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LETTER OF INVITATION

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Do not hesitate to contact us if you have any question.

Dimitris Kondarides

dimi@chemeng.upatras.gr

Theofilos Ioannides

theo@iceht.forth.gr

Dionissios Mantzavinos

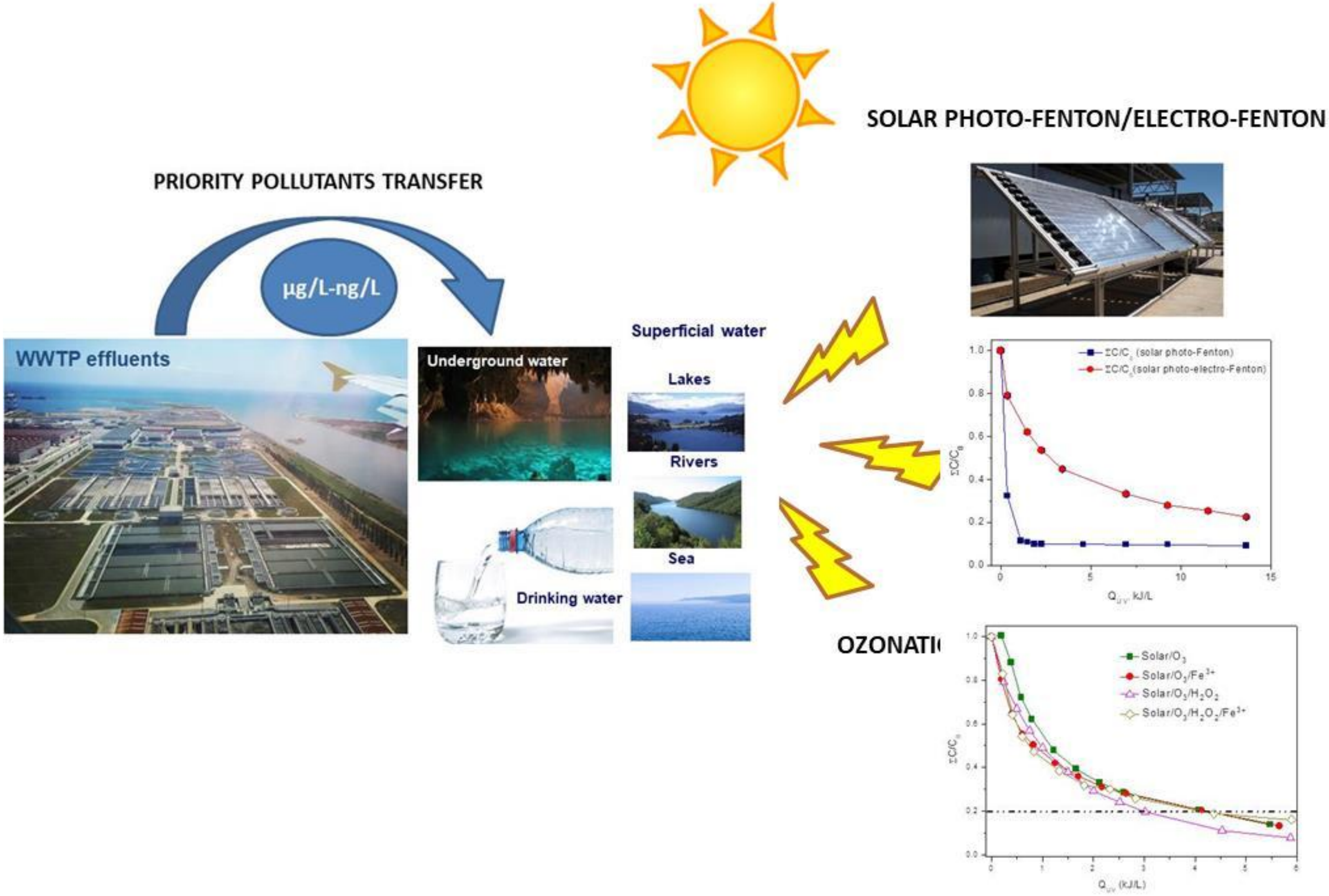
mantzavinos@chemeng.upatras.gr

Guest Editors: Catalysis Today-Special issue ***CATALYSIS FOR ENERGY & ENVIRONMENTAL APPLICATIONS***

Highlights

- New application of solar photo-electro-Fenton at neutral pH at pilot plant scale.
- Higher microcontaminants degradation rate in solar photo-Fenton compared to solar photo-electro-Fenton.
- No significant improvement detected when ozone was combined with Fenton´s reagent.
- Significant low consumption of ozone was observed when combined with solar energy.

***Graphical Abstract (for review)**



New approaches to solar Advanced Oxidation Processes for elimination of priority substances based on electrooxidation and ozonation at pilot plant scale

Melina Roccamante[a,b], Irene Salmerón [a,b], Ana Ruiz[a,b], Isabel Oller [a,b *],
~~Manuel I. Maldonado[a,b] ,~~ Sixto Malato [a,b]

[a] *Plataforma Solar de Almería-CIEMAT, Ctra Senés km 4, 04200 Tabernas (Almería), Spain*
[b] *CIESOL, Joint Centre of the University of Almería-CIEMAT, 04120 Almería, Spain*

Abstract

The main objective of this work is the comparison of various Advanced Oxidation Processes based on solar photo-Fenton at circumneutral pH (by adding EDDS as iron complexing agent), such as solar photo-electro-Fenton process and solar ozonation in combination with Fenton like processes ($O_3/Fe^{2+}/H_2O_2$, $O_3/Fe^{3+}/H_2O_2$ and Solar/$Fe^{3+}/O_3/H_2O_2$), for the elimination of four microcontaminants (Terbutryn, chlorfenvinphos, pentachlorophenol and diclofenac) at 200 µg/L each and in different water matrices. These compounds were selected as Priority Substances listed in European Commission directives (2013/39/EC and 2008/105/EC Directives). Research was carried out at pilot plant scale in a 30 L electrochemical system (cells made by an anode of boron-doped diamond thin film on a niobium mesh (Nb-BDD) and a carbon-polytetrafluoroethylene (PTFE) GDE as the cathode), a 20 L ozone reactor and three different solar photoreactors (39 L, 45L and 120 L) based on compound parabolic collectors (CPC) and connected to the non-solar oxidation systems. Results showed successful elimination of at least 80% of MCs for all the technologies tested. However, solar photo-Fenton at circumneutral pH showed better performance than solar photo-electro-Fenton and even electro-Fenton processes. In addition, the combination of ozone with solar radiation showed promising results as almost complete elimination of MCs was attained with a significant lower ozone consumption that when applying ozone in the dark (with or without the assistance of Fenton´s reagent).

Keywords: Mild Solar photo-Fenton; ozonation; photo-electro-Fenton, priority substances, solar energy.

1. Introduction

The growing development of the personal care and pharmaceutical industry has led to the presence of substances as antiseptics, pesticides, hormons, etc., in water bodies, for instance in municipal wastewater treatment plant (MWWTP) effluents, in a very low concentration that have being detected thanks to the development of advanced analytical methods [1]. Among these microcontaminants (MCs) there are pesticides, industrial compounds, antibiotics, steroids, drugs, etc. Many of these trace contaminants are referred as Contaminants of Emerging Concern (CECs) because they have recently been analysed, they are not still regulated and are believed to affect the environment and human health, not only for themselves but also for the degradation by-products that they can generate, sometimes presenting even higher toxicity than the parent compounds. Although there are no discharge limits for most MCs, some regulations have been published and therefore some CECs identified with high risk (based on available data of acute and chronic effects to aquatic environment and human health) entered in the regulations and therefore they are called

Priority substances (PS). A new strategy was defined by the European Directive 2000/60/EC identifying some PS. Later, a list of 33 PS was established by the Directive 2008/105/EC. The last Directive 2013/39/EU updated previous regulations introducing the polluter pays principle. Therefore, the development of non-expensive-innovative wastewater treatment technologies are needed [2] not only for removing PS but also CECs, all of them considered MCs.

Considering that conventional wastewater treatments based on biological systems are normally designed focusing on carbon, nitrogen and phosphorous elimination, only partial MCs removal is usually achieved since most of the compounds cannot be metabolized by microorganisms as source of carbon and may even inhibit the activity of the microorganisms or produce their bioaccumulation in the food chain [3]. The application of tertiary treatments for refining these treated waters so as to avoid PS and other CECs reaching both irrigation water (as they could accumulate in crops products [4, 5], and water natural bodies, and to prevent their bioaccumulation and the consequent aggravation of their detrimental effects on human health, has been widely studied in the last years [6].

Recently, membrane separation and advanced oxidation processes (AOPs) are becoming consolidated as effective technologies to remove MCs [Westerhoff, P., Moon, H., Minakata, D., Crittenden, J. Oxidation of organics in retentates from reverse osmosis wastewater reuse facilities. Water Research, 43, 3992-3998, 2009. Pérez-González, A., Urtiaga, A.M., Ibáñez, R., Ortiz, I. State of the art and review on the treatment technologies of water reverse osmosis concentrates. Water Research, 46, 267-283, 2012. Justo, A., González, O., Aceña, J., Pérez, S., Barceló, D., Sans, C., Esplugas, S. Pharmaceuticals and organic pollution mitigation in reclamation osmosis brines by UV/H2O2 and ozone.

Journal of Hazardous Materials, 263, 268-274, 2013. 7]. In this context, the treatment of membrane rejection streams (highly concentrated in salts and contaminants) has open the door to the application of electrochemical processes for MCs removal, as these processes need high conductivity in water to be effective [Pérez, G., Fernández-Alba, A.R., Urtiaga, A.M., Ortiz, I. Electro-oxidation of reverse osmosis concentrates generated in tertiary water treatment. Water Research, 44, 2763-2772, 2010; Radjenovic, J., Bagastyo, A., Rozendal, R.A., Mu, Y., Keller, J., Rabaey, K. Electrochemical oxidation of trace organic contaminants in reverse osmosis concentrate using RuO2/IrO2-coated titanium anodes. Water Research, 45, 1579-1586, 2011. Urtiaga, A.M., Pérez, G., Ibáñez, R., Ortiz, I. Removal of pharmaceuticals from a WWTP secondary effluent by ultrafiltration/reverse osmosis followed by electrochemical oxidation of the RO concentrate. Desalination, 331, pp. 26-34, 2013.; 8]. Usually, wastewater containing MCs resembles to natural sweet waters in its physic-chemical characteristics, such as MWWTP effluents.

Nowadays, it is booming the combination of processes looking for an increase in treatments effectiveness, therefore it has emerged a high trend on the application of electro-Fenton (EF) processes, based on the application of two oxidative systems simultaneously. On the one hand, $^{\bullet}$OH are electrogenerated on the anode surface by electrolysis of water, and on the other hand, hydrogen peroxide is electrogenerated in the cathode, so Fenton reaction takes place when adding iron [9]. According to the published works in this topic, there is a niche for research on the elimination of MCs by EF processes and so several challenges needs to be addressed [10-13]. Critical challenges to wider adoption of electrochemical oxidation for wastewater treatment is the high cost of electrodes and that it is strongly pH dependent. Usually, the oxidation potential of an electrochemical system in acidic medium is higher than that in alkaline medium. Boron-doped diamond (BDD) electrodes have been studied extensively in recent years but the performance of the process in removing MCs is affected by the presence of inorganic anions and DOM intrinsically present in wastewater, which can react with the electro-generated hydroxyl radicals and other reactive oxygen species [Sirés I., Brillas E., 2012. Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review. Environment International 40, 212-229]. One of the challenges regards their implementation in continuous mode to provide high H_2O_2 amounts from the start. Moreover, EF operation at acidic pH is a known drawbacks that need to be solved. A comprehensive review on the application of EF and other processes for the abatement of MCs was recently published [Francisca C. Moreira, Rui A.R. Boaventura, Enric Brillas, Vítor J.P. Vilar. Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. Applied Catalysis B: Environmental Volume 202, March 2017, Pages 217-261].

Since most water bodies containing MCs come from MWWTP effluents and these are in pH ranges near neutrality, it is necessary to consider that the ideal situation would be the application of tertiary treatments which are known to be effective at natural pH such as ozone based processes [14]. The treatment of MWWTP effluents with ozonation has already been implemented in Switzerland with the target in the elimination of a selection of CECs from a defined list of compounds. The studies evaluate the suitable process configurations depending on the individual features of the treatment plants [15].

The wide diversity of MCs and local specificity of their composition indicates the need for development and integration of different treatments. Therefore, the aim of this study is to propose alternative solar treatments, all of them operated at circumneutral pH in combination with electro-oxidation or O_3-based processes. The most tested solar-based treatment in the recent years for elimination of MCs has been photo-Fenton, known to be optimal at pH around 3, but successfully applied at circumneutral pH by using different complexing agents such as citric acid, EDTA, EDDS, etc [16]. This statement has been widely demonstrated in several works [17-20] so any other technology to be applied must be successfully compared to photo-Fenton process at neutral pH.

The main objective of this work is the comparison of various AOPs based on solar photo-Fenton at circumneutral pH, such as photo-electro-Fenton process and solar ozonation in combination with Fenton like processes ($O_3/Fe^{2+}/H_2O_2$, $O_3/Fe^{3+}/H_2O_2$ and Solar/$Fe^{3+}/O_3/H_2O_2$), for the elimination of selected target MCs (terbutryn, chlorfenvinphos, pentachlorophenol and diclofenac) at pilot plant scale contained in different water matrices (demineralized water, natural water, simulated fresh water and simulated MWWTP effluent). Conventional photo-Fenton process and ozonation were also performed as a matter for comparison. Target MCs have been selected as PS included in Directive 2013/39/EU, including a set of compounds of different structure (aromatic and not aromatic), considered highly toxic, with different heteroatoms (Cl, N, P) and possible to analyze by HPLC/UV at low concentration (LOQ < 5 μg/L).~~.~~

2. Materials and methods

2.1. Chemicals and wastewater characterization

Pentachlorophenol (PCP), terbutryn (TBT), chlorfenvinphos (CFP) and diclofenac (DFC) high-purity grade (>99%) all were purchased from Sigma-Aldrich. As iron source it was used Iron (III) Sulphate ($Fe_2(SO_4)\cdot 3H_2O$, 75% purity) from Panreac. Anhydrous sodium sulfate (Fluka) was employed as background electrolyte in electrochemical processes at 0.05 M. Reagent grade hydrogen peroxide (35% w/v), sulphuric acid and sodium hydroxide (for pH adjustment) were acquired from J.T. Baker. Ethylenediamine-N,N'-disuccinic acid (EDDS) 35% in H_2O was purchased from Aldrich. Acetonitrile (ACN) and formic acid for the HPLC method were HPLC-grade from Panreac. Millipore 0.2 µm syringe-driven Millex hydrophobic Fluoropore (PTFE) membrane filters were utilized for particles removal.

Experiments were conducted in demineralized water, natural water (NW) (pH 6.2 and 1.1 mS/cm of conductivity), ~~simulated fresh water (SW)~~ and simulated effluent from a MWWTP (SE). ~~SW~~ SE was ~~prepared according to~~based in the following receipt for simulated water [21]: 96 mg/L of $NaHCO_3$, 60 mg/L of $CaSO_4.2H_2O$, 60 mg/L of $MgSO_4$ and 4 mg/L of KCl. ~~A slightly modified~~ SE from the American Standard Methods [21] was prepared by adding the following chemicals to ~~SW~~simulated water: beef extract (1.8 mg/L), peptone (2.7 mg/L), humic acid (4.2 mg/L), tannic acid (4.2 mg/L), sodium lignin sulfonate (2.4 mg/L), sodium lauryle sulphate (0.9 mg/L), acacia gum powder (4.7 mg/L), Arabic acid (5.0 mg/L), $(NH_4)_2SO_4$ (23.6 mg/L) and K_2HPO_4 (7.0 mg/L), contributing 10 mg/L of dissolved organic carbon (DOC) [22].

2.2. Analytical methods

Hydrogen peroxide was measured by spectophotometry at 410 nm by adding Ti(IV) oxysulfate, according to DIN 38409 H15 and iron concentration was measured following ISO 6332 using for both a Unicam UV/Vis UV2 spectrophotometer (at 510 nm).

Ozone concentration in solution was measured by the indigo method based on the decolorization of indigo trisulfonate (600 nm) by ozone [21, 23].

~~A Shimadzu TOC-VCSN analyzer was used to monitor Dissolved Organic Carbon (DOC) after sample filtration through a 0.22 µm Nylon filter.~~ The degradation rate of the MCs was monitored by a UPLC/UV Agilent Technologies Series 1260, equipped with a C-18 ZORBAX XDB C-18 analytical column. The gradient started at 90/10 (v/v) ultrapure water (with formic acid 25 mM) and acetonitrile (ACN) that progress till 100% ACN in 14 min at a flow rate of 1 mL/min. The UV signal for each compound was: 220 nm for Pentachlorophenol, 230 nm for Terbutryn, 240 nm for Chlorofenvinphos and 285 nm for Diclofenac. Limits of quantification (LOQ) of Pentachlorophenol, Terbutryn, Chlorofenvinphos and Diclofenac were 4.4, 3.8, 3.2 and 3.4 µg/L respectively. 9 mL of sample was filtered with a 0.22 µm PTFE filter. The filter was washed with 1 ml of ACN to extract any absorbed compound, mixing it with 9 mL of filtered sample before injection in HPLC. Inyection volume was 100µL. Mineralization of MCs (TOC results) was not determined because treating MCs at 200 µg/L is out of the analytical limits of this technique and/or not realible due to the presence of other organics.

Fe^{3+}:EDDS concentration was measured by liquid chromatography (HPLC Agilent 1100 Series) by using an Ion-Pair method with a reversed-phase column (Luna C18, 150X3 mm, 5µm particle size) [24].

2.3. Pilot plants and experimental procedures

2.3.1. Solar photo-Fenton treatment

Compound parabolic collector (CPC) solar pilot plant used for solar photo-Fenton experiments is located in Plataforma Solar de Almería (latitude 37ºN, longitude 2.4ºW). ~~The volume inside the absorber tubes is 22 L being the total irradiated area 3.08 m^2 and the total volume 39 L.~~ Table 1 describes the characteristics of CPC photo-reactor. A global solar UV radiometer (KIPP&ZONEN, Model CUV 3) tilted 37º as the CPC reactor quantifies the solar ultraviolet radiation (UV). More details can be obtained in [25]. Solar accumulated UV energy has been quantified according to Eq. 1 where:

$$Q_{UV,n+1} = Q_{UV} + \Delta t_n \cdot \overline{UV}_{G,n+1} \cdot \frac{A_i}{V_T}\ ; \qquad \Delta t_n = t_{n+1} - t_n \qquad (1)$$

t_n: experimental time for each sample.

UV: average solar ultraviolet radiation measured during the period Δt_n.

A_i: illuminated area (m^2).

$Q_{UV,n}$: accumulated energy per unit of volume (kJ/L) at t_n.

Solar photo-Fenton experiments at near neutral pH would require the addition of a complexing agent such as EDDS for maintaining iron in solution [26]. In such a case, 5.5 mg/L of Fe^{3+} was complexed with EDDS maintaining the molar ratio 1:2 Fe^{3+}: EDDS as better operating condition according to Miralles-Cuevas et al. [27]. For the complex formation in the dark, iron was dissolved in the minimum amount of acidified water, and then the required amount of EDDS was added. The complex was immediately formed showing a strong yellow color.

2.3.2. Solar photo-electro-Fenton treatment

Solar photo-electro-Fenton pilot plant consisted of four electrochemical cells acquired from ElectroCell coupled to a CPC photo-reactor. Each cell was composed by an anode made of boron-doped diamond thin film on a niobium mesh (Nb-BDD) and a carbon-polytetrafluoroethylene (PTFE) GDE as the cathode, both with 0.01 m^2 effective area. The GDE cathode was fed with compressed air (ABAC air compressor, 1.5 kW) at 10 L/min. The experiments were carried at a constant *j* using a Delta Electronika power supply limited to 70 V and 22 A.

Solar CPC photoreactor combined with the electro-Fenton plant is described in Table 1, consists of 10 borosilicate tubes mounted in an aluminum frame on a platform tilted 37º (PSA, 37º N, 2.4º W)~~ with a total illuminated area of 2 m^2, and an irradiated volume of 23 L~~. Scheme of the pilot plant is shown in elsewhere [28]. The working volume was 30 L for electro-Fenton (EF) assays~~ and 75 L to perform the solar photo-electro-Fenton (SPEF) tests~~.

Accumulated UV energy in each experiment was obtained by using equation 1 (as explained for solar photo-Fenton experiments previously).

Experiments were developed by using 50 mM solution of Na_2SO_4 (Sigma –Aldrich) as supporting electrolyte dissolved on demineralized water. First of all, Fe:EDDS complex prepared as described above, was added in a 1:2 ratio. Then, 200 µg/L of each target contaminant was also added to directly to the recirculation tank of the pilot plant. Letting homogenize the solution for a time equal to 3 times the recirculation of the total volume, a sample was taken to check initial MCs concentration. After this, experiment started and samples were taken in intervals of 5 minutes during the first 30 min, then every 15 min till 90 min of test and finally every 30 min.

2.3.3. Ozonation treatment

The ozonation system is an Anseros PAP-pilot plant (Ansero Klaus Nonnenmacher GmbH, Germany) for batch operation. The reactor is a 20 L column with an inlet O_3 diffuser and a gas dehumidifier in the sampling point. It was also equipped with an ozone destroyer, two nondispersive UV analyzers (Ozomat GM-6000-OEM) to measure inlet and outlet ozone gas concentration, a flow-meter for inlet air regulation, an ~~air~~ oxygen generator (Anseros SEP100) and an ozone generator (Anseros COM-AD02).

During experiments with ozonation, the mix of four MCs was added directly from stock solution into the reactor. The samples were collected every 5-10 min and residual ozone was removed with N_2 to stop the reaction. The ozone generator was set at 20% power with a constant 1.5 g O_3/h production. Ozone gas was measured at the system inlet ($C_{O_{3},i}$, g/Nm^3) and outlet ($C_{O_{3},o}$, g/Nm^3), so that ozone consumption of each sample $O_{3cons,n}$, g/L could be calculated by Eq. (2) taking the inlet air flow Q_a Nm^3/h of 0.06 Nm^3/h and ozone consumption in the previous sample into account:

$$O_{3cons,n}\left(\frac{g}{L}\right) = O_{3cons,n-1} + \frac{Q_a\cdot\left(C_{O_{3,i,n}} - C_{O_{3,o,n}}\right)\cdot(t_n - t_{n-1})}{V_r} \qquad (2)$$

In some experiments ozonation pilot plant was combined with a solar CPC photo-reactor (different to that described in section 2.3.1.) for the assessment of Solar/Fe^{3+}/O_3/H_2O_2

process (see Figure 1). Table 1 presents the characteristics of CPC photo-reactor used. Eq. 1 was used to determine $Q_{UV,n}$.

Figure 1 - Ozonation Plant Pilot

Table 1. CPC solar photo-reactor used for ~~Solar/Fe^{3+}/O$_3$/H$_2$O$_2$~~the different ~~tests~~ processes

PARAMETER	photo-Fenton	photo-electro-Fenton	Solar/Fe3+/O3/H2O2
Illuminated volume	22 L	23 L	68.2 L
Reactor area	3.08 m^2	2 m^2	2 m^2
Glass tubes diameter	32 mm	45 mm	75 mm
CPC inclination	37º	37º	37º
Total volume	39L	75 L	120 L

3. Results and discussion

3.1. ~~Solar p~~Photo~~-electro~~-Fenton and photo/electro-Fenton processes ~~treatment~~

3.1.a. Solar photo-Fenton and photo-electro-Fenton comparison

Elimination of target MCs (200 µg/L of each) in demineralized water by solar photo-Fenton process under well-known operating conditions [26], at pilot plant scale and at near neutral pH by using Fe:EDDS 1:2, and 0.1 mM of Fe^{3+}, was first evaluated (Figure 2 shows the degradation profile of the sum of MCs). Diclofenac and Pentachlorophenol were completely degraded after a solar-UV accumulated energy of 0.83 kJ/L (after around 5 minutes of solar illumination) and requiring 31 mg/L of H_2O_2, though Chlorfenvinphos and Terbutryn were more resistant and 85% of elimination was attained after 11 kJ/L (corresponding to around 60 minutes of solar illumination) and a H_2O_2 consumption of 60 mg/L. Final pH at the end of the experiment was 6.

The degradation of ~~the same concentration of selected~~ MCs was also tested by electro-oxidation in demineralized water containing a required electrolyte, in this case Na_2SO_4 (50 mM), in the ~~electro-oxidation~~ pilot plant described in section 2.3.2. ~~Taking into account the p~~Previously reported results ~~related to the optimization of~~optimized this experimental system for in-situ electrogeneration of hydrogen peroxide [28] and~~,~~ 73.6 mA/cm^2 was selected with a hydrogen peroxide production rate between 30 and 60 mg/min~~for carrying out the degradation tests~~. However, though optimum pH obtained in the previous work was 3, in this occasion it was selected to operate at circumneutral pH. ~~and so, cathodic electrogeneration of hydrogen peroxide was checked under such new operating conditions. As a result, hydrogen peroxide production rate was observed to be between 30 and 60 mg/min.~~The following paragraphs discuss results obtained under these conditions checking the stability of the complex Fe:EDDS in the dark and applying SPEF (Figure 2).

Before applying solar photoelectro-Fenton (SPEF) process by using also Fe:EDDS 1:2 at circumneutral pH, it was required checking the stability of the complex Fe:EDDS in the dark during electro-oxidation. Under our knowledge any previous study on the use of EDDS in electro-oxidation systems has been reported. Therefore, an electro-Fenton (EF) test was performed at 73.6 mA/cm^2 and pH 6 for 240 min monitoring Fe:EDDS complex at 0.1 mM of Fe^{3+}. During 120 minutes of treatment the complex remained stable and from then it began to decay. After 180 minutes (14.9 kWh/m^3) Fe:EDDS complex showed a 18% of decay and 40% at the end of the assay with an energy consumption of 20 kWh/m^3. In consequence, 180 minutes were considered as the maximum process time for the rest of assays developed in the study to guaranty the stability of the complex and so at least 80% of Fe^{3+} would be present as Fe:EDDS.

Then, SPEF experiment was carried out at a current density of 73.6 mA/cm^2 and 0.1 mM of Fe^{3+} with Fe:EDDS 1:2 (Figure 2). It is important to highlight that the exposure of the complex to sunlight promotes its degradation. Accordingly to this, iron in solution decreased from 0.1 mM to 0.062 mM after 60 minutes of SPEF. Despite this, after 180 minutes, with 5.1 kWh/m^3 of energy consumption it was achieved 77.5% of MCs degradation in the electro-oxidation process. At that point, iron dissolved in the system was only 0.036 mM, confirming the instability of the complex and the degradation of EDDS.

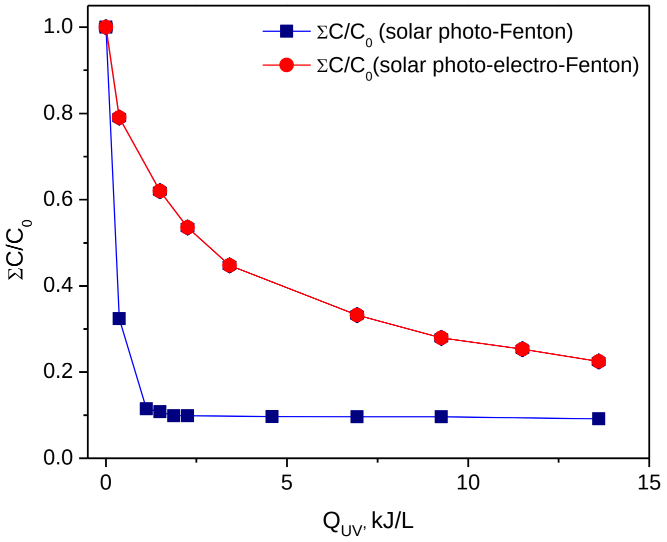


Figure 2. MCs degradation ($\Sigma C_0 \approx$ 800 µg/L) by SPEF (*j* 73.6 mA/cm^2) with 0.1 mM of Fe^{3+} at neutral pH by adding Fe:EDDS 1:2 in demineralized water (Na$_2$SO$_4$ 50 mM in SPEF).

SPEF treatment showed less efficiency in the target MCs abatement compared with solar photo-Fenton process. Indeed initial reaction rate corresponding to the degradation of the sum of MCs was 77.8 µg/L.min for solar photo-Fenton against 10.6 µg/L.min for SPEF process. Both experiments were carried out in demineralized water though the presence of the electrolyte (Na$_2$SO$_4$ 50 mM) required for the adequate performance of SPEF provoked ~~the~~ lower ~~reduction on the~~ removal rate in SPEF compared with solar photo-Fenton. Generation of hydroxyl radicals was lower because of (i) the formation of sulfato-Fe(III) complexes and (ii) scavenging of hydroxyl radicals by sulfate and formation of sulfate radicals which are less reactive than HO radicals. In addition, the absence of an external source of hydrogen peroxide was also responsible of the removal rate slowed down and therefore, it must be stated that cathodic electrogeneration of hydrogen peroxide governed

MCs removal rate. Using higher amount of hydrogen peroxide, a better performance of the electrochemical cells or advanced concepts and new materials of such cells, could increase SPEF efficiency as H_2O_2 production rate is a key issue in this kind of AOPs.

3.1.b. Electro-Fenton process

EF experiments were also carried out in order to evaluate MCs degradation without combining with solar energy. For that purpose, first, pure anodic oxidation (AO) was carried out at 73.6 mA/cm^2. Afterwards, EF was applied also at 73.6 mA/cm^2 in the presence of Fe^{3+} but testing different concentrations: 0.1, 0.2 and 0.5 mM (Figure 3 and Table 2). In addition, and regarding the current density *(j)*, 30, 73.6 and 100 mA/cm^2 were tested at Fe^{3+} 0.1 mM. Lowest current density slowed down the generation of hydrogen peroxide, though it also showed a lowest energy consumption (2.2 kWh/m^3) for attaining 80% degradation of MCs after 150 minutes of EF treatment. This result brought to light the necessity of increasing *j* to improve the ratio between energy consumption and MCs elimination. Nevertheless, when applying the highest *j* value (100 mA/cm^2), EF treatment time was significantly reduced to 60 min due to the larger oxidizing power of the anode and the higher production of hydrogen peroxide that favored the Fenton reaction and consequently, MCs elimination. Nevertheless, that positive result was countered by the important increase detected on the related energy consumption, attaining 6.5 kWh/m^3. Best compromise between MCs degradation and energy consumption was obtained when applying *j* of 73.6 mA/cm^2, which did not entail a significant increase in current density, compared with 30 mA/cm^{2,} but more than 80% degradation after 45 minutes of EF was reached with an energy consumption of 3.45 kWh/m^3.

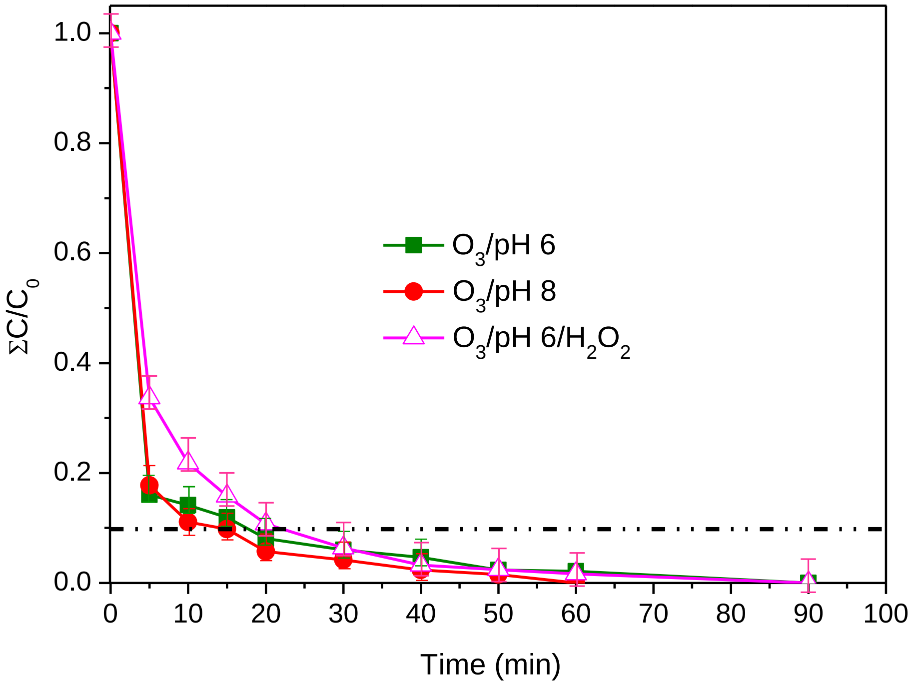


Figure 3. MCs degradation ($\Sigma C_0 \approx$ 800 µg/L) by AO and EF (Fe:EDDS, 1:2) at neutral pH in demineralized water (Na_2SO_4 50 mM in SPEF).~~.~~

It must be noticed that an increase in Fe^{3+} concentration from 0.1mM to 0.2 and 0.5 mM at 73.6 mA/cm^2 in the EF treatment always involves an increase in EDDS amount for maintaining the ratio Fe:EDDS of 1:2. In consequence, higher concentration of EDDS would mean also higher organic carbon in solution that would act as radicals' scavenger. This fact explains the increase on the energy required for attaining 80% of MCs removal associated to a higher concentration of Fe^{3+} (Figure 3). However, when Fe^{3+} was increased from 0.2 mM to 0.5 mM, the energy demanded was lower than when using Fe^{3+} 0.2 mM but still higher than at Fe^{3+} 0.1 mM. At higher Fe^{3+} concentration dark-Fenton process was so fast that all hydrogen peroxide generated was consumed rapidly.

Finally, the AO test at *j* 73.6 mA/cm^2 corroborated higher required treatment time and energy consumption compared to EF process with 0.1 mM of Fe^{3+}. It should be highlighted that AO was very effective for Pentachlorophenol, Terbutryn and Diclofenac removal, but not for the more recalcitrant MC, Chlorofenvinphos (Table 2). AO does not require iron removal after the treatment, which would simplify electrooxidation operation.

Table 2. Summary of the results obtained in the electro-oxidation pilot plant to attain 80% of total MCs degradation at pH 6 by using AO or EF (with Fe:EDDS).

	0.1 mM Fe^{3+}			**73.6 mA/cm^2**		
	30 mA/cm^2	**73.6 mA/cm^2**	**100 mA/cm^2**	**AO**	**0.2 mM Fe^{3+}**	**0.5 mM Fe^{3+}**
Time (min.)	150	45	60	75	120	180
Energy consumption kWh/m^3	2.2	3.5	6.5	5.0	12.1	8.1
MCs removal (%)						
Pentachlorophenol	87.8	78.8	91.7	100	89	85.8
Terbutryn	66.2	84.2	79.5	84.1	72.1	68.3
Chlorofenvinphos	58.4	57.4	57.3	46.2	61.5	62.9
Diclofenac	100	97.3	100	100	100	100

3.~~3~~2. ~~Solar ozonation treatment~~Ozonation and solar ozonation systems

3.2.a. Ozonation tests

Ozonation treatment of the target MCs spiked on different types of water (demineralized water, NW and SE) was performed varying pH from 6 to 11 (direct ozonation and indirect free radical oxidation). Initial concentration of each target MC was maintained in 200 µg/L. The effect assessment of H_2O_2 addition (at 1.5 mM) as well as Fenton like reactions by using Fe^{2+} or Fe^{3+}at 0.1 mM, were also carried out. Same operating conditions were evaluated in combination with solar radiation.

Ozonation results in demineralized water at pH 6 and pH 11 showed more than 99% degradation of all contaminants (after 50 minutes of treatment) in both situations. It should be noted that, working at pH 11, ozone consumption was higher (32 mg O_3/L) than when working at lower pH (13 mg O_3/L) due to the reaction of ozone with generated hydroxyl radicals at high pH (Eq. 3). It is important to stress that more oxidizing conditions at pH 11 did not entail higher degradation rates due to the low concentration of MCs. Therefore, pH 11 was disregarded for further tests as indirect free radical oxidation route showed any substantial interest for this application. Lower pH (around 8) was selected instead as it is a normal value for natural waters and wastewater containing MCs.

$$O_3 + H_2O_2 \rightarrow HO^{\cdot} + HO_2^{\cdot} + O_2 \qquad (3)$$

Afterwards, ozonation was tested in NW at pH 6 and 8. It was observed an increment of the degradation rate and on the consumption of ozone, 14 mg O_3/L at pH 6 and 19 mg O_3/L at pH 8, for attaining more than 99% of MCs degradation (Figure 4). Substantially lower consumption of ozone was required to degrade 90% of MCs (1.8 mg O_3/L at pH 6 and 4.4 mg O_3/L at pH 8). It was clearly observed that higher pH resulted in higher reaction rates but accompanied of higher ozone consumption. Consequently, it should be remarked that application of ozone treatment for elimination of MCs must be always tested at pH around 8 (normal pH of natural waters and MWWTP effluents) and not at pH 6. These results are consistent with ozone application at large scale for treatment of MCs in Switzerland, where a specific ozone dose of 1.5-2.5 mg/L is required for 80% of MCs abatement [29]. It is important to highlight that when adding H_2O_2 at natural pH (8), the consumption of O_3 slightly increased to 5 mg/L to degrade >90% of MCs, without an improvement on the MCs elimination rate. The reaction of ozone with of H_2O_2 (peroxone process) gives rise to the generation of $^{\bullet}OH$ radicals [30] but, as in the case of ozonation at pH 11, it did not provoke a better degradation rate due to the low concentration of MCs and so ozone reacted with H_2O_2.

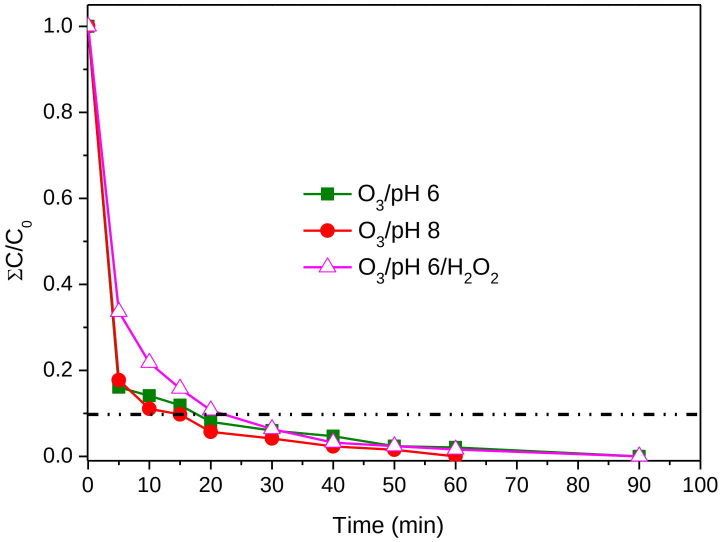


Figure 4. MCs degradation ($\Sigma C_0 \approx$ 800 µg/L) by ozonation in NW at two different pHs and with addition of H_2O_2 (50 mg/L).

After demonstrating the bad performance of ozone at pH 11 for MCs elimination and that the process was efficient at pH close to the typical pH of MWWTP effluents (pH around 8) the final objective was to study if any combination between ozonation and Fenton ~~or photo-Fenton~~ would be interesting for the enhancement of MCs removal. Figure 5 shows results with SE at natural pH (8) showing a consumption of ozone of 6.4 mg/L to degrade >90% of MCs. In Figure 5 it is also shown experimental results obtained in the presence of iron with and without its combination with H_2O_2. When applying Fe^{2+} or Fe^{3+} (both at 0.1 mM), ozone consumption was 6.6 and 9.6 mg O_3/L, respectively. Recent studies reported that the co-presence of O_3 and Fenton reagents favored the generation of $^{\bullet}OH$ [31]. Experiments with addition of iron to the ozonation system have been carried out to evaluate the direct reaction of ozone with Fe^{2+} and reduction to Fe^{3+} with extra $^{\bullet}OH$ generation according to Eqs. 4-7 [32]. But no improvement was observed in the reaction rate or in ozone consumption. Initial degradation rate was 61.7 µg/L.min for ozonation (pH 8) almost equal to those obtained when Fe^{2+} or Fe^{3+} were added (59.5 µg/L.min and 60.6 µg/L.min, respectively).

$$Fe^{2+} + O_3 \rightarrow Fe^{3+} + O_3^{\bullet-} \qquad (4)$$

$$O_3^{\bullet-} + H^+ \rightarrow O_2 + HO^{\bullet} \qquad (5)$$

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \qquad (6)$$

$$FeO^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \qquad (7)$$

When testing ozonization in combination with Fenton process (Fe/H_2O_2), both consumption of ozone and treatment times were similar, so any significant improvement took place. In addition, initial degradation rates were 58.6 µg/L.min and 50.2 µg/L.min, when adding H_2O_2 to Fe^{2+} and Fe^{3+}, respectively.

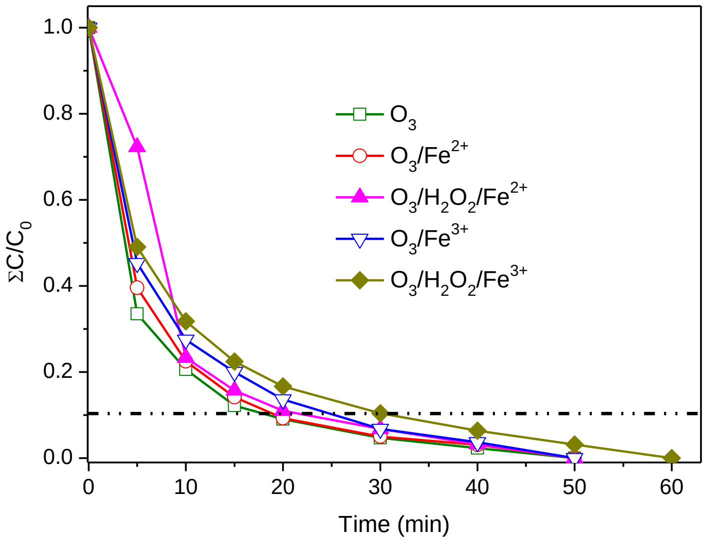


Figure 5. MCs degradation ($\Sigma C_0 \approx$ 800 µg/L) by ozonation in SE at pH 8 with addition of Fe^{2+}, Fe^{3+} (0.1 mM) and H_2O_2 (1.5 mM).

3.2.b. S~~s~~olar ozonation tests

Finally, the combination of ozone with a solar CPC photo-reactor working at natural pH (8) for the elimination of MCs in SE was performed (figure 6).

Dissolved ozone molecules absorb UV light with a peak absorbance at 260 nm and a molar absorptivity of 3292±70 M/cm [33]. Upon the irradiation of UV, the dissolved ozone molecules undergo photolysis reactions to yield hydrogen peroxide [34]. The application of ozone in the presence of solar radiation led to an enhancement of MCs removal as lower consumption of ozone was required. Indeed, for 80% degradation of MCs the consumption of ozone was 0.52 mg/L (O_3), 0.30 mg/L (O_3/Fe^{3+}), 0.23 mg/L (O_3/H_2O_2) and 0.6 mg/L ($O_3/Fe^{3+}/H_2O_2$). The so important reduction in ozone consumption for solar/O_3 compared with results obtained with ozonation in the dark was due to a new source of $^{\bullet}OH$ generated under solar UV (λ< 315 nm) from H_2O_2 photolysis as H_2O_2 could be produced by Eq. 8 [35]. The consumption of ozone in solar/O_3/H_2O_2 was still low against an enhancement in the reaction rate. In that cases in which ozone was combined with iron under solar illumination, the contribution of photo-Fenton process was not clear as both ozone consumption and reaction rate were quite similar to solar/O_3 process. It is interesting to remark that during solar treatments, the temperature in the photo-reactor increased (up to c.a. 40º C). This also favored MCs elimination since ozone reaction rates increase with temperature [36].

$$O_3 + H_2O \xrightarrow{h\nu} O_2 + H_2O_2 \quad (8)$$

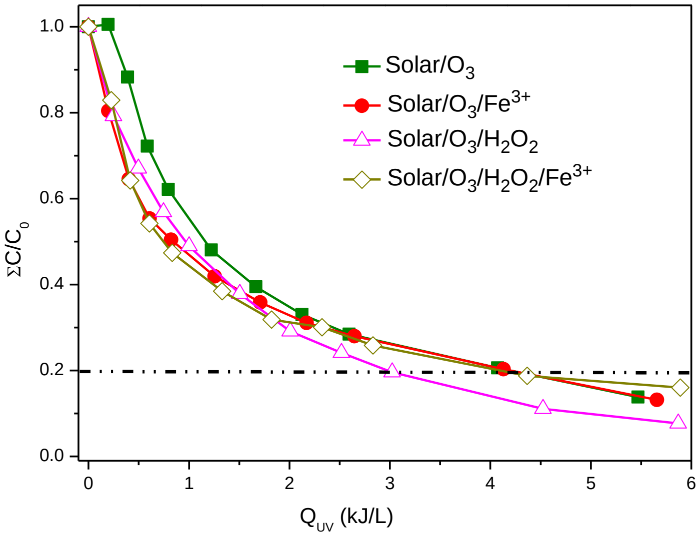


Figure 6. MCs degradation ($\Sigma C_0 \approx$ 800 µg/L) by ozonation combined with a CPC photo-reactor in SE at pH 8 with addition of Fe^{2+}, Fe^{3+} (0.1 mM) and H_2O_2 (50 mg/L).

It is important also to stress that initial degradation rate did not improve when combining ozone with solar radiation, as it decreased to 28.3 µg/L.min. Similar values where obtained when Fe^{3+} or H_2O_2 were added separately (24.7 µg/L.min and 24.9 µg/L.min, respectively), or even in combination of both reagents, giving 30.4 µg/L.min of initial degradation rate. These results expose the evidence that main advantage on combining ozonation with solar radiation lays on the significant reduction on ozone consumption.

4. Conclusions

It has been demonstrated that Fe:EDDS complex is able to maintain iron in solution for EF and SPEF treatments and so it can be considered a useful tool for performing electrochemical processes at circumneutral pH.

SPEF treatment showed less efficiency compared with solar photo-Fenton process at circumneutral pH due to the hydroxyl radicals' scavenger effect provoked by the necessity of adding an electrolyte in wastewater with low ionic strength. SPEF was also less efficient than EF treatment due to a limited electro-generation of H_2O_2. An improvement on the in-situ production rate of hydrogen peroxide would enhance SPEF process. Better performance of target MCs elimination was obtained when applying EF with Fe^{3+} at 0.1 mM. These results bring to light the interest on EF, SPEF and electro-oxidation processes in general as a suitable technology for MCs removal only when they are contained on specific wastewaters characterized by high conductivity values, such as membrane processes rejection streams.

Finally, Ozonation treatment demonstrated to be successful in the almost complete removal of studied MCs present in different water matrices at different pH in dark conditions. However, it is important to stress that higher pH values increased ozone consumption due to the very low concentration of contaminants to be oxidized, and so the reaction of generated H_2O_2 with O_3.

In general, the removal of MCs do not need the generation of high concentrations of hydroxyl radicals, this is why the combination of ozone with other treatments based on the addition of iron and hydrogen peroxide in the dark did not show an enhancement in the efficiency of the process. Nevertheless, the application of ozone in the presence of solar radiation led to an improvement on the MCs degradation and a reduction on ozone consumption compared with ozonation in the dark. This interesting result must be explored in detail and optimized taking into account economic aspects such as electricity requirements and the consequent depletion of ozone generation costs.

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New approaches to solar Advanced Oxidation Processes for elimination of priority substances based on electrooxidation and ozonation at pilot plant scale

Melina Roccamante[a,b], Irene Salmerón [a,b], Ana Ruiz[a,b], Isabel Oller [a,b *], Sixto Malato [a,b]

[a] *Plataforma Solar de Almería-CIEMAT, Ctra Senés km 4, 04200 Tabernas (Almería), Spain*

[b] *CIESOL, Joint Centre of the University of Almería-CIEMAT, 04120 Almería, Spain*

Abstract

The main objective of this work is to compare various Advanced Oxidation Processes based on solar photo-Fenton at circumneutral pH (by adding EDDS as iron complexing agent), such as solar photo-electro-Fenton process and solar ozonation in combination with Fenton like processes ($O_3/Fe^{2+}/H_2O_2$, $O_3/Fe^{3+}/H_2O_2$ and Solar/$Fe^{3+}/O_3/H_2O_2$), for the elimination of four microcontaminants (Terbutryn, chlorfenvinphos, pentachlorophenol and diclofenac) at 200 µg/L each and in different water matrices. These compounds were selected as Priority Substances listed in European Commission directives (2013/39/EC and 2008/105/EC Directives). Research was carried out at pilot plant scale in a 30 L electrochemical system (cells made by an anode of boron-doped diamond thin film on a niobium mesh (Nb-BDD) and a carbon-polytetrafluoroethylene (PTFE) GDE as the cathode), a 20 L ozone reactor and three different solar photoreactors (39 L, 45L and 120 L) based on compound parabolic collectors (CPC) and connected to the non-solar oxidation systems. Results showed successful elimination of at least 80% of MCs for all the technologies tested. However, solar photo-Fenton at circumneutral pH showed better performance than solar photo-electro-Fenton and even electro-Fenton processes. In addition, the combination of ozone with solar radiation showed promising results since almost a complete elimination of MCs was attained with a significant lower ozone consumption than when applying ozone in the dark (with or without the assistance of Fenton´s reagent).

Keywords: Mild Solar photo-Fenton; ozonation; photo-electro-Fenton, priority substances, solar energy.

1. Introduction

The growing development of the personal care and pharmaceutical industry has led to the presence of substances such as antiseptics, pesticides, hormons, etc., in water bodies, for instance in municipal wastewater treatment plant (MWWTP) effluents, in such a low concentration that they have been detected thanks to the development of advanced analytical methods [1]. Among these microcontaminants (MCs) there are pesticides, industrial compounds, antibiotics, steroids, drugs, etc. Many of these trace contaminants are referred as Contaminants of Emerging Concern (CECs) because they have recently been analysed, they are not still regulated and are believed to affect the environment and human health, not only for themselves but also for the degradation by-products that they can generate, sometimes presenting even higher toxicity than the parent compounds. Although there are no discharge limits for most MCs, some regulations have been published and therefore some CECs identified with high risk (based on available data of acute and chronic effects to aquatic environment and human health) entered in the regulations and therefore they are called Priority substances (PS). A new strategy was defined by the European Directive 2000/60/EC identifying some PS. Later, a list of 33 PS was established by the Directive 2008/105/EC. The last Directive 2013/39/EU updated previous regulations introducing the polluter pays principle. Therefore, the development of non-expensive-innovative wastewater treatment technologies are needed [2] not only for removing PS but also CECs, all of them considered MCs.

Considering that conventional wastewater treatments based on biological systems are normally designed focusing on carbon, nitrogen and phosphorous elimination, MCs are only partially removed since most of the compounds cannot be metabolized by microorganisms and may even inhibit their activity or produce their bioaccumulation in the food chain [3]. The application of tertiary treatments for refining these treated waters so as to avoid PS and other CECs reaching both irrigation water (as they could accumulate in crop products [4, 5], and water natural bodies, and to prevent their bioaccumulation and the consequent aggravation of their detrimental effects on human health, has been widely studied in the last years [6].

Recently, membrane separation and advanced oxidation processes (AOPs) are becoming consolidated as effective technologies to remove MCs [7-10]. In this context, the treatment of membrane rejection streams (highly concentrated in salts and contaminants) has open the door to the application of electrochemical processes for MCs removal, as these processes need high conductivity in water to be effective [11-14]. Usually, wastewater containing MCs resembles to natural sweet waters in its physic-chemical characteristics, such as MWWTP effluents.

Nowadays, the combination of processes looking for an increase in treatments effectiveness is booming, therefore a high trend on the application of electro-Fenton (EF) processes has emerged, based on the simultaneous application of two oxidative systems. On the one hand, $^{\bullet}OH$ are electrogenerated on the anode surface by electrolysis of water, and on the other hand, hydrogen peroxide is electrogenerated in the cathode, so Fenton reaction takes place when adding iron [15]. According to the published works regarding this topic, there is a niche for research on the elimination of MCs by EF processes and so, several challenges need to be addressed [16-19]. Critical challenges in order to wider the adoption of electrochemical oxidation for wastewater treatment are the high cost of electrodes and that it is strongly pH dependent. Usually, the oxidation potential of an electrochemical system in acidic medium is higher than in alkaline medium. Boron-doped diamond (BDD) electrodes have been studied extensively in the recent years but their performance in the process of removing MCs is affected by the presence of inorganic anions and DOM, intrinsically present in wastewater, which can react with the electro-generated hydroxyl radicals and other reactive oxygen species [20]. One of the challenges is their implementation in a continuous mode in order to provide high H_2O_2 amounts from the start. Moreover, EF operation at acidic pH is known as a drawback that needs to be solved. A comprehensive review on the application of EF and other processes for the abatement of MCs was recently published [21].

Since most water bodies containing MCs come from MWWTP effluents and these are in pH ranges near neutrality, it is necessary to consider that the ideal situation would be the application of tertiary treatments which are known to be effective at natural pH, such as ozone based processes [22]. The treatment of MWWTP effluents with ozonation has already been implemented in Switzerland with the aim of removing a selection of CECs from a defined list of compounds. The studies evaluate the suitable process configurations depending on the individual features of the treatment plants [23].

The wide diversity of MCs and local specificity of their composition indicates the need for developing and integrating different treatments. Therefore, the aim of this study is to propose alternative solar treatments, all of them operated at circumneutral pH in combination with electro-oxidation or O_3-based processes. The most tested solar-based treatment in the recent years for elimination of MCs has been photo-Fenton, known to be optimal at pH around 3, but successfully applied at circumneutral pH by using different complexing agents, such as citric acid, EDTA, EDDS, etc [24]. This statement has been widely demonstrated in several works [25-28] so, any other technology applied, must be successfully compared to photo-Fenton process at neutral pH.

The main objective of this work is the comparison of various AOPs based on solar photo-Fenton at circumneutral pH, such as photo-electro-Fenton process and solar ozonation in combination with Fenton like processes ($O_3/Fe^{2+}/H_2O_2$, $O_3/Fe^{3+}/H_2O_2$ and Solar/$Fe^{3+}/O_3/H_2O_2$), for the elimination of selected target MCs (terbutryn, chlorfenvinphos, pentachlorophenol and diclofenac) at a pilot plant scale contained in different water matrices (demineralized water, natural water, simulated fresh water and simulated MWWTP effluent). Conventional photo-Fenton process and ozonation were also performed for comparison. Target MCs have been selected as PS included in Directive 2013/39/EU, including a set of compounds with different structures (aromatic and not aromatic), considered highly toxic, with different heteroatoms (Cl, N, P) and possible to analyze by HPLC/UV at low concentration (LOQ < 5 µg/L).

2. Materials and methods

2.1. Chemicals and wastewater characterization

Pentachlorophenol (PCP), terbutryn (TBT), chlorfenvinphos (CFP) and diclofenac (DFC) high-purity grade (>99%) were all purchased from Sigma-Aldrich. As iron source Iron (III) Sulphate ($Fe_2(SO_4)\cdot 3H_2O$, 75% purity) from Panreac was used. Anhydrous sodium sulfate (Fluka) was employed as background electrolyte in electrochemical processes at 0.05 M. Reagent grade hydrogen peroxide (35% w/v), sulphuric acid and sodium hydroxide (for pH adjustment) were acquired from J.T. Baker. Ethylenediamine-N,N'-disuccinic acid (EDDS) 35% in H_2O was purchased from Aldrich. Acetonitrile (ACN) and formic acid for the HPLC method were HPLC-grade from Panreac. Millipore 0.2 µm syringe-driven Millex hydrophobic Fluoropore (PTFE) membrane filters were used for particles removal.

Experiments were conducted in demineralized water, natural water (NW) (pH 6.2 and 1.1 mS/cm of conductivity), and simulated effluent from a MWWTP (SE). SE was based in the following receipt for simulated water [29]: 96 mg/L of $NaHCO_3$, 60 mg/L of $CaSO_4.2H_2O$, 60 mg/L of $MgSO_4$ and 4 mg/L of KCl. SE from the American Standard Methods [29] was prepared by adding the following chemicals to simulated water: beef extract (1.8 mg/L), peptone (2.7 mg/L), humic acid (4.2 mg/L), tannic acid (4.2 mg/L), sodium lignin sulfonate (2.4 mg/L), sodium lauryle sulphate (0.9 mg/L), acacia gum powder (4.7 mg/L), Arabic acid (5.0 mg/L), $(NH_4)_2SO_4$ (23.6 mg/L) and K_2HPO_4 (7.0 mg/L), contributing 10 mg/L of dissolved organic carbon (DOC) [30].

2.2. Analytical methods

Hydrogen peroxide was measured by spectophotometry at 410 nm by adding Ti(IV) oxysulfate, according to DIN 38409 H15 and iron concentration was measured following ISO 6332 using for both a Unicam UV/Vis UV2 spectrophotometer (at 510 nm).

Ozone concentration in solution was measured by the indigo method based on the decolorization of indigo trisulfonate (600 nm) by ozone [29,31].

The degradation rate of the MCs was monitored by a UPLC/UV Agilent Technologies Series 1260, equipped with a C-18 ZORBAX XDB C-18 analytical column. The gradient started at 90/10 (v/v) ultrapure water (with formic acid 25 mM) and acetonitrile (ACN) that progress till 100% ACN in 14 min at a flow rate of 1 mL/min. The UV signal for each compound was: 220 nm for Pentachlorophenol, 230 nm for Terbutryn, 240 nm for Chlorofenvinphos and 285 nm for Diclofenac. Limits of quantification (LOQ) of Pentachlorophenol, Terbutryn, Chlorofenvinphos and Diclofenac were 4.4, 3.8, 3.2 and 3.4 µg/L respectively. 9 mL of sample was filtered with a 0.22 µm PTFE filter. The filter was washed with 1 ml of ACN to extract any absorbed compound, mixing it with 9 mL of filtered sample before injection in HPLC. Inyection volume was 100µL. Mineralization of MCs (TOC results) was not determined because treating MCs at 200 µg/L is out of the analytical limits of this technique and/or not realible due to the presence of other organics.

Fe^{3+}:EDDS concentration was measured by liquid chromatography (HPLC Agilent 1100 Series) by using an Ion-Pair method with a reversed-phase column (Luna C18, 150X3 mm, 5µm particle size) [32].

2.3. Pilot plants and experimental procedures

2.3.1. Solar photo-Fenton treatment

Compound parabolic collector (CPC) solar pilot plant used for solar photo-Fenton experiments is located at Plataforma Solar de Almería (latitude 37ºN, longitude 2.4ºW). Table 1 describes the characteristics of CPC photo-reactor. A global solar UV radiometer (KIPP&ZONEN, Model CUV 3) tilted 37º as the CPC reactor quantifies the solar ultraviolet radiation (UV). More details can be obtained in [33]. Solar accumulated UV energy has been quantified according to Eq. 1 where:

$$Q_{UV,n+1} = Q_{UV} + \Delta t_n \cdot \overline{UV}_{G,n+1} \cdot \frac{A_i}{V_T} \; ; \qquad \Delta t_n = t_{n+1} - t_n \qquad (1)$$

t_n: experimental time for each sample.

UV: average solar ultraviolet radiation measured during the period Δt_n.

A_i: illuminated area (m^2).

$Q_{UV,n}$: accumulated energy per unit of volume (kJ/L) at t_n.

Solar photo-Fenton experiments at near neutral pH would require the addition of a complexing agent, such as EDDS, for maintaining iron in solution [34]. In such a case, 5.5 mg/L of Fe^{3+} was complexed with EDDS maintaining the molar ratio 1:2 Fe^{3+}: EDDS as better operating condition according to Miralles-Cuevas et al. [35]. For the complex formation in the dark, iron was dissolved in the minimum amount of acidified water, and then the required amount of EDDS was added. The complex was immediately formed showing a strong yellow color.

2.3.2. Solar photo-electro-Fenton treatment

Solar photo-electro-Fenton pilot plant consisted of four electrochemical cells acquired from ElectroCell coupled to a CPC photo-reactor. Each cell was composed by an anode made of a boron-doped diamond thin film on a niobium mesh (Nb-BDD) and a carbon-polytetrafluoroethylene (PTFE) GDE as the cathode, both with 0.01 m^2 effective area. The GDE cathode was fed with compressed air (ABAC air compressor, 1.5 kW) at 10 L/min. The experiments were carried at a constant *j* using a Delta Electronika power supply limited to 70 V and 22 A.

Solar CPC photoreactor combined with the electro-Fenton plant is described in Table 1, it consists of 10 borosilicate tubes mounted in an aluminum frame on a platform tilted 37º (PSA, 37º N, 2.4º W). Scheme of the pilot plant is shown in elsewhere [36]. The working volume was 30 L for electro-Fenton (EF) assays.

Accumulated UV energy in each experiment was obtained by using equation 1 (as explained for solar photo-Fenton experiments previously).

Experiments were developed by using 50 mM solution of Na_2SO_4 (Sigma –Aldrich) as supporting electrolyte dissolved on demineralized water. First of all, Fe:EDDS complex prepared as described above, was added in a 1:2 ratio. Then, 200 µg/L of each target contaminant was also added directly to the recirculation tank of the pilot plant. After homogenizing the solution for a time equal to 3 times the recirculation of the total volume, a sample was taken to check initial MCs concentration. After this, the experiment started and samples were taken in intervals of 5 minutes during the first 30 min, then every 15 min till 90 min of test and finally every 30 min.

2.3.3. Ozonation treatment

The ozonation system is an Anseros PAP-pilot plant (Ansero Klaus Nonnenmacher GmbH, Germany) for batch operation. The reactor is a 20 L column with an inlet O_3 diffuser and a gas dehumidifier in the sampling point. It was also equipped with an ozone destroyer, two nondispersive UV analyzers (Ozomat GM-6000-OEM) to measure inlet and outlet ozone gas concentration, a flow-meter for inlet air regulation, an oxygen generator (Anseros SEP100) and an ozone generator (Anseros COM-AD02).

During experiments with ozonation, the mix of four MCs was added directly from stock solution into the reactor. The samples were collected every 5-10 min and residual ozone was removed with N_2 to stop the reaction. The ozone generator was set at 20% power with a constant 1.5 g O_3/h production. Ozone gas was measured at the system inlet ($\mathrm{C_{O_{3,i}}}, \mathrm{g/Nm^3}$) and outlet ($\mathrm{C_{O_{3,o}}}, \mathrm{g/Nm^3}$), so that ozone consumption of each sample $\mathrm{O_{3cons,n}}, \mathrm{g/L}$ could be calculated by Eq. (2) taking the inlet air flow $\mathrm{Q_a}$ $\mathrm{Nm^3/h}$ of 0.06 $\mathrm{Nm^3/h}$ and ozone consumption in the previous sample into account:

$$O_{3cons,n}\left(\frac{g}{L}\right) = O_{3cons,n-1} + \frac{Q_a \cdot \left(C_{O_{3,i,n}} - C_{O_{3,o,n}}\right) \cdot (t_n - t_{n-1})}{V_r} \qquad (2)$$

In some experiments, the ozonation pilot plant was combined with a solar CPC photo-reactor (different to that described in section 2.3.1.) for the assessment of Solar/Fe^{3+}/O_3/H_2O_2 process (see Figure 1). Table 1 presents the characteristics of the CPC photo-reactor used. Eq. 1 was used to determine $Q_{UV,n}$.

Figure 1 - Ozonation Pilot plant

Table 1. CPC solar photo-reactors used in the differenttestedprocesses

PARAMETER	photo-Fenton	photo-electro-Fenton	Solar/Fe^{3+}/O_3/H_2O_2
Illuminated volume	22 L	23 L	68.2 L
Reactor area	3.08 m^2	2 m^2	2 m^2
Glass tubes diameter	32 mm	45 mm	75 mm
CPC inclination	37º	37º	37º
Total volume	39L	75 L	120 L

3. Results and discussion

3.1. Photo-Fenton and photo/electro-Fenton processes

3.1.a. Solar photo-Fenton and photo-electro-Fenton comparison

Elimination of target MCs (200 µg/L of each) in demineralized water by solar photo-Fenton process under well-known operating conditions [34]~~,~~ at pilot plant scale and at near neutral pH by using Fe:EDDS 1:2, and 0.1 mM of Fe^{3+}, was first evaluated (Figure 2 shows the degradation profile of the sum of MCs). Diclofenac and Pentachlorophenol were completely degraded after a solar-UV accumulated energy of 0.83 kJ/L (after around 5 minutes of solar illumination) and requiring 31 mg/L of H_2O_2, though Chlorfenvinphos and Terbutryn were more resistant and 85% of elimination was attained after 11 kJ/L (corresponding to around 60 minutes of solar illumination) and a H_2O_2 consumption of 60 mg/L. Final pH at the end of the experiment was 6.

The degradation of MCs was also tested by electro-oxidation in demineralized water containing the required electrolyte, in this case Na_2SO_4 (50 mM), in the pilot plant described in section 2.3.2. Previously reported results, optimized this experimental system for in-situ electrogeneration of hydrogen peroxide [36] and 73.6 mA/cm^2 was selected with a hydrogen peroxide production rate between 30 and 60 mg/min. However, though optimum pH obtained in the previous work was 3, in this occasion it was selected to operate at circumneutral pH. The following paragraphs discuss results obtained under these conditions checking the stability of the complex Fe:EDDS in the dark and applying SPEF (Figure 2).

Before applying solar photoelectro-Fenton (SPEF) process by using also Fe:EDDS 1:2 at circumneutral pH, it was required to check the stability of the complex Fe:EDDS in the dark during electro-oxidation. To our knowledge, no previous study on the use of EDDS in electro-oxidation systems has been reported. Therefore, an electro-Fenton (EF) test was performed at 73.6 mA/cm^2 and pH 6 for 240 min monitoring Fe:EDDS complex at 0.1 mM of Fe^{3+}. During 120 minutes of treatment, the complex remained stable and from then it began to decay. After 180 minutes (14.9 kWh/m^3) Fe:EDDS complex showed a 18% of decay and 40% at the end of the assay, with an energy consumption of 20 kWh/m^3. In consequence, 180 minutes were considered to be the maximum process time for the rest of assays developed in the study in order to guaranty the stability of the complex and so at least 80% of Fe^{3+} would be present as Fe:EDDS.

Then, SPEF experiment was carried out at a current density of 73.6 mA/cm^2 and 0.1 mM of Fe^{3+} with Fe:EDDS 1:2 (Figure 2). It is important to highlight that the exposure of the complex to sunlight promotes its degradation. Accordingly to this, iron in solution decreased from 0.1 mM to 0.062 mM after 60 minutes of SPEF. Despite this, after 180 minutes, with 5.1 kWh/m^3 of energy consumption, 77.5% of MCs degradation was achieved in the electro-oxidation process. At that point, iron dissolved in the system was only 0.036 mM, confirming the instability of the complex and the degradation of EDDS.

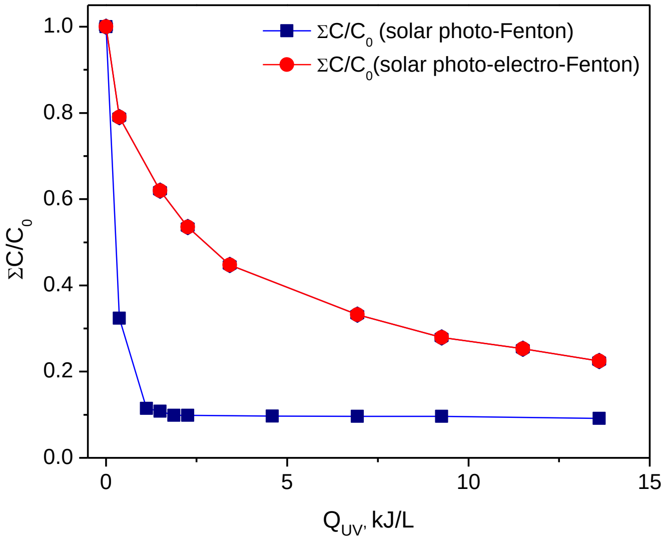

Figure 2. MCs degradation ($\Sigma C_0 \approx 800$ µg/L) by SPEF (*j* 73.6 mA/cm^2) with 0.1 mM of Fe^{3+} at neutral pH by adding Fe:EDDS 1:2 in demineralized water (Na_2SO_4 50 mM in SPEF).

SPEF treatment showed less efficiency in MCs removal compared with solar photo-Fenton process. Indeed initial reaction rate, corresponding to the degradation of the sum of MCs, was 77.8 µg/L.min for solar photo-Fenton against 10.6 µg/L.min for SPEF process. Both experiments were carried out in demineralized water though the presence of the electrolyte (Na_2SO_4 50 mM) required for the adequate performance of SPEF provoked lower removal rate in SPEF compared with solar photo-Fenton. Generation of hydroxyl radicals was lower because of (i) the formation of sulfato-Fe(III) complexes and (ii) scavenging of hydroxyl radicals by sulfate and the formation of sulfate radicals which are less reactive than HO radicals. In addition, the absence of an external source of hydrogen peroxide was also responsible of the removal rate slow down and therefore, it must be stated that cathodic electrogeneration of hydrogen peroxide governed MCs removal rate. Using higher amount of hydrogen peroxide, a better performance of the electrochemical cells or advanced concepts and new materials of such cells, could increase SPEF efficiency as H_2O_2 production rate is a key issue in this kind of AOPs.

3.1.b. Electro-Fenton process

EF experiments were also carried out in order to evaluate MCs degradation without combining with solar energy. For that purpose, first, pure anodic oxidation (AO) was carried out at 73.6 mA/cm^2. Afterwards, EF was applied also at 73.6 mA/cm^2 in the presence of Fe^{3+} but testing different concentrations: 0.1, 0.2 and 0.5 mM (Figure 3 and

Table 2). In addition, and regarding the current density *(j)*, 30, 73.6 and 100 mA/cm^2 were tested at Fe^{3+} 0.1 mM. Lowest current density slowed down the generation of hydrogen peroxide, though it also showed the lowest energy consumption (2.2 kWh/m^3) for attaining 80% degradation of MCs after 150 minutes of EF treatment. This result brought to light the necessity of increasing *j* in order to improve the ratio between energy consumption and MCs elimination. Nevertheless, when applying the highest *j* value (100 mA/cm^2), EF treatment time was significantly reduced to 60 min due to the larger oxidizing power of the anode and the higher production of hydrogen peroxide that favored the Fenton reaction and consequently, MCs elimination. Nevertheless, that positive result was countered by the important increase detected on the related energy consumption, attaining 6.5 kWh/m^3. Best compromise between MCs degradation and energy consumption was obtained when applying *j* of 73.6 mA/cm^2, which did not entail a significant increase in current density, compared with 30 mA/cm^{2,} but more than 80% degradation after 45 minutes of EF was reached with an energy consumption of 3.45 kWh/m^3.

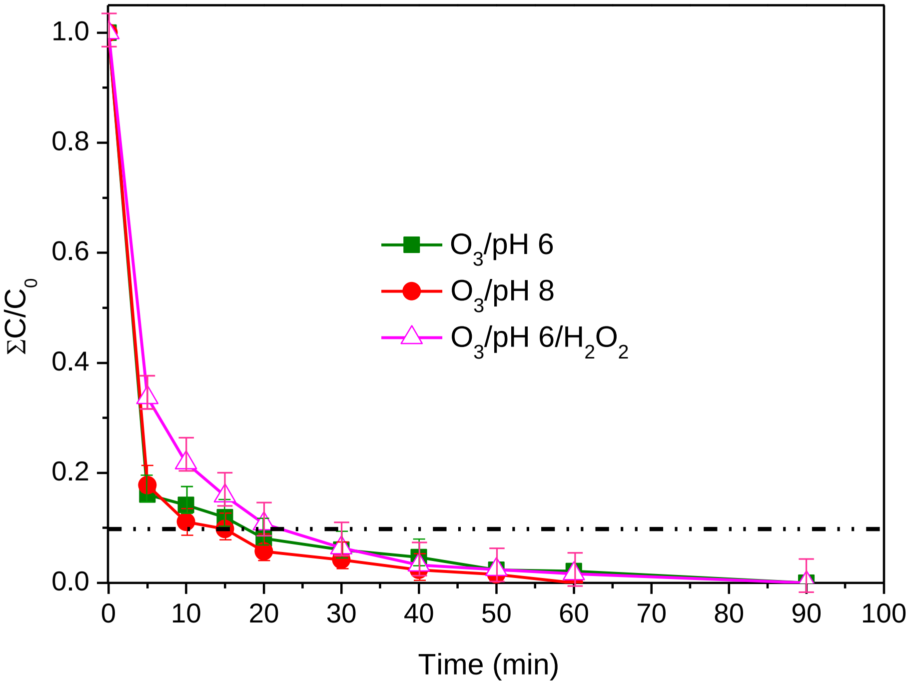

Figure 3. MCs degradation ($\Sigma C_0 \approx$ 800 µg/L) by AO and EF (Fe:EDDS, 1:2) at neutral pH in demineralized water (Na_2SO_4 50 mM in SPEF).

It must be noticed that an increase in Fe^{3+} concentration from 0.1mM to 0.2 and 0.5 mM at 73.6 mA/cm^2 in the EF treatment always involves an increase in EDDS amount for maintaining the ratio Fe:EDDS of 1:2. In consequence, a higher concentration of EDDS would mean also higher organic carbon in solution that would act as radicals' scavenger. This fact explains the increase on the energy required for attaining 80% of MCs removal associated to a higher concentration of Fe^{3+} (Figure 3). However, when Fe^{3+} was increased from 0.2 mM to 0.5 mM, the energy demand was lower than when using Fe^{3+} 0.2 mM, although still higher than at Fe^{3+} 0.1 mM. At higher Fe^{3+} concentration, dark-Fenton process was so fast that all hydrogen peroxide generated was consumed rapidly.

Finally, the AO test at *j* 73.6 mA/cm^2 corroborated that higher treatment time and energy consumption was required compared to EF process with 0.1 mM of Fe^{3+}. It should be highlighted that AO was very effective for Pentachlorophenol, Terbutryn and Diclofenac removal, but not for the more recalcitrant MC, Chlorofenvinphos (Table 2). AO does not require iron removal after the treatment, which would simplify electrooxidation operation.

Table 2. Summary of the results obtained in the electro-oxidation pilot plant to attain 80% of total MCs degradation at pH 6 by using AO or EF (with Fe:EDDS).

	0.1 mM Fe^{3+}			**73.6 mA/cm^2**		
	30 mA/cm^2	**73.6 mA/cm^2**	**100 mA/cm^2**	**AO**	**0.2 mM Fe^{3+}**	**0.5 mM Fe^{3+}**
Time (min.)	150	45	60	75	120	180
Energy consumption kWh/m^3	2.2	3.5	6.5	5.0	12.1	8.1
MCs removal (%)						
Pentachlorophenol	87.8	78.8	91.7	100	89	85.8
Terbutryn	66.2	84.2	79.5	84.1	72.1	68.3
Chlorofenvinphos	58.4	57.4	57.3	46.2	61.5	62.9
Diclofenac	100	97.3	100	100	100	100

3.2. Ozonation and solar ozonation systems

3.2.a. Ozonation tests

Ozonation treatment of the target MCs spiked on different types of water (demineralized water, NW and SE) was performed varying pH from 6 to 11 (direct ozonation and indirect free radical oxidation). Initial concentration of each target MC was maintained in 200 µg/L. The effect assessment on H_2O_2 addition (at 1.5 mM) as well as Fenton like reactions by using Fe^{2+} or Fe^{3+}at 0.1 mM, were also carried out. Same operating conditions were evaluated in combination with solar radiation.

Ozonation results in demineralized water at pH 6 and pH 11 showed more than 99% degradation of all contaminants (after 50 minutes of treatment) in both situations. It should be noted that, working at pH 11, ozone consumption was higher (32 mg O_3/L) than when working at lower pH (13 mg O_3/L) due to the reaction of ozone with generated hydroxyl radicals at high pH (Eq. 3). It is important to stress that more oxidizing conditions at pH 11 did not entail higher degradation rates due to the low concentration of MCs. Therefore, pH 11 was disregarded for further tests as indirect free radical oxidation route showed no substantial interest for this application. Lower pH (around 8) was selected instead as it is a normal value for natural water and wastewater containing MCs.

$$O_3 + H_2O_2 \rightarrow HO^{\cdot} + HO_2^{\cdot} + O_2 \qquad (3)$$

Afterwards, ozonation was tested in NW at pH 6 and 8. An increment of the degradation rate and on the consumption of ozone was observed, 14 mg O_3/L at pH 6 and 19 mg O_3/L at pH 8, for attaining more than 99% of MCs degradation (Figure 4). Substantially lower consumption of ozone was required to degrade 90% of MCs (1.8 mg O_3/L at pH 6 and 4.4 mg O_3/L at pH 8). It was clearly observed that higher pH resulted in higher reaction rates but accompanied with a higher ozone consumption. Consequently, it should be remarked that application of ozone treatment for elimination of MCs must be always tested at pH around 8 (normal pH of natural waters and MWWTP effluents) and not at pH 6. These results are consistent with ozone application at large scale for treatment of MCs in Switzerland, where a specific ozone dose of 1.5-2.5 mg/L is required for 80% of MCs abatement [37]. It is important to highlight that when adding H_2O_2 at natural pH (8), the consumption of O_3 slightly increased to 5 mg/L to degrade >90% of MCs, without an improvement on the MCs elimination rate. The reaction of ozone with of H_2O_2 (peroxone process) rises the generation of $^{\bullet}OH$ radicals [38] but, as in the case of ozonation at pH 11, it did not provoke a better degradation rate due to the low concentration of MCs and so ozone reacted with H_2O_2.

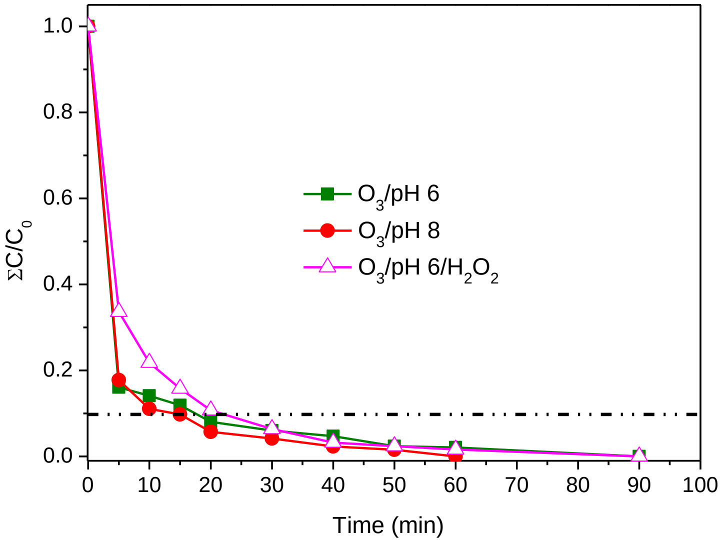

Figure 4. MCs degradation ($\Sigma C_0 \approx$ 800 µg/L) by ozonation in NW at two different pHs and with addition of H_2O_2 (50 mg/L).

After demonstrating the bad performance of ozone at pH 11 for MCs elimination and that the process was efficient at pH close to the typical pH of MWWTP effluents (pH around 8) the final objective was to study if any combination between ozonation and Fenton would be interesting for the enhancement of MCs removal. Figure 5 shows results with SE at natural pH (8) showing a consumption of ozone of 6.4 mg/L to degrade >90% of MCs. In Figure 5, the experimental results obtained in the presence of iron with and without its combination with H_2O_2 are shown. When applying Fe^{2+} or Fe^{3+} (both at 0.1 mM), ozone consumption was 6.6 and 9.6 mg O_3/L, respectively. Recent studies reported that the co-presence of O_3 and Fenton reagents favored the generation of $^{\bullet}OH$ [39]. Experiments with addition of iron to the ozonation system have been carried out to evaluate the direct reaction of ozone with Fe^{2+} and reduction to Fe^{3+} with extra $^{\bullet}OH$ generation according to Eqs. 4-7 [40], but no improvement was observed in the reaction rate or in the ozone consumption. Initial degradation rate was 61.7 µg/L.min for ozonation (pH 8), almost equal to those obtained when Fe^{2+} or Fe^{3+} were added (59.5 µg/L.min and 60.6 µg/L.min, respectively).

$$Fe^{2+} + O_3 \rightarrow Fe^{3+} + O_3^{\bullet-} \quad (4)$$

$$O_3^{\bullet-} + H^+ \rightarrow O_2 + HO^{\bullet} \quad (5)$$

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \quad (6)$$

$$FeO^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \quad (7)$$

When testing ozonization in combination with Fenton process (Fe/H_2O_2) both, consumption of ozone and treatment times, were similar so no significant improvement took place. In addition, initial degradation rates were 58.6 µg/L.min and 50.2 µg/L.min, when adding H_2O_2 to Fe^{2+} and Fe^{3+}, respectively.

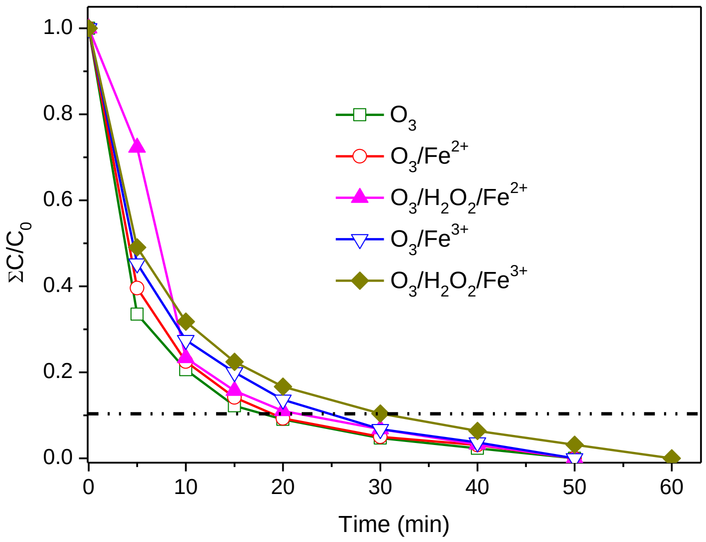

Figure 5. MCs degradation ($\Sigma C_0 \approx$ 800 µg/L) by ozonation in SE at pH 8 with addition of Fe^{2+}, Fe^{3+} (0.1 mM) and H_2O_2 (1.5 mM).

3.2.b. Solar ozonation tests

Finally, the combination of ozone with a solar CPC photo-reactor working at natural pH (8) for the elimination of MCs in SE was performed (figure 6).

As it has been previously reported, dissolved ozone molecules absorb UV light with a peak absorbance at 260 nm and a molar absorptivity of 3292±70 M/cm [41]. Upon the irradiation of UV, the dissolved ozone molecules undergo photolysis reactions to yield hydrogen peroxide [42]. The application of ozone in the presence of solar radiation led to an enhancement of MCs removal as lower consumption of ozone was required. Indeed, to obtain 80% degradation of MCs the consumption of ozone was 0.52 mg/L (O_3), 0.30 mg/L (O_3/Fe^{3+}), 0.23 mg/L (O_3/H_2O_2) and 0.6 mg/L ($O_3/Fe^{3+}/H_2O_2$). The so important reduction in ozone consumption for solar/O_3 compared with results obtained with ozonation in the dark was due to a new source of $^{\bullet}$OH generated under solar UV (λ< 315 nm) from H_2O_2

photolysis as H_2O_2 could be produced by Eq. 8 [43]. The consumption of ozone in solar/O_3/H_2O_2 was still low against an enhancement in the reaction rate. In the cases in which ozone was combined with iron under solar illumination, the contribution of photo-Fenton process was not clear as both ozone consumption and reaction rate were quite similar to solar/O_3 process. It is interesting to remark that during solar treatments, the temperature in the photo-reactor increased (up to c.a. 40º C). This also favored MCs elimination since ozone reaction rates increase with temperature [44].

$$O_3 + H_2O \xrightarrow{h\nu} O_2 + H_2O_2 \tag{8}$$

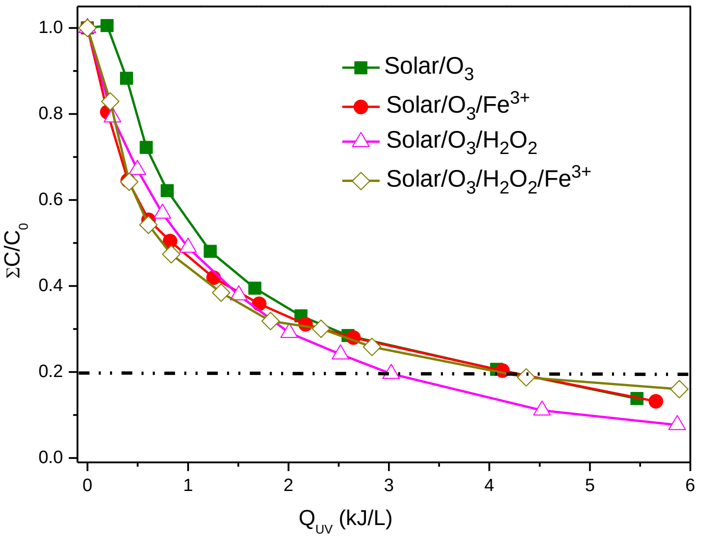

Figure 6. MCs degradation ($\Sigma C_0 \approx$ 800 µg/L) by ozonation combined with a CPC photo-reactor in SE at pH 8 with addition of Fe^{2+}, Fe^{3+} (0.1 mM) and H_2O_2 (50 mg/L).

It is important also to stress that initial degradation rate did not improve when combining ozone with solar radiation, as it decreased to 28.3 µg/L.min. Similar values where obtained when Fe^{3+} or H_2O_2 were added separately (24.7 µg/L.min and 24.9 µg/L.min, respectively), or even combining both reagents, giving 30.4 µg/L.min of initial degradation rate. These results show that the main advantage in combining ozonation with solar radiation lays on the significant reduction on ozone consumption.

4. Conclusions

It has been demonstrated that Fe:EDDS complex is able to maintain iron in solution for EF and SPEF treatments and so, it can be considered a useful tool for performing electrochemical processes at circumneutral pH.

SPEF treatment showed less efficiency compared with solar photo-Fenton process at circumneutral pH due to the hydroxyl radicals' scavenger effect provoked by the need of adding an electrolyte in wastewater with low ionic strength. SPEF was also less efficient than EF treatment due to a limited electro-generation of H_2O_2. An improvement on the in-situ production rate of hydrogen peroxide would enhance the SPEF process. A better performance of target MCs elimination was obtained when applying EF with Fe^{3+} at 0.1 mM. These results bring to light the interest on EF, SPEF and electro-oxidation processes in general as a suitable technology for MCs removal only when they are contained in specific wastewaters characterized by high conductivity values, such as membrane processes rejection streams.

Finally, Ozonation treatment demonstrated to be successful in almost the complete removal of studied MCs present in different water matrices at different pH in dark conditions. However, it is important to stress that higher pH values increased ozone consumption due to the very low concentration of contaminants to be oxidized, and the reaction of generated H_2O_2 with O_3.

In general, the removal of MCs does not need the generation of high concentrations of hydroxyl radicals, this is why the combination of ozone with other treatments based on the addition of iron and hydrogen peroxide in the dark did not show an enhancement in the efficiency of the process. Nevertheless, the application of ozone in the presence of solar radiation led to an improvement on the MCs degradation and a reduction on ozone consumption compared with ozonation in the dark. This interesting result must be explored in detail and optimized taking into account economic aspects, such as electricity requirements and the consequent depletion of ozone generation costs.

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