 2.00 % for MET, SMX and ACMP respectively.

The improvements between recirculation and non-recirculation systems are given by a lower DOC concentration, less presence of total suspended solids and a higher percentage of elution in the absorbance at 254 nm in the recirculation systems. A lower DOC concentration means that there is less organic matter. If the presence of total suspended solids is lower the concentration of organic matter is also lower as in the case of absorbance at 254 nm, if the percentage removal is higher, it means that less organic matter is present. Organic matter is one of the competitors of MPs for hydroxyl radicals. Therefore, in systems with recirculation, having less organic matter, the competition for hydroxyl radicals is less and therefore more MPs are degraded.
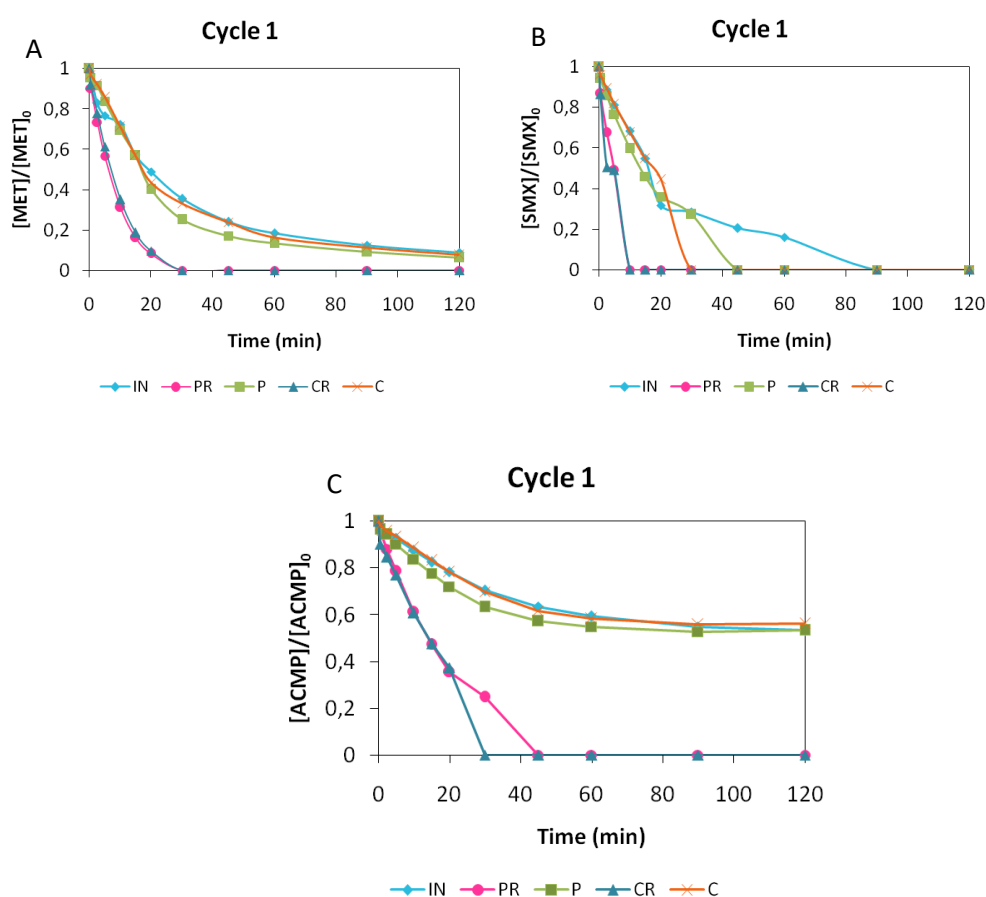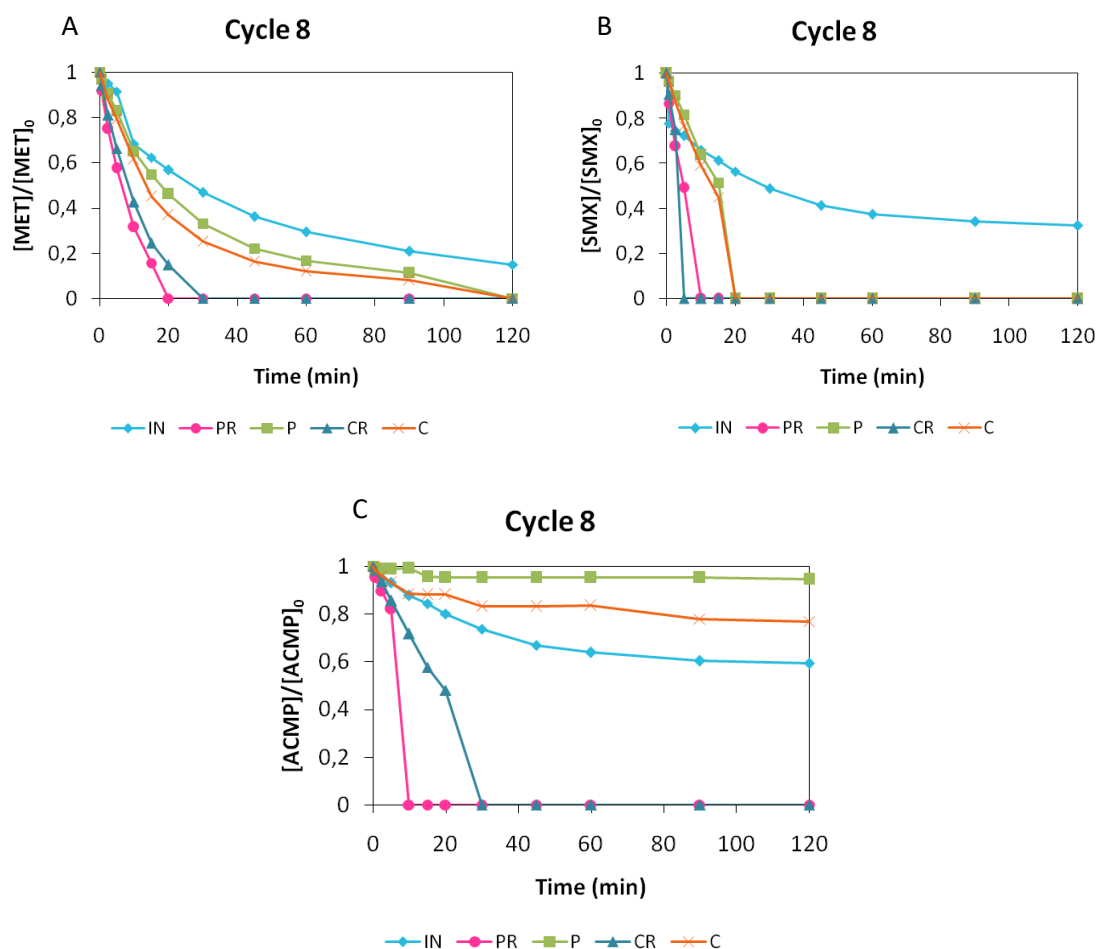
Figure 16 MPs degradation by Photo-Fenton at neutral pH over time for each system and plant type in the cycle 8 using DTPA-Fe at a) Metronidazole; b) Sulfamethoxazole c) Acetamiprid; [Fe] =10 mg/L [H_2O_2]=50 mg/L [MET]$_0$=[SMX]$_0$ =[$ACMP$]$_0$=0.2 mg/L. Irradiance =500 W/m^2.

The main differences in Figures 15 and 16 are that the IN sample never degrades with any of the compounds, this may be because both DOC and absorbance at 254 nm are higher in cycle 8 than in cycle 1, and therefore the amount of organic matter is higher and therefore there is more competition for hydroxyl radicals. Even so, the trend between the systems is the same, except in the case of the systems without recirculation for the MPs ACMP. Over time the trend remains the same, which means that the performance does not change significantly over time.
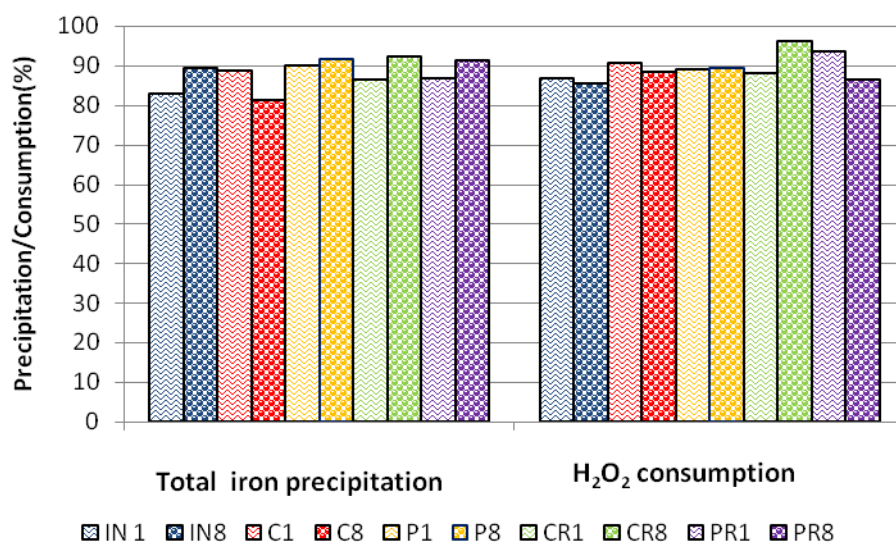
Figure 17 Removal of total iron precipitation and H₂O₂ consumption.

In the Figure 17 shows the amount of precipitated iron and the consumption of hydrogen peroxide. The amount of precipitated iron in all samples, both in cycle 1 and cycle 8, has a value between 80 and 95 %. This percentage is very high, which may be due to the fact that iron at pH 7 is not soluble in water and forms iron hydroxides that precipitate. Even if it is complexed, the hydroxyl radials and light can break the complex and cause the iron to be free and form these iron hydroxides. Iron hydroxide is less photoactive than dissolved iron and therefore the reaction no longer has a catalyst that is responsible for the production of hydroxyl radicals. This event affects especially the more recalcitrant compounds such as ACMP, which needs longer treatment time, as shown in figures 15 and 16, which have plate zone curves. This can also occur with effluents that are dirty.

As for the H₂O₂ consumption, it is very high in all samples, being in the range of 85 to 95%. This high consumption is due to the fact that iron acts as a catalyst and therefore consumes hydrogen peroxide to form hydroxyl radicals. Hydrogen peroxide also reacts with light, giving rise to more hydroxyl radicals. Although in this way the amount of hydroxyl radicals is less, as we are at the limit wavelengths where it can react. Finally, hydrogen peroxide can be consumed by reacting with the organic matter present in the samples.

5. **CONCLUSIONS**

From the results obtained in this investigation, it can be observed that constructed wetlands present good performances on the removal of different MPs. The best removals were obtained with the *C. haspan* plant and with recirculation. However, the differences observed whit two plants were not significative. As for the two modes of operation, it is better with recirculation than without recirculation. With the results obtained we can also see that the more the sample passes through the CWs the more it resembles log K_{ow}. *C. haspan* has longer roots and therefore may have better removal; in recirculation systems a biofilm can be created which would increase biodegradability and also adsorption.

It has been seen that CWs have good removals of total suspended solids and absorbance at 254 nm in recirculation systems. As far as DOC concentration is concerned, the best results were also obtained in recirculation systems. The differences between the types of plants in the mentioned experiments are not very significant.

In the case of NO_2^- concentration, the lowest concentration is achieved with the recirculation experiments, since with the presence of oxygen the nitrification process is carried out.

With the performance of the photo-Fenton process, the results obtained display clear evidence of the improvement in MPs removal in the experiments performed with pretreated effluents in CW with recirculation than the other experiments. For instance, in SMX, the treatment time in experiments using PR or CR was reduced by 9 times compared to experiments without pre-treatment (IN). No significant differences were seen between plants; the best systems for all MPs are the recirculation systems. The differences between the MPs degradations are due to the different photolysis and kinetics with the hydroxyl radial presented by the different MPs.

Good results have been seen in the removal of DOC, TSS, UV 254, MPS in CWs and with the hybrid technology an improvement has been seen in the removal of MPs in the photo-Fenton process, thus allowing to reduce the time of this process. In addition, the removal of very recalcitrant compounds such as ACMP, which has low kinetics with hydroxyl radicals, has been achieved.

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7. NOMENCLATURE

NSAID: Non-steroidal anti-inflammatory drugs.

WWTP: Wastewater treatment plants.

AOP: Advanced oxidation processes.

CWs: constructed wetlands.

MP: micropollutants.

ACMP: Acetamiprid.

SMX: Sulfamethoxazole.

MET: Metronidazole.

IN: input sample without pretreatment

C: *Cyperus haspan*

P: *Phragmites australis*

CR: *Cyperus haspan* with recirculation

PR: *Phragmites australis* with recirculation

Log K_{ow}: coefficient octanol-water

8. ANNEXES

ANNEX I

The following table shows the micropollutants used in the experiments.

Types of micropollutants

Micropollutant	Abbreviation	Category	Log K_{OW}
Atrazine	ATZ	Herbicide	2,61 [61]
Benzotriazole	BZT	Corrosion inhibition	1,44[61]
Bisphenol A	BPA	Plasticizer	3,32 [61]
Caffeine		Physchoactive Drug	-0,07[61]
Carbamazepine	CBZ	Anticonvulsant	2,45[61]
Clofibric acid	CLO	Herbicide	-
Diclofenac	DCF	NSAID	4,51[62]
Fluconazole	FCZ	Antifungal	0,25[63]
Gemfibrozil	GEM	Lipid regulator	4,77[64]
Hydrochlorotiazide	HTZ	Diuretic	-0,07[61]
Ibuprufen	IBU	NSAID	3,97[65]
Iopromide	IPM	Contrast media	-
Metoprolol	METR	Beta blocker	1,88[61]
Narpoxen		NSAID	3,18[61]
Phenytoin	PYT	Anticonvulsant	2,47[61]
Primidone	PMD	Anticonvulsant	0,91[61]
Sulfamethoxazole	SMX	Antibiotic	0,89[61]
TCEP	TCEP	Flame retardant	-
Trimethoprim		Antibiotic	0,91[61]
Venlafaxine	VLF	Antidepressant	3,20[66]

ANNEX II

Compound	ESI (+/-)	Internal standard	Precursor ion > MS/MS fragment ions	Cone (V)	Cell (eV)	Rt
Atrazine	+	Carbamazepine-d10	216 > 174 216 > 96	10	10 20	15.46
Bisphenol A	-	Bisphenol A-d8	227 > 133 227 > 211	5	30	15.46
Benzotriazole	+	Benzotriazole-d4	120 > 65 120 > 92	25	20 15	7.98
Caffeine	+	Caffeine-13C, d3	195 > 138 195 > 110	10	15 30	6.95
Carbamazepine	+	Carbamazepine-d10	237 > 194	20	10	14.63
Clofibric acid	-	Hydrochlorothiazide-13C, d2	213 > 127 213 > 85	10	15 10	10.16
Diclofenac	-	Diclofenac-13C, d6	295 > 251 295 > 215	5	15	14.90
Diclofenac	+	Diclofenac-13C, d6	298>214 298 >252	10	30 10	16.80
Fluconazole	+	Fluconazole-13C, d3	307 > 220 307 > 169	10	20 25	10.08
Gemfibrozil	-	Gemfibrozil-d6	249 > 121	5	15	17.27
Hydrochlorothiazide	-	Hydrochlorothiazide-13C, d2	296.9 > 270 296.9 > 206	5	20 25	7.13
Ibuprofen	-	Ibuprofen-d3	205> 161	5	10	15.98
Iopromide	-	Hydrochlorothiazide-13C, d2	789.6 > 127 789.6 > 750	10	20 25	1.66
Iopromide	+					
Metoprolol	+	Metoprolol-d7	268 > 74 268 > 133	20	25	10.55
Naproxen	-	Diclofenac-13C, d6	229 > 170 229 > 185	5	15	13.86
Phenytoin	-	Diclofenac-13C, d6	251 > 102 251 > 208	5	20	14.58
Primidone	+	Metoprolol-d7	219 > 162.15 219 > 91	10	15 20	9.72
Sulfamethoxazole	+	Sulfamethoxazole-13C, d6	254 > 92 254 > 156.15	10	20	11.70
TCEP	+	Carbamazepine-d10	285 > 99 285 > 63	10	20 35	15.06
Trimethoprim	+	Trimethoprim-d9	291 > 123 291 > 110	15	40	8.16

| Venlafaxine | + | Venlafaxine-d6 | 278 > 58
278 > 121.2 | 40 | 25
20 | 12.99 |

Deuterados	ESI (+/-)	Precursor ion > MS/MS fragment ions	Cone (V)	Cell (eV)	Rt
Benzotriazole-d4	+	124 > 68.85	35	25	7.54
Bisphenol A-d8	-	235.1 > 137	25	30	15.41
Caffeine-13C, d3	+	198 > 140	15	25	5.77
Carbamazepine-d10	+	247 > 204.1	5	20	14.56
Diclofenac-13C, d6	+	303> 221	10	25	14.92
Diclofenac-13C, d6	-	301 > 257	10	15	14.92
Fluconazole-13C, d3	+	310 > 223	10	20	10.09
Gemfibrozil-d6	-	255.11 > 121	15	20	17.26
Hydrochlorothiazide-13C, d2	-	299.91 > 271	20	20	6.80
Ibuprofen-d3	-	208 > 164	15	10	15.99
Metoprolol-d7	+	275 > 79	30	25	10.55
Sulfamethoxazole-13C, d6	+	260 > 98	10	20	11.62
Trimethoprim-d9	+	300 > 123	10	35	8.05
Venlafaxine-d6	+	284 > 64	15	25	12.91