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Title: Assessment of solar raceway pond reactors for removal of contaminants of emerging concern by photo-Fenton at circumneutral pH from very different municipal wastewater effluents

Article Type: Research Paper

Keywords: Chloride radicals; Sulfate radicals; EDDS; Micropollutant; Organic matter; Solar photocatalysis

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Abstract: This paper presents for the first time the treatment of contaminants of emerging concern (CECs) in a systematic study in different municipal wastewater treatment plants (MWWTPs) of the Mediterranean area, more than 1000 km away. Solar photo-Fenton process at neutral pH with Fe3+-EDDS has been demonstrated to be very efficient under controlled conditions and must be validated in realistic and variable conditions such as real MWWTP effluents of different composition. To this end, CEC removal was studied in effluents from 5 treatment plants in the Mediterranean area of Spain, the inorganic and organic composition varying in the range 161 - 641 mg L-1 (sulfate), 133 - 538 mg L-1 (chloride) and 10 - 20 mg L-1 (dissolved organic carbon). More than 45 CECs were quantified in MWW and results showed that the effect on CEC elimination of the concentration of anions and organic matter was interfered by the nature of the organic matter. However, origin and composition of MWW was not critic for attaining >80% degradation of CECs after 15 min of reaction. Moreover, conventional anions (sulfate, chloride) had a positive effect on CEC degradation rate. This paper demonstrates the consistency and predictability of the solar photo-Fenton process at circumneutral pH for treating CECs in simple and cheap photoreactors.

Response to Reviewers: Response to reviewers

Reviewers' comments:

Reviewer #1: You have included all my suggestions in your revised manuscript. You have also calculated cost effectiveness of this project. It would be more attractive to the reader if you include few more lines on the "need of this research" as pointed out by one of the reviewers.

Response:

Following reviewer´s comment, a new paragraph at the end on the introduction section has been included to emphasize there are no studies comparing different real effluents and this assessment is crucial to predict process applicability and robustness as well as identifying the factors with highest impact on results when comparing different water matrices (Page 6).

Reviewer #4: I see the authors well responded to most of the reviewer comments. They also defend their manuscripts against some controversial points. Although I still disagree with some of their defense, I think the manuscript could be published as long as these points are well discussed. So the authors need to make further improvements to better address the comments

Response:
Following reviewer´s comment, the manuscript has been revised to better address the main comments.

Comment:
- It is important to monitor the intermediates that formed during the oxidation of the considered CECs. May be additional irradiation time is required for complete degeneration.

Response:
This issue been included in the introduction section of the revised manuscript (Page 4).

Comment:
- The treatment of wastewater at neutral condition is a merit, however it is preferred (If it is still possible) to test the performance of photo-Fenton at acidic conditions because faster and more efficient degradation may be attained. If the difference is not significant then it can be reported that the processing under neutral condition is the optimal.

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The efficiency of the photo-Fenton process at its optimal pH (2.8) has been widely demonstrated. However, the need for a previous acidification pretreatment and neutralization post-treatment as well as pH control to ensure that Fe2+ and Fe3+ species exert their catalytic role increases the effluent salinity and treatment costs. A new sentence and reference has been included in the revised manuscript (Page 3)
L. Clarizia, D. Russo, I. Di Somma, R. Marotta, R. Andreozzi, Homogeneous photo-Fenton processes at near neutral pH: A review, Appl. Catal. B: Environ. 209 (2017) 358–371, doi:10.1016/j.apcatb.2017.03.011.

Reviewer #5: Introduction
"There is a large number of publications about solar photo-Fenton",. The authors need to do a better literature review without self citations.

Response:

Following Reviewer #5’s comment we have revised the introduction and included six new references in the revised version of the manuscript (Pages 3, 4 and 6) and three self citations have been removed. Due to the pionering work with RPR, some self citations have no alternative references.

UNIVERSIDAD DE ALMERÍA
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Almería, February 8th 2019

Dear Dionysios Dionysiou,

We thank to the reviewers for their comments, which have been followed indicating the changes (in yellow) made in the revised manuscript with reference CEJ-D-18-13135R1. We trust the response to the reviewers' comments and the revised manuscript fully address the points raised by the reviewers.

We could understand the doubts of the reviewers about many technical aspects of the paper. Indeed, most of their comments were so useful for improving the paper. But we do not agree in any comment related with the "need of this research". We are aware of the research done all over the world about treatment by AOPs of CECs in effluents from municipal wastewater treatment plants and we must point out the following:

1. There is no paper using raceway pond reactors (RPRs) treating CECs in real effluents including a deep evaluation of all CECs by LC/MS. RPR are well-known photoreactors for algae culture, but only recently applied in solar AOPs.
2. There is no paper focused on the solar photo-Fenton treatment of several real effluents from FIVE different locations and water characteristics.
3. There is no paper where AOPs (and not only photo-Fenton) have been applied to different real effluents, including a deep evaluation of all CECs. Only so interesting papers dealing with the Switzerland pioneer experience based on implementation of a new Water Protection Act in 2016, which regulates the removal of CECs from urban wastewater. But the Switzerland pioneer experience is based on ozonation and active carbon.
4. There is no paper focused on solar photo-Fenton and including treatment costs based on the results obtained with FIVE real effluents in RPR.

Therefore, from our point of view, impact and novelty of the paper have no doubt.

We look forward to your acceptance of the revised submission. Thank you for assisting with this manuscript.

Yours sincerely,

José Antonio Sánchez Pérez

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Graphical Abstract

***Highlights (for review)**

- Photo-Fenton with Fe^{3+}-EDDS removes CECs regardless water composition
- 80% CEC removal after 15 min in 5 real WWTP effluents
- Nature and not the load of organic matter has impact on CEC removal
- Short reaction time to remove CECs encourages continuous flow operation
- Mechanism developed with synthetic effluent explains reactions in real wastewater

Assessment of solar raceway pond reactors for removal of contaminants of emerging concern by photo-Fenton at circumneutral pH from very different municipal wastewater effluents

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Abstract

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1. Introduction

In many regions of the world with water scarcity, the reuse of effluents from wastewater treatment plants (WWTP) becomes an increasingly widespread and desirable alternative. In recent years, the presence of contaminants of emerging concern (CECs) in WWTP effluents has become evident, thanks to the development of advanced analytical techniques capable of detecting contaminants at a very low concentration [1–3]. Within these techniques, the direct injection-based method by ultra-high-performance liquid chromatography quadrupole-linear ion trap analyzer (LC-QqLIT-MS/MS) stands out for being a fast and very sensitive method [4]. Contaminants such as pharmaceuticals, antibiotics, biocides, pesticides and personal care products are detected at low concentrations ($\mu g\ L^{-1}$ – $ng\ L^{-1}$), but their accumulation in the ecosystems can cause negative effects on the aquatic organisms, crops (if the water is re-used for irrigation), and consequently, on human health [5,6]. Conventional WWTPs are not designed to eliminate this type of contaminants, and the legislation is becoming stricter with its discharge [7,8]. Therefore, an additional treatment is necessary for the removal of these compounds, which may be the advanced oxidation processes (AOPs), mainly based on the generation of $HO^{\bullet}$ radicals with a high oxidative potential to degrade a wide variety of organic compounds [9,10]. One of the most efficient AOPs is the photo-Fenton process, which consists of the generation of hydroxyl radicals through the reaction between Fe^{2+}/Fe^{3+} and H_2O_2 under UV radiation. This process has been widely studied at its optimum pH, 2.8 [11,12]. However, the need for a previous acidification pretreatment and further neutralization before reusing or discharging as well as pH control to ensure the catalytic activity of iron species increases the effluent salinity as well as the costs of the process [13].

To deal with these drawbacks, the current studies are focused on the operation at neutral pH and the use of low-cost reactors, such as raceway pond reactors (RPRs). These reactors, consisting of two open channels through which water is recirculated, are provided with a paddle wheel connected to an engine to vary the flow conditions. Furthermore, the liquid depth can be changed according to the availability of UV radiation [14]. Previous works show that high CEC removal efficiencies are achieved, both in synthetic municipal and industrial wastewater, in RPRs with different liquid depths (5 - 15 cm) [15,16]. Indeed, they are more efficient in reference to treatment capacity than the conventional tubular reactors with compound parabolic collectors (CPCs) [15,17]. To carry out the process at neutral pH, the use of EDDS, a biodegradable chelating agent which complex iron and avoid its precipitation, has been widely studied [18–21]. This Fe^{3+}-EDDS complex stands out for its high absorptivity, which allows high removal rates to be achieved at short reaction times [16,22,23]. As for the transformation products (TPs) formed during the oxidation of the CECs, additional irradiation time may be required for complete degradation. Indeed TPs products of some single CECs (spiked at concentration in the range of a few mg/L) after photo-Fenton treatment have been recently reported [24,25]. However, it is not technically possible to quantify TPs generated from dozens of parent compounds found in real secondary effluents at concentration level of ng/L along with tens of mg/L of natural organic matter and other organic compounds, preventing from any reliable study about TPs. As a detailed evaluation of CEC TPs is not possible, studies are focused on environmental impact of TP discharge. Reported studies show the potential phytotoxicity and cytotoxicity of the treated wastewater is attenuated, and the androgenic/glucorticoid activity and estrogenicity are removed after the treatment with Fe^{3+}-EDDS [26].

When working with real MWWTP effluents, the variability of water composition, as well as the lack of analytical techniques to determine all the matter present in the water, hinders the study of the process. Among the ions, HCO_3^-/CO_3^{2-}, chloride and sulfate can have an important effect on the process. Concerning the HCO_3^-/CO_3^{2-} ions, its effect is negative since they act as a scavenger of hydroxyl radicals [27]. As for chloride and sulfate, the corresponding radicals could be formed but with oxidation potentials lower than that of hydroxyl radicals. Otherwise they can contribute to the oxidation of contaminants, since $SO_4^{\bullet-}$ reacts with Cl^- generating $Cl^\bullet$, and finally Cl^- reacts with the generated $Cl^\bullet$ yielding $Cl_2^{\bullet-}$, which exhibits a higher reactivity with organic pollutants than with other species [28]. Nonetheless, both ions can retard the efficiency of the process by forming complexes with iron and also by scavenging the $HO^\bullet$ radicals [29–31].

Previous experiments have shown that it is possible to degrade CECs in a MWWTP effluent with a Fe^{3+}-EDDS molar ratio of 1:2 and H_2O_2 in CPC photoreactors [32]. The drawback of working at a Fe^{3+}-EDDS ratio of 1:2, instead of 1:1, is not only the increase in operating costs, but the concentration of dissolved organic carbon (DOC) added by the EDDS to the water is doubled. When working with 0.1 mM Fe^{3+}-EDDS at a ratio of 1:1, DOC added to the water is 12 mg L^{-1} being DOC content of MWWTP around 20 mg L^{-1}. For instance, taking into account the daily emission limit for DOC to surface waters established by the Andalusian Regional Government, 45.9 mg L^{-1} [33], this limit could be exceeded when working at a Fe^{3+}-EDDS ratio of 1:2. Recently, the efficiency of using Fe^{3+}-EDDS at 1:1 molar ratio for acetamiprid removal, a neonicotinoid, by photo-Fenton process with synthetic secondary effluents has been demonstrated [16].

In this regard, among the great number of publications on photo-Fenton only a few are related to microcontaminant removal in wastewater, most of them using demineralized water or synthetic wastewater [34-36]. Working under these conditions is necessary to understand the phenomenology of the process and the reaction mechanisms. Then, the results must be validated under real conditions. Real wastewater is a very complex and variable water matrix and there is a lack of papers dealing with the removal of CECs in real WWTP effluents, as recently reported not only on photo-Fenton process, but also on advanced oxidation processes [37]. Nonetheless, no studies comparing different real effluents have yet been reported and this assessment is crucial to predict process applicability and robustness because results can largely change from one case to another due to real water variability.

The main objective of this study was to determine if photo-Fenton best operating conditions developed during several years of experimentation with model and real effluents are suitable for treating MWWTP effluents of very different composition. Additionally, identifying the factors with highest impact on results when comparing different water matrices is of paramount interest. Experiments were carried out at neutral pH, with 0.1 mM Fe^{3+}-EDDS at 1:1 molar ratio, in secondary effluents from five MWWTPs (see Table 1) located in different areas of Spain more than 1000 km away, with variability in salinity (conductivity 0.9 up to 2.2 mS cm^{-1}) as well as in organic matter (DOC 10 – 20 mg L^{-1}). This paper is aimed at gaining know-how about the effect of effluent composition on CEC removal kinetics and process efficiency.

2. Materials and methods

2.1. Chemicals

Ferric sulfate (75%), hydrogen peroxide (33%), hydrochloric acid (37%) and acetic acid were obtained from Panreac (Barcelona, Spain). Sodium formate was acquired from Merck Millipore (Darmstadt, Germany). Ultrapure water was generated with a Millipore Direct-Q® Ultrapure Water System (Bedford, MA, USA) (18.2 MΩ cm^{-1} resistance and 2 mg L^{-1} total organic carbon). Methanol (MeOH), acetonitrile (AcN) and formic acid (purity, 98%) were HPLC grade and supplied by Honeywell-Riedel-de Haën (Seelze, Germany). Ethylenediamine disuccinic acid (35%), titanium (IV) oxysulfate, tetrabutylammonium bisulfate, sulfuric acid (99%), formic acid (98%), ascorbic acid, o-phenantroline and methanol were purchased from Sigma-Aldrich (Steinheim, Germany). All high purity analytical standards (purity >97%) were also purchased from Sigma-Aldrich comprising a group of CECs including pharmaceuticals, antibiotics, pesticides and some of their metabolites. ^{13}C-caffeine (Sigma-Aldrich) was used as injection standard.

For the determination of CECs by LC–MS/MS analysis, individual stock solutions of each compound were prepared in MeOH or AcN at 1000 mg L^{-1} and stored in amber glass vials at −20 °C. Stock standard solutions containing the compounds were prepared by mixing and diluting the individual stock solutions. A working solution containing all the analytes was prepared daily from the stock solution at 1 μg mL^{-1} in AcN.

2.2. MWWTP effluents

The experiments were carried out in secondary effluents from MWWTPs located in different areas of Spain: El Bobar (Almeria city, southeast of Spain), El Toyo (Almeria province), El Ejido (Almeria province), Alcoy (Alicante province, east of Spain) and Girona (Catalonia, northeast of Spain). The plants have a capacity of 315000, 52000, 108000, 120679 and 206250 population equivalents, respectively. El Bobar and Girona WWTPs treat wastewater from the city and nearby villages. Due to its location, El Ejido WWTP treats wastewater from a nearby hospital and it is placed in an area surrounded by an intensive greenhouse agricultural production. In all WWTPs the water line consists of a pretreatment (roughing filtration, desanding and degreasing), a primary treatment (primary decantation), a conventional activated sludge biological treatment (except in El Toyo WWTP provided with extended aeration) followed by a secondary decantation. Furthermore, all the effluents (except El Ejido wastewater) were collected after filtration through sand filters.

In the case of the MWWTP effluents from Alcoy and Girona, once the water was collected from the MWWTP, it was refrigerated and transported to Almeria within the following two days. In this way, all the effluents were used in the experimentation within the same week they were collected. Due to HCO_3^-/CO_3^{2-} ions inhibit CEC degradation, the inorganic carbon (IC) was reduced to around 15 mg L^{-1} by adding H_2SO_4 prior to the experimentation. In this way, the effect related to the scavenger effect of CO_3^{2-}/HCO_3^- was the same in all the effluents, thus avoiding interferences. Table 1 shows the characteristics of the effluents before the treatment. The highest concentration of Chemical oxygen demand (COD) was 58.3

mg L^{-1}. As there was no mineralization, COD was not reduced after the treatment. Indeed, it increased around 20 mg L^{-1}, mainly due to the DOC added by the EDDS to the water. This is not a drawback, since the limit for COD discharge established by the Andalusian Regional Government is 138 mg L^{-1} [33]. Regarding the anionic content, sulfate and chloride were the most abundant anions in all the effluents (sulfate ranged from 161 to 641 mg L^{-1} and chloride from 133 to 538 mg L^{-1}). To study the possible effect of these anions, effluents were classified according to sulfate and chloride concentration level: effluent from El Ejido = high-level, effluent from El Bobar = medium-level A, effluent from El Toyo = medium-level B, effluent from Girona = low-level A and effluent from Alcoy = low-level B.

2.3. Experimental set-up

The experiments were carried out in outdoor conditions at the Solar Energy Research Center (CIESOL) located in Almeria (36°50′17″N, 02°27′35″W). The volume capacity to transport water from the MWWTPs to the research center (specifically from Girona and Alcoy) limited the volume of wastewater collected. Consequently, an RPR with 19-L capacity was used. The reactor consisted of a perfectly mixed RPR with 5-cm liquid depth, 22-cm channel width, and a mixing time of 2 min. Concerning the reactants, the experiments were conducted under mild oxidation conditions with 0.88 mM H_2O_2 (30 mg L^{-1}, the minimum concentration to guarantee the conditions of a Fenton-like process and permitting water disposal at the end of the treatment), and 0.1 mM Fe^{3+} (5.6 mg L^{-1}, the optimal concentration reported for photo-Fenton in RPRs [14]), at a Fe^{3+}-EDDS molar ratio of 1:1. These oxidation conditions were demonstrated to be efficient for CEC removal in synthetic secondary effluents [16]. During the reaction time, the temperature and pH were measured with probes connected to a LabJack USB/Ethernet data acquisition device. The pH ranged between 7 and 8 and the water temperature between 22 and 28 °C. Regarding the incident UV radiation, it was measured with a global UV radiometer (Delta Ohm, LPUVA02AV) in the wavelength range 327-384 nm.

All the experiments were replicated and conducted around noon during sunny days, at a global UV radiation comprised between 28 and 35 W m^{-2}. To compare the results, they were normalized to a constant irradiance of 30 W m^{-2}. The illumination time normalized to this radiation was calculated with Eq. (1), well established for kinetic calculations in solar photoreactors [38]:

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \cdot \frac{\overline{UV}_G}{30} \cdot \frac{V_i}{V_T} \qquad \text{Eq. (1)}$$

where t_{30W} is the normalized illumination time, t_n is the experimental time for each sample $(n=1,\ t_{30W}=0)$, $\overline{UV}_G$ is the average global UV irradiance measured during Δt_n $(t_n - t_{n-1})$, V_i and V_T are the illuminated and the total volume of the photoreactor, respectively. Factor $V_i/V_T = 1$ for RPR.

2.4. Chemicals analysis

At each sampling time, two samples were taken from the photoreactor, one for reactant quantification and another for determination of CECs. For the quantification of reagents, the samples were filtered by 0.2-µm nylon filters from Millipore. As for the CECs, 5 mL of sample were taken from the reactor to a 7-mL amber glass bottle (pre-rinsed with ultra-pure water) containing 0.5 mL of AcN. Acetonitrile acts as $HO^{\bullet}$ scavenger, stopping the reaction [39]. Then, an aliquot of this mixture was filtered by 0.22-µm PTFE syringe filters (Aisimo Corporation, London, UK) into a 2-mL injection vial.

Total dissolved iron was spectrophotometrically measured at 510 nm, according to the 1,10-phenanthroline method (ISO 6332). H_2O_2 was determined at 410 nm with titanium (IV) oxysulfate solution (DIN 38 402 H15). For iron, the limit of quantification (LOQ) and the standard deviation (SD) were 4.5 10^{-3} mM and 6.1 10^{-4} mM, respectively. As for H_2O_2, LOQ and SD were 2.9 10^{-2} mM and 4 10^{-3} mM, respectively.

IC and DOC were measured with a Shimadzu-V CPH TOC analyzer (Shimadzu Corporation, Kyoto, Japan), the LOQ being 1 mg L^{-1}.

The Fe^{3+}-EDDS complex was measured by a 1200 Series system consisting of an ultra-high pressure liquid chromatography with diode array detector (UHPLC-DAD) from Agilent Technologies (Waldbronn, Germany). Isocratic elution was used. The organic phase was MeOH and the aqueous phase consisted of a mixture of sodium formiate (15 mM) and tetrabutylamonium hydrogen sulfate (2 mM) in Milli-Q water at pH 4, in a percentage of 95% and 5%, respectively, the flow being of 0.5 mL min^{-1}. The LOQ and the SD were 3.5 10^{-3} mM and 3.5 10^{-4} mM, respectively.

The concentration of anions was determined using ion chromatography Metrohm 881 Compact IC pro (Herisau, Switzerland). The system worked with an anionic column, Metrosep A Supp 7, 250-4.0 mm and 5 µm from Metrohm. The eluent was a solution of Na_2CO_3, and the flow was 0.8 mL min^{-1}, and the LOQ was 0.5 mg L^{-1}.

The CECs were monitored using the protocol previously developed and validated by Campos-Mañas et al. [40]. The direct injection technique was applied (no sample pre-treatment) using a sample volume of 10 µL. Sample dilution (1/10) with water was applied when necessary for an adequate quantification. The analyses were carried out by LC coupled to a hybrid quadrupole lineal ion trap MS analyzer (LC-QqLIT-MS/MS). The instrumentation consisted of an Agilent 1200 LC system (Agilent Technologies, Foster City, CA, USA) and a 5500 QTRAP analyzer (AB Sciex Instruments, Wilmington, DE, USA). Table 2 shows the concentration of the CECs detected at the highest concentrations in the five effluents.

2.5. Cost estimation

A cost estimation of the treatment of real secondary effluents by solar photo-Fenton at neutral pH in RPRs operated in continuous flow mode has been carried out. To this end, a design flow rate of 400 m^3 d^{-1} was set to fulfill the European Urban Wastewater Directive 91/271/EEC [41] which establishes the need of wastewater treatment in agglomerations larger than 2000 population equivalents, the wastewater generated per population equivalent being close to 200 L d^{-1}.

Total costs were estimated as the sum of the operating costs (OC) and the amortization costs (AC). Taxes, staff and land costs were not considered, since they are highly dependent on labour regulation as well as the treatment plant location. Operating costs were estimated by Eq. (2), considering maintenance costs as 2% of amortization costs [42].

$$OC = C_R + C_E + 0.02\,AC \qquad \text{Eq. (2)}$$

Where C_R and C_E are the reactant and energy costs, respectively.

Concerning the unitary reactant cost, industrial price was considered: 0.45 € L^{-1} H_2O_2 (33% w/v), 0.71 € kg^{-1} $Fe_2(SO_4)_3 \cdot H_2O$, 0.1 € L^{-1} H_2SO_4 (98% w/v). In the case of EDDS, 3.5 € L^{-1} EDDS (35% w/v) is the lowest reported cost because no industrial price is available yet. As for energy costs, the price of electricity was considered 0.1 € kW^{-1} h^{-1}. For mixing in the RPR, the unitary power requirement is 4 W m^{-3} [14]. Moreover, the cost of an 18 kW centrifugal pump, for effluent circulation to the reactor, was included, as well as four 50 W pumps for reactant dosing.

Regarding the amortization costs, Eq. (3), the investment cost (I) was referred to the RPR and the pumping systems. The RPR cost was calculated with Eq. (4), the cost per unit area being 10 € m^{-2}. A life cycle (L) of 20 years was assumed.

$$AC = \frac{I}{L} \qquad \text{Eq. (3)}$$

$$C_{RPR} = 10\, A_{RPR} \qquad \text{Eq. (4)}$$

3. Results and discussion

3.1. Effect of water matrix on reagents consumption and on the removal of contaminants of emerging concern

In a previous work, a reaction mechanism for solar photo-Fenton process at neutral pH was proposed and validated in a synthetic secondary effluent. Briefly, the main steps are the following: firstly, the Fe^{3+}-EDDS is photoreduced by UV radiation. Fe^{2+}-EDDS, as an intermediate state before being decomposed to Fe^{2+} and $EDDS^{\bullet 3-}$, reacts with H_2O_2 giving rise to $HO^{\bullet}$ and Fe^{3+}-EDDS. Finally, Fe^{2+} is oxidized by H_2O_2 (classic Fenton) yielding $HO^{\bullet}$ and Fe^{3+}, which instantaneously precipitates as $Fe(OH)_3$. The hydroxyl radicals oxidize CECs, as well as the Fe^{3+}-EDDS, the organic matter, the inorganic carbon and the H_2O_2 yielding their respective oxidation products. All the reactions and more details about the mechanism were previously reported [43].

$$Fe^{3+} - EDDS + h\upsilon \rightarrow [Fe^{3+} - EDDS]^{*} \qquad \text{R. (1)}$$

$$[Fe^{3+} - EDDS]^{*} \rightarrow Fe^{2+} - EDDS + H^{+} \qquad \text{R. (2)}$$

$$Fe^{2+} - EDDS + H_2O_2 \rightarrow Fe^{3+} - EDDS + HO^{\bullet} + HO^{-} \qquad \text{R. (3)}$$

$$Fe^{2+} - EDDS \rightarrow Fe^{2+} + EDDS^{\bullet 3-} \qquad \text{R. (4)}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)_3 + HO^{\bullet} + HO^{-} \qquad \text{R. (5)}$$

Concerning the Fe^{3+}-EDDS profiles in the real MWWTP effluents, in all cases the complex totally decomposed after 15 minutes of the reaction, Fig. 1a. Furthermore, the profiles were similar to those obtained in a synthetic effluent at a global average irradiance close to 30 W m^{-2} [16], same as that used for normalizing illumination time according to Eq. 1. This fact shows that complex decomposition depends on the photochemical reactions and its subsequent oxidation with H_2O_2 rather than the water composition, in concordance with the proposed reaction mechanism.

In all cases, some iron remained in solution after complex decomposition. In this case, differences were observed in total dissolved iron profiles between the different MWWTP effluents, Fig. 1b. Whereas the profiles were similar in medium-level A, low-level A and B, the iron precipitated faster in high-level and medium-level B, the fastest precipitation being in medium-level B. It must be mentioned that in medium-level B, the iron profile was similar to that observed in a synthetic secondary effluent [43]. According to the mechanism, total dissolved iron concentration is the sum of the concentrations corresponding to the different species of Fe-EDDS. However, the fact that in the different MWWTP effluents the profiles are different could be related to the formation of other iron complexes, dependent on water composition. Although anions, such as chloride and sulfate can complex iron and therefore keep it in solution, the results show that these differences in iron concentration are not directly related to the concentration of anions, and it could be due to the generation of iron complexes with the organic matter present in the different effluents [44–46]. It should be highlighted that the total dissolved iron profiles are not related to the concentration of DOC, since in high-level (with around 20 mg L^{-1} DOC) the iron precipitated faster than in low-level A and slower than medium-level B (with around 10 mg L^{-1} DOC in both effluents). Therefore it could be concluded that the type of organic matter, which is difficult to determine due to its heterogeneity, structural complexity [47] and variability (between different MWWTP and in the same MWWTP at different hours of the day or seasons) could determine iron in solution.

Concerning H_2O_2 profiles, difference between MWWTP effluents was more significant after Fe^{3+}-EDDS decomposition. During the first minutes of the reaction, in which the complex is present, the H_2O_2 consumption is mainly due to the fast reaction between H_2O_2 and the photoreduced complex. Therefore, H_2O_2 consumption was very similar in the different effluents. However, once the concentration of the complex is low, the reactions of H_2O_2 with the organic matter would compete with those of the photo-Fenton process, substantially lower than during the first minutes as iron in solution was lower. In fact, a slightly higher H_2O_2

consumption can be observed in the high-level effluent, which was the effluent with the highest DOC concentration. It should be noticed that if the iron complexes formed with the organic matter after Fe^{3+}-EDDS decomposition would be photochemically active, it would be reflected in the H_2O_2 consumption profiles: the higher concentration of iron in solution, the higher H_2O_2 consumption. However, Figure 1 shows that there is no direct relationship between consumption of H_2O_2 and the total dissolved iron profiles. In medium-level A, H_2O_2 consumption was lower than in other effluents, while the iron concentration was higher. This phenomenon could be explained by the formation of iron complexes with the organic matter of the medium that could avoid iron photoreduction and its subsequent reaction with H_2O_2 to generate hydroxyl radicals.

Substantial differences were observed in the CEC degradation during the first minutes of reaction. In concordance with the reaction mechanism, CEC removal rate was substantially lower after 15 min of reaction, once the Fe^{3+}-EDDS was decomposed. The pseudo-first order rate constants, Table 3, show that there is no relationship between CEC removal rate and the concentration of organic matter and anions present in the reaction medium. Therefore, although organic matter and anions act as $HO^{\bullet}$ scavengers, degradation of CECs could be mainly affected by organic matter composition. The rate constants obtained in high level and medium-level B effluents (0.23 – 0.38 min^{-1}) are in concordance with the results reported for synthetic secondary effluents doped with 100 μg L^{-1} of the pesticide acetamiprid (a highly recalcitrant CEC), being its pseudo-first order rate constant 0.43 min^{-1} at 30 W m^{-2} of UV irradiance [16].

The highest percentage of removal was achieved in medium-level B (98% after t_{30W}=15 min), despite it being the effluent with the fastest iron precipitation and not the effluent with lower initial concentration. This could be explained by the fact that this effluent came from a MWWTP located in a small area with the lowest population equivalents (52000) in comparison with the other effluents, and its DOC concentration was also low (around 11 mg L^{-1}). As it is known, the lower the DOC, the lower the scavenger effect of hydroxyl radicals. Furthermore, there would be less organic matter to complex the iron, and more iron would be available to contribute to the Fenton reaction once the complex is photoreduced. As for the high-level effluent, it also showed a fast CEC removal (94% of CEC removal after t_{30W}=17 min) despite it being the effluent with the highest total load of CECs. Furthermore, the lower the CEC concentration, the more hydroxyl radicals react with the organic matter instead of oxidizing the CECs. Even so, 87% and 82% of CEC removal was achieved after t_{30W}= 17 and 16 min in low-level effluents, respectively. In medium-level A only 56% of CEC removal was achieved after t_{30W} = 15 min. This effluent corresponds to the MWWTP with the highest population equivalents, despite it not being the effluent with the highest DOC concentration.

Although chloride and sulfate radicals are less reactive than hydroxyl radicals, previous experiments carried out in demineralized water showed that these ions could have a positive or negative effect on the kinetics of the process, depending on the process conditions [27–31]. Therefore, it is interesting to study the effect of the initial concentration of these ions on CEC removal in real MWWTP effluents. In Fig. 2a, it is observed that the CECs removed increased with the concentration of chlorides present in the effluent until 386 mg L^{-1} (Medium level A). This is consistent with reported results which point out that the addition of 350 mg L^{-1}

chloride to the system contributed to accelerate the kinetics of pollutant removal [28]. Nevertheless, from 386 to 481 mg L^{-1} chloride the load of CEC removed was practically the same, whereas the total load removed increased strongly in the effluent with concentration of chlorides of 538 mg L^{-1}. In the case of sulfates, the same effect was observed. From these results, it could be deduced that there is not any detrimental effect of the initial concentration of the main anions on the reaction rate or total load removed, and therefore, on the process efficiency. Within the usual concentration found in natural sweet waters, higher concentration of chloride and sulfate presented higher kinetics.

Concisely, all these results show that the Fe^{3+}-EDDS photo-decomposition does not significantly depend on the secondary effluents composition, but on the photochemical reactions of the process, according to the mechanism already developed with a synthetic effluent and described elsewhere [43]. During the first minutes of the reaction there is not effect of the water composition on the hydrogen peroxide consumption. This is in concordance with the fast reaction between the photoactivated complex and the hydrogen peroxide proposed in the reaction mechanism, giving rise to the fast generation of $HO^{\bullet}$ and most of the CEC removal. Once the Fe^{3+}-EDDS complex is decomposed, an effect of the water composition on the H_2O_2 consumption is observed. Furthermore, there is a remnant of iron in solution as non-photoactive organocomplexes, which do not depend on the organic matter concentration, but on its composition. According to the pseudo-first order kinetics, high degradation rates can be achieved in effluents with a high load of CECs. Although main anions affect the process, there is not any direct relationship between increasing concentration of the anions and a detrimental effect on CEC removal. The composition of the organic matter present in MWWTP effluents is proposed to cause a higher impact on the process than its initial concentration. Overall, CECs were efficiently removed regardless water composition although the kinetics in each type of effluents must be specifically determined case by case.

3.2. CEC removal in the MWWTP effluents

In the five effluents studied, a range from 18 to 45 compounds were identified by LC–MS/MS. These compounds were mainly pharmaceuticals, some pesticides, antibiotics and opioids were also found. The degradation profiles of all compounds over time and the removal percentages in each effluent are shown in Tables S1-S5. Fig. 3 shows the degradation profiles of the six most abundant compounds in each effluent (eleven different CECs). In all cases, the sum of the non-biodegradable metabolites of dipyrone [48] (4-aminoantipyrine,4-acetylaminoantipyrine, 4-formylaminoantipyrine, 4-methylaminoantipyrine), named as DPR-M, represented the highest concentration of CECs (between 33% and 55% of the total load of CECs). Gabapentin, *O*-desmethylvenlafaxine (metabolite of venlafaxine), tramadol and its metabolite *O*-desmethyltramadol were also found with the highest initial concentrations in most wastewaters. DPR-M and tramadol are low-cost analgesics, which can be consumed without medical prescription, and gabapentin and venlafaxine are pharmaceuticals commonly used as anticonvulsant and antidepressant, respectively. Therefore, it is usual to find all these compounds or their metabolites at high concentrations in MWWTP effluents [49,50]. In the case of the high-level effluent, naproxen (anti-inflamatory) was found among the compounds in the highest concentrations. This could be due to the localization of the MWWTP near a hospital. Moreover, theophylline and cotinine, two alkaloids related to the consumption of tea and tobacco, were also often detected.

Despite DPR-M representing the highest load, around 80-100% was removed after a t_{30W} of 15 min in all effluents, except in medium-level A, in which DPR-M was removed 60%. The other five pollutants with the highest initial concentration were removed between 70 and 100% after a t_{30W} of 15 min in all effluents, except in medium-level A, where the percentages were lower again, between 30 and 90%. Therefore, the low percentage of degradation achieved in medium-level A (in comparison with the other effluents) was not due to the degree of recalcitrance of the CECs, since CECs found in the highest concentrations in this effluent were also found and rapidly degraded in other wastewaters. It reinforces the proposed statement that composition of the organic matter present in MWWTP effluents is the key point that governs kinetics under the same treatment conditions.

It is worth mentioning that 88% of the total initial load was removed in the high-level effluent at t_{30W}= 11 min, with a ratio Fe^{3+}-EDDS 1:1 and 0.88 mM H_2O_2 in an RPR. This agrees with the 88% reported at t_{30W}= 8 min for an effluent from the same MWWTP, with a ratio Fe^{3+}-EDDS 1:2 and 1.47 mM H_2O_2 in a CPC reactor [32]. Thus, the results obtained show the similar removal rate in the low-cost RPRs for the treatment of municipal wastewater in comparison with the CPCs.

The average removal of CECs in the five effluents was 83% at a t_{30W} of 15 min. The new Swiss water protection act entered into force on January 2016 and requires WWTPs upgrade within the next twenty years [51]. According to that, CECs need to be removed by 80% relative to the raw wastewater. The treatment target is defined by the elimination of a selection of CECs from a list of twelve defined compounds [52]. So far, few plants are in full-scale operation in Switzerland, either with ozonation or activated carbon treatment and less than 50% CEC removal is expected from the advanced tertiary treatment. But, to date, results about CEC removal are scarce in full-scale. Therefore, even the lowest percentage of removal attained in this work would fulfill these rules.

3.3. Economic assessment

Once the technical feasibility of the process has been demonstrated, an estimation of the treatment cost gives insight of the potential applicability of the treatment. Nonetheless, to carry out a rigorous economic assessment data from demonstration plants are needed. Due to the high percentages of CEC removal achieved at short reaction time, the process should be operated in continuous flow mode at large scale [53]. In this work, only the order of magnitude of the cost was estimated considering the operation of an RPR in continuous flow mode at a hydraulic residence time of 15 min, being long enough to achieve more than 80% CEC removal. The treatment capacity would be 1600 L m^{-2} d^{-1} for the continuous flow operation of a 5-cm deep RPR with 0.1 mM Fe^{3+}-EDDS and 0.88 mM H_2O_2 at 15 min of hydraulic residence time (HRT) for 8 hour a day, the annual average sun hours per day in Almería (Spain) [54]. This estimated treatment capacity is 77% higher than the value reported at acidic pH with 20 min HRT [53]. With these data, the estimated area of the RPR was 250 m^2 to treat 400 m^3 d^{-1}, resulting in an amortization cost of 188 € y^{-1}.

Concerning operating costs, the reactant cost, mainly affected by the high cost of EDDS, represented 94% of the total value (67492 € y^{-1}). Energy cost, mainly affected by wastewater pumping, represented 6%. Maintenance cost was less than 0.1%, thus it could be considered negligible.

Finally, unitary total cost of the treatment was estimated to be 0.46 € m^{-3}. This value is in the reported range for AOPs [55]. Furthermore, it is competitive with the reported costs for the operation of a CPC solar pilot plant at neutral pH with Fe^{3+}-EDDS (in the range 0.71 - 1.31 € m^{-3} for the treatment of 500 m^3 d^{-1}) [56].

This economic assessment is only a rough estimation, based on the scaling of the results obtained in a 19L-RPR operated in batch mode. In future works, the technical feasibility of the process in continuous flow must be demonstrated. Then, from the results obtained on a larger scale, the economic feasibility could be evaluated. Furthermore, operating cost could be strongly reduced by using chelating agents cheaper than EDDS, such as natural complexing agents, which encourages to continue the study of the process at neutral pH.

4. Conclusions

As far as authors known, the efficiency of the photo-Fenton process for treating MWWTP effluents of very different composition has been demonstrated for the first time. Using a low-cost RPR, more than 80% removal of total load of contaminants of emerging concern was achieved regardless the origin of the secondary effluent in less than 15 min of treatment. No dependence of the photo-Fenton process with the inorganic components of secondary effluents was found, but results show that effluents with high load of chloride or sulfate can contribute to the improvement of the process efficiency. The nature (and not the load, at least until 20 mg L^{-1}) of the organic matter has a great effect on CEC degradation. Composition of the organic matter present in MWWTP effluents is the key point that governs kinetics under given treatment conditions (iron and EDDS concentration, H_2O_2 dose, photoreactor design). It should be highlighted that the results obtained in different real MWWTP effluents can be explained based on reaction mechanisms developed under controlled conditions with synthetic effluents. Finally, the short reaction time to reach substantial removal of CECs and the estimated cost in the range reported for AOPs encourage the study of the process in continuous flow.

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Assessment of solar raceway pond reactors for removal of contaminants of emerging concern by photo-Fenton at circumneutral pH from very different municipal wastewater effluents

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Abstract

This paper presents for the first time the treatment of contaminants of emerging concern (CECs) in a systematic study in different municipal wastewater treatment plants (MWWTPs) of the Mediterranean area, more than 1000 km away. Solar photo-Fenton process at neutral pH with Fe^{3+}-EDDS has been demonstrated to be very efficient under controlled conditions and must be validated in realistic and variable conditions such as real MWWTP effluents of different composition. To this end, CEC removal was studied in effluents from 5 treatment plants in the Mediterranean area of Spain, the inorganic and organic composition varying in the range 161 - 641 mg L^{-1} (sulfate), 133 - 538 mg L^{-1} (chloride) and 10 - 20 mg L^{-1} (dissolved organic carbon). More than 45 CECs were quantified in MWW and results showed that the effect on CEC elimination of the concentration of anions and organic matter was interfered by the nature of the organic matter. However, origin and composition of MWW was not critic for attaining >80% degradation of CECs after 15 min of reaction. Moreover, conventional anions (sulfate, chloride) had a positive effect on CEC degradation rate. This paper demonstrates the consistency and predictability of the solar photo-Fenton process at circumneutral pH for treating CECs in simple and cheap photoreactors.

Key words: Chloride radicals; Sulfate radicals; EDDS; Micropollutant; Organic matter; Solar photocatalysis

1. Introduction

In many regions of the world with water scarcity, the reuse of effluents from wastewater treatment plants (WWTP) becomes an increasingly widespread and desirable alternative. In recent years, the presence of contaminants of emerging concern (CECs) in WWTP effluents has become evident, thanks to the development of advanced analytical techniques capable of detecting contaminants at a very low concentration [1–3]. Within these techniques, the direct injection-based method by ultra-high-performance liquid chromatography quadrupole-linear ion trap analyzer (LC-QqLIT-MS/MS) stands out for being a fast and very sensitive method [4]. Contaminants such as pharmaceuticals, antibiotics, biocides, pesticides and personal care products are detected at low concentrations ($\mu g\ L^{-1}$ – $ng\ L^{-1}$), but their accumulation in the ecosystems can cause negative effects on the aquatic organisms, crops (if the water is re-used for irrigation), and consequently, on human health [5,6]. Conventional WWTPs are not designed to eliminate this type of contaminants, and the legislation is becoming stricter with its discharge [7,8]. Therefore, an additional treatment is necessary for the removal of these compounds, which may be the advanced oxidation processes (AOPs), mainly based on the generation of $HO^{\bullet}$ radicals with a high oxidative potential to degrade a wide variety of organic compounds [9,10]. One of the most efficient AOPs is the photo-Fenton process, which consists of the generation of hydroxyl radicals through the reaction between Fe^{2+}/Fe^{3+} and H_2O_2 under UV radiation. This process has been widely studied at its optimum pH, 2.8 [11,12]. However, the need for a previous acidification pretreatment and further neutralization before reusing or discharging as well as pH control to ensure the catalytic activity of iron species increases the effluent salinity as well as the costs of the process [13].

To deal with these drawbacks, the current studies are focused on the operation at neutral pH and the use of low-cost reactors, such as raceway pond reactors (RPRs). These reactors, consisting of two open channels through which water is recirculated, are provided with a paddle wheel connected to an engine to vary the flow conditions. Furthermore, the liquid depth can be changed according to the availability of UV radiation [14]. Previous works show that high CEC removal efficiencies are achieved, both in synthetic municipal and industrial wastewater, in RPRs with different liquid depths (5 - 15 cm) [15,16]. Indeed, they are more efficient in reference to treatment capacity than the conventional tubular reactors with compound parabolic collectors (CPCs) [15,17]. To carry out the process at neutral pH, the use of EDDS, a biodegradable chelating agent which complex iron and avoid its precipitation, has been widely studied [18–21]. This Fe^{3+}-EDDS complex stands out for its high absorptivity, which allows high removal rates to be achieved at short reaction times [16,22,23]. As for the transformation products (TPs) formed during the oxidation of the CECs, additional irradiation time may be required for complete degradation. Indeed TPs products of some single CECs (spiked at concentration in the range of a few mg/L) after photo-Fenton treatment have been recently reported [24,25]. However, it is not technically possible to quantify TPs generated from dozens of parent compounds found in real secondary effluents at concentration level of ng/L along with tens of mg/L of natural organic matter and other organic compounds, preventing from any reliable study about TPs. As a detailed evaluation of CEC TPs is not possible, studies are focused on environmental impact of TP discharge. Reported studies show the potential phytotoxicity and cytotoxicity of the treated wastewater is attenuated, and the androgenic/glucorticoid activity and estrogenicity are removed after the treatment with Fe^{3+}-EDDS [26].

When working with real MWWTP effluents, the variability of water composition, as well as the lack of analytical techniques to determine all the matter present in the water, hinders the study of the process. Among the ions, HCO_3^-/CO_3^{2-}, chloride and sulfate can have an important effect on the process. Concerning the HCO_3^-/CO_3^{2-} ions, its effect is negative since they act as a scavenger of hydroxyl radicals [27]. As for chloride and sulfate, the corresponding radicals could be formed but with oxidation potentials lower than that of hydroxyl radicals. Otherwise they can contribute to the oxidation of contaminants, since $SO_4^{\bullet-}$ reacts with Cl^- generating $Cl^\bullet$, and finally Cl^- reacts with the generated $Cl^\bullet$ yielding $Cl_2^{\bullet-}$, which exhibits a higher reactivity with organic pollutants than with other species [28]. Nonetheless, both ions can retard the efficiency of the process by forming complexes with iron and also by scavenging the $HO^\bullet$ radicals [29–31].

Previous experiments have shown that it is possible to degrade CECs in a MWWTP effluent with a Fe^{3+}-EDDS molar ratio of 1:2 and H_2O_2 in CPC photoreactors [32]. The drawback of working at a Fe^{3+}-EDDS ratio of 1:2, instead of 1:1, is not only the increase in operating costs, but the concentration of dissolved organic carbon (DOC) added by the EDDS to the water is doubled. When working with 0.1 mM Fe^{3+}-EDDS at a ratio of 1:1, DOC added to the water is 12 mg L^{-1} being DOC content of MWWTP around 20 mg L^{-1}. For instance, taking into account the daily emission limit for DOC to surface waters established by the Andalusian Regional Government, 45.9 mg L^{-1} [33], this limit could be exceeded when working at a Fe^{3+}-EDDS ratio of 1:2. Recently, the efficiency of using Fe^{3+}-EDDS at 1:1 molar ratio for acetamiprid removal, a neonicotinoid, by photo-Fenton process with synthetic secondary effluents has been demonstrated [16].

In this regard, among the great number of publications on photo-Fenton only a few are related to microcontaminant removal in wastewater, most of them using demineralized water or synthetic wastewater [34-36]. Working under these conditions is necessary to understand the phenomenology of the process and the reaction mechanisms. Then, the results must be validated under real conditions. Real wastewater is a very complex and variable water matrix and there is a lack of papers dealing with the removal of CECs in real WWTP effluents, as recently reported not only on photo-Fenton process, but also on advanced oxidation processes [37]. Nonetheless, no studies comparing different real effluents have yet been reported and this assessment is crucial to predict process applicability and robustness because results can largely change from one case to another due to real water variability.

The main objective of this study was to determine if photo-Fenton best operating conditions developed during several years of experimentation with model and real effluents are suitable for treating MWWTP effluents of very different composition. Additionally, identifying the factors with highest impact on results when comparing different water matrices is of paramount interest. Experiments were carried out at neutral pH, with 0.1 mM Fe^{3+}-EDDS at 1:1 molar ratio, in secondary effluents from five MWWTPs (see Table 1) located in different areas of Spain more than 1000 km away, with variability in salinity (conductivity 0.9 up to 2.2 mS cm^{-1}) as well as in organic matter (DOC 10 – 20 mg L^{-1}). This paper is aimed at gaining know-how about the effect of effluent composition on CEC removal kinetics and process efficiency.

2. Materials and methods

2.1. Chemicals

Ferric sulfate (75%), hydrogen peroxide (33%), hydrochloric acid (37%) and acetic acid were obtained from Panreac (Barcelona, Spain). Sodium formate was acquired from Merck Millipore (Darmstadt, Germany). Ultrapure water was generated with a Millipore Direct-Q® Ultrapure Water System (Bedford, MA, USA) (18.2 MΩ cm^{-1} resistance and 2 mg L^{-1} total organic carbon). Methanol (MeOH), acetonitrile (AcN) and formic acid (purity, 98%) were HPLC grade and supplied by Honeywell-Riedel-de Haën (Seelze, Germany). Ethylenediamine disuccinic acid (35%), titanium (IV) oxysulfate, tetrabutylammonium bisulfate, sulfuric acid (99%), formic acid (98%), ascorbic acid, o-phenantroline and methanol were purchased from Sigma-Aldrich (Steinheim, Germany). All high purity analytical standards (purity >97%) were also purchased from Sigma-Aldrich comprising a group of CECs including pharmaceuticals, antibiotics, pesticides and some of their metabolites. ^{13}C-caffeine (Sigma-Aldrich) was used as injection standard.

For the determination of CECs by LC–MS/MS analysis, individual stock solutions of each compound were prepared in MeOH or AcN at 1000 mg L^{-1} and stored in amber glass vials at −20 °C. Stock standard solutions containing the compounds were prepared by mixing and diluting the individual stock solutions. A working solution containing all the analytes was prepared daily from the stock solution at 1 μg mL^{-1} in AcN.

2.2. MWWTP effluents

The experiments were carried out in secondary effluents from MWWTPs located in different areas of Spain: El Bobar (Almeria city, southeast of Spain), El Toyo (Almeria province), El Ejido (Almeria province), Alcoy (Alicante province, east of Spain) and Girona (Catalonia, northeast of Spain). The plants have a capacity of 315000, 52000, 108000, 120679 and 206250 population equivalents, respectively. El Bobar and Girona WWTPs treat wastewater from the city and nearby villages. Due to its location, El Ejido WWTP treats wastewater from a nearby hospital and it is placed in an area surrounded by an intensive greenhouse agricultural production. In all WWTPs the water line consists of a pretreatment (roughing filtration, desanding and degreasing), a primary treatment (primary decantation), a conventional activated sludge biological treatment (except in El Toyo WWTP provided with extended aeration) followed by a secondary decantation. Furthermore, all the effluents (except El Ejido wastewater) were collected after filtration through sand filters.

In the case of the MWWTP effluents from Alcoy and Girona, once the water was collected from the MWWTP, it was refrigerated and transported to Almeria within the following two days. In this way, all the effluents were used in the experimentation within the same week they were collected. Due to HCO_3^-/CO_3^{2-} ions inhibit CEC degradation, the inorganic carbon (IC) was reduced to around 15 mg L^{-1} by adding H_2SO_4 prior to the experimentation. In this way, the effect related to the scavenger effect of CO_3^{2-}/HCO_3^- was the same in all the effluents, thus avoiding interferences. Table 1 shows the characteristics of the effluents before the treatment. The highest concentration of Chemical oxygen demand (COD) was 58.3

mg L^{-1}. As there was no mineralization, COD was not reduced after the treatment. Indeed, it increased around 20 mg L^{-1}, mainly due to the DOC added by the EDDS to the water. This is not a drawback, since the limit for COD discharge established by the Andalusian Regional Government is 138 mg L^{-1} [33]. Regarding the anionic content, sulfate and chloride were the most abundant anions in all the effluents (sulfate ranged from 161 to 641 mg L^{-1} and chloride from 133 to 538 mg L^{-1}). To study the possible effect of these anions, effluents were classified according to sulfate and chloride concentration level: effluent from El Ejido = high-level, effluent from El Bobar = medium-level A, effluent from El Toyo = medium-level B, effluent from Girona = low-level A and effluent from Alcoy = low-level B.

2.3. Experimental set-up

The experiments were carried out in outdoor conditions at the Solar Energy Research Center (CIESOL) located in Almeria (36°50′17″N, 02°27′35″W). The volume capacity to transport water from the MWWTPs to the research center (specifically from Girona and Alcoy) limited the volume of wastewater collected. Consequently, an RPR with 19-L capacity was used. The reactor consisted of a perfectly mixed RPR with 5-cm liquid depth, 22-cm channel width, and a mixing time of 2 min. Concerning the reactants, the experiments were conducted under mild oxidation conditions with 0.88 mM H_2O_2 (30 mg L^{-1}, the minimum concentration to guarantee the conditions of a Fenton-like process and permitting water disposal at the end of the treatment), and 0.1 mM Fe^{3+} (5.6 mg L^{-1}, the optimal concentration reported for photo-Fenton in RPRs [14]), at a Fe^{3+}-EDDS molar ratio of 1:1. These oxidation conditions were demonstrated to be efficient for CEC removal in synthetic secondary effluents [16]. During the reaction time, the temperature and pH were measured with probes connected to a LabJack USB/Ethernet data acquisition device. The pH ranged between 7 and 8 and the water temperature between 22 and 28 °C. Regarding the incident UV radiation, it was measured with a global UV radiometer (Delta Ohm, LPUVA02AV) in the wavelength range 327-384 nm.

All the experiments were replicated and conducted around noon during sunny days, at a global UV radiation comprised between 28 and 35 W m^{-2}. To compare the results, they were normalized to a constant irradiance of 30 W m^{-2}. The illumination time normalized to this radiation was calculated with Eq. (1), well established for kinetic calculations in solar photoreactors [38]:

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \cdot \frac{\overline{UV}_G}{30} \cdot \frac{V_i}{V_T} \qquad \text{Eq. (1)}$$

where t_{30W} is the normalized illumination time, t_n is the experimental time for each sample $(n=1,\ t_{30W}=0)$, $\overline{UV}_G$ is the average global UV irradiance measured during Δt_n $(t_n - t_{n-1})$, V_i and V_T are the illuminated and the total volume of the photoreactor, respectively. Factor $V_i/V_T = 1$ for RPR.

2.4. Chemicals analysis

At each sampling time, two samples were taken from the photoreactor, one for reactant quantification and another for determination of CECs. For the quantification of reagents, the samples were filtered by 0.2-µm nylon filters from Millipore. As for the CECs, 5 mL of sample were taken from the reactor to a 7-mL amber glass bottle (pre-rinsed with ultra-pure water) containing 0.5 mL of AcN. Acetonitrile acts as $HO^\bullet$ scavenger, stopping the reaction [39]. Then, an aliquot of this mixture was filtered by 0.22-µm PTFE syringe filters (Aisimo Corporation, London, UK) into a 2-mL injection vial.

Total dissolved iron was spectrophotometrically measured at 510 nm, according to the 1,10-phenanthroline method (ISO 6332). H_2O_2 was determined at 410 nm with titanium (IV) oxysulfate solution (DIN 38 402 H15). For iron, the limit of quantification (LOQ) and the standard deviation (SD) were 4.5 10^{-3} mM and 6.1 10^{-4} mM, respectively. As for H_2O_2, LOQ and SD were 2.9 10^{-2} mM and 4 10^{-3} mM, respectively.

IC and DOC were measured with a Shimadzu-V CPH TOC analyzer (Shimadzu Corporation, Kyoto, Japan), the LOQ being 1 mg L^{-1}.

The Fe^{3+}-EDDS complex was measured by a 1200 Series system consisting of an ultra-high pressure liquid chromatography with diode array detector (UHPLC-DAD) from Agilent Technologies (Waldbronn, Germany). Isocratic elution was used. The organic phase was MeOH and the aqueous phase consisted of a mixture of sodium formiate (15 mM) and tetrabutylamonium hydrogen sulfate (2 mM) in Milli-Q water at pH 4, in a percentage of 95% and 5%, respectively, the flow being of 0.5 mL min^{-1}. The LOQ and the SD were 3.5 10^{-3} mM and 3.5 10^{-4} mM, respectively.

The concentration of anions was determined using ion chromatography Metrohm 881 Compact IC pro (Herisau, Switzerland). The system worked with an anionic column, Metrosep A Supp 7, 250-4.0 mm and 5 µm from Metrohm. The eluent was a solution of Na_2CO_3, and the flow was 0.8 mL min^{-1}, and the LOQ was 0.5 mg L^{-1}.

The CECs were monitored using the protocol previously developed and validated by Campos-Mañas et al. [40]. The direct injection technique was applied (no sample pre-treatment) using a sample volume of 10 ⍰L. Sample dilution (1/10) with water was applied when necessary for an adequate quantification. The analyses were carried out by LC coupled to a hybrid quadrupole lineal ion trap MS analyzer (LC-QqLIT-MS/MS). The instrumentation consisted of an Agilent 1200 LC system (Agilent Technologies, Foster City, CA, USA) and a 5500 QTRAP analyzer (AB Sciex Instruments, Wilmington, DE, USA). Table 2 shows the concentration of the CECs detected at the highest concentrations in the five effluents.

2.5. Cost estimation

A cost estimation of the treatment of real secondary effluents by solar photo-Fenton at neutral pH in RPRs operated in continuous flow mode has been carried out. To this end, a design flow rate of 400 m^3 d^{-1} was set to fulfill the European Urban Wastewater Directive 91/271/EEC [41] which establishes the need of wastewater treatment in agglomerations larger than 2000 population equivalents, the wastewater generated per population equivalent being close to 200 L d^{-1}.

Total costs were estimated as the sum of the operating costs (OC) and the amortization costs (AC). Taxes, staff and land costs were not considered, since they are highly dependent on labour regulation as well as the treatment plant location. Operating costs were estimated by Eq. (2), considering maintenance costs as 2% of amortization costs [42].

$$OC = C_R + C_E + 0.02\,AC \qquad \text{Eq. (2)}$$

Where C_R and C_E are the reactant and energy costs, respectively.

Concerning the unitary reactant cost, industrial price was considered: 0.45 € L^{-1} H_2O_2 (33% w/v), 0.71 € kg^{-1} $Fe_2(SO_4)_3 \cdot H_2O$, 0.1 € L^{-1} H_2SO_4 (98% w/v). In the case of EDDS, 3.5 € L^{-1} EDDS (35% w/v) is the lowest reported cost because no industrial price is available yet. As for energy costs, the price of electricity was considered 0.1 € kW^{-1} h^{-1}. For mixing in the RPR, the unitary power requirement is 4 W m^{-3} [14]. Moreover, the cost of an 18 kW centrifugal pump, for effluent circulation to the reactor, was included, as well as four 50 W pumps for reactant dosing.

Regarding the amortization costs, Eq. (3), the investment cost (I) was referred to the RPR and the pumping systems. The RPR cost was calculated with Eq. (4), the cost per unit area being 10 € m^{-2}. A life cycle (L) of 20 years was assumed.

$$AC = \frac{I}{L} \qquad \text{Eq. (3)}$$

$$C_{RPR} = 10\, A_{RPR} \qquad \text{Eq. (4)}$$

3. Results and discussion

3.1. Effect of water matrix on reagents consumption and on the removal of contaminants of emerging concern

In a previous work, a reaction mechanism for solar photo-Fenton process at neutral pH was proposed and validated in a synthetic secondary effluent. Briefly, the main steps are the following: firstly, the Fe^{3+}-EDDS is photoreduced by UV radiation. Fe^{2+}-EDDS, as an intermediate state before being decomposed to Fe^{2+} and $EDDS^{\bullet 3-}$, reacts with H_2O_2 giving rise to $HO^{\bullet}$ and Fe^{3+}-EDDS. Finally, Fe^{2+} is oxidized by H_2O_2 (classic Fenton) yielding $HO^{\bullet}$ and Fe^{3+}, which instantaneously precipitates as $Fe(OH)_3$. The hydroxyl radicals oxidize CECs, as well as the Fe^{3+}-EDDS, the organic matter, the inorganic carbon and the H_2O_2 yielding their respective oxidation products. All the reactions and more details about the mechanism were previously reported [43].

$$Fe^{3+} - EDDS + hv \rightarrow [Fe^{3+} - EDDS]^* \qquad \text{R. (1)}$$

$$[Fe^{3+} - EDDS]^* \rightarrow Fe^{2+} - EDDS + H^+ \qquad \text{R. (2)}$$

$$Fe^{2+} - EDDS + \ H_2O_2 \rightarrow Fe^{3+} - EDDS + HO^\bullet + \ HO^- \qquad \text{R. (3)}$$

$$Fe^{2+} - EDDS \rightarrow Fe^{2+} + EDDS^{\bullet 3-} \qquad \text{R. (4)}$$

$$Fe^{2+} + \ H_2O_2 \rightarrow Fe(OH)_3 + HO^\bullet + \ HO^- \qquad \text{R. (5)}$$

Concerning the Fe^{3+}-EDDS profiles in the real MWWTP effluents, in all cases the complex totally decomposed after 15 minutes of the reaction, Fig. 1a. Furthermore, the profiles were similar to those obtained in a synthetic effluent at a global average irradiance close to 30 W m^{-2} [16], same as that used for normalizing illumination time according to Eq. 1. This fact shows that complex decomposition depends on the photochemical reactions and its subsequent oxidation with H_2O_2 rather than the water composition, in concordance with the proposed reaction mechanism.

In all cases, some iron remained in solution after complex decomposition. In this case, differences were observed in total dissolved iron profiles between the different MWWTP effluents, Fig. 1b. Whereas the profiles were similar in medium-level A, low-level A and B, the iron precipitated faster in high-level and medium-level B, the fastest precipitation being in medium-level B. It must be mentioned that in medium-level B, the iron profile was similar to that observed in a synthetic secondary effluent [43]. According to the mechanism, total dissolved iron concentration is the sum of the concentrations corresponding to the different species of Fe-EDDS. However, the fact that in the different MWWTP effluents the profiles are different could be related to the formation of other iron complexes, dependent on water composition. Although anions, such as chloride and sulfate can complex iron and therefore keep it in solution, the results show that these differences in iron concentration are not directly related to the concentration of anions, and it could be due to the generation of iron complexes with the organic matter present in the different effluents [44–46]. It should be highlighted that the total dissolved iron profiles are not related to the concentration of DOC, since in high-level (with around 20 mg L^{-1} DOC) the iron precipitated faster than in low-level A and slower than medium-level B (with around 10 mg L^{-1} DOC in both effluents). Therefore it could be concluded that the type of organic matter, which is difficult to determine due to its heterogeneity, structural complexity [47] and variability (between different MWWTP and in the same MWWTP at different hours of the day or seasons) could determine iron in solution.

Concerning H_2O_2 profiles, difference between MWWTP effluents was more significant after Fe^{3+}-EDDS decomposition. During the first minutes of the reaction, in which the complex is present, the H_2O_2 consumption is mainly due to the fast reaction between H_2O_2 and the photoreduced complex. Therefore, H_2O_2 consumption was very similar in the different effluents. However, once the concentration of the complex is low, the reactions of H_2O_2 with the organic matter would compete with those of the photo-Fenton process, substantially lower than during the first minutes as iron in solution was lower. In fact, a slightly higher H_2O_2

consumption can be observed in the high-level effluent, which was the effluent with the highest DOC concentration. It should be noticed that if the iron complexes formed with the organic matter after Fe^{3+}-EDDS decomposition would be photochemically active, it would be reflected in the H_2O_2 consumption profiles: the higher concentration of iron in solution, the higher H_2O_2 consumption. However, Figure 1 shows that there is no direct relationship between consumption of H_2O_2 and the total dissolved iron profiles. In medium-level A, H_2O_2 consumption was lower than in other effluents, while the iron concentration was higher. This phenomenon could be explained by the formation of iron complexes with the organic matter of the medium that could avoid iron photoreduction and its subsequent reaction with H_2O_2 to generate hydroxyl radicals.

Substantial differences were observed in the CEC degradation during the first minutes of reaction. In concordance with the reaction mechanism, CEC removal rate was substantially lower after 15 min of reaction, once the Fe^{3+}-EDDS was decomposed. The pseudo-first order rate constants, Table 3, show that there is no relationship between CEC removal rate and the concentration of organic matter and anions present in the reaction medium. Therefore, although organic matter and anions act as $HO^{\bullet}$ scavengers, degradation of CECs could be mainly affected by organic matter composition. The rate constants obtained in high level and medium-level B effluents (0.23 – 0.38 min^{-1}) are in concordance with the results reported for synthetic secondary effluents doped with 100 μg L^{-1} of the pesticide acetamiprid (a highly recalcitrant CEC), being its pseudo-first order rate constant 0.43 min^{-1} at 30 W m^{-2} of UV irradiance [16].

The highest percentage of removal was achieved in medium-level B (98% after t_{30W}=15 min), despite it being the effluent with the fastest iron precipitation and not the effluent with lower initial concentration. This could be explained by the fact that this effluent came from a MWWTP located in a small area with the lowest population equivalents (52000) in comparison with the other effluents, and its DOC concentration was also low (around 11 mg L^{-1}). As it is known, the lower the DOC, the lower the scavenger effect of hydroxyl radicals. Furthermore, there would be less organic matter to complex the iron, and more iron would be available to contribute to the Fenton reaction once the complex is photoreduced. As for the high-level effluent, it also showed a fast CEC removal (94% of CEC removal after t_{30W}=17 min) despite it being the effluent with the highest total load of CECs. Furthermore, the lower the CEC concentration, the more hydroxyl radicals react with the organic matter instead of oxidizing the CECs. Even so, 87% and 82% of CEC removal was achieved after t_{30W}= 17 and 16 min in low-level effluents, respectively. In medium-level A only 56% of CEC removal was achieved after t_{30W} = 15 min. This effluent corresponds to the MWWTP with the highest population equivalents, despite it not being the effluent with the highest DOC concentration.

Although chloride and sulfate radicals are less reactive than hydroxyl radicals, previous experiments carried out in demineralized water showed that these ions could have a positive or negative effect on the kinetics of the process, depending on the process conditions [27–31]. Therefore, it is interesting to study the effect of the initial concentration of these ions on CEC removal in real MWWTP effluents. In Fig. 2a, it is observed that the CECs removed increased with the concentration of chlorides present in the effluent until 386 mg L^{-1} (Medium level A). This is consistent with reported results which point out that the addition of 350 mg L^{-1}

chloride to the system contributed to accelerate the kinetics of pollutant removal [28]. Nevertheless, from 386 to 481 mg L^{-1} chloride the load of CEC removed was practically the same, whereas the total load removed increased strongly in the effluent with concentration of chlorides of 538 mg L^{-1}. In the case of sulfates, the same effect was observed. From these results, it could be deduced that there is not any detrimental effect of the initial concentration of the main anions on the reaction rate or total load removed, and therefore, on the process efficiency. Within the usual concentration found in natural sweet waters, higher concentration of chloride and sulfate presented higher kinetics.

Concisely, all these results show that the Fe^{3+}-EDDS photo-decomposition does not significantly depend on the secondary effluents composition, but on the photochemical reactions of the process, according to the mechanism already developed with a synthetic effluent and described elsewhere [43]. During the first minutes of the reaction there is not effect of the water composition on the hydrogen peroxide consumption. This is in concordance with the fast reaction between the photoactivated complex and the hydrogen peroxide proposed in the reaction mechanism, giving rise to the fast generation of $HO^{\bullet}$ and most of the CEC removal. Once the Fe^{3+}-EDDS complex is decomposed, an effect of the water composition on the H_2O_2 consumption is observed. Furthermore, there is a remnant of iron in solution as non-photoactive organocomplexes, which do not depend on the organic matter concentration, but on its composition. According to the pseudo-first order kinetics, high degradation rates can be achieved in effluents with a high load of CECs. Although main anions affect the process, there is not any direct relationship between increasing concentration of the anions and a detrimental effect on CEC removal. The composition of the organic matter present in MWWTP effluents is proposed to cause a higher impact on the process than its initial concentration. Overall, CECs were efficiently removed regardless water composition although the kinetics in each type of effluents must be specifically determined case by case.

3.2. CEC removal in the MWWTP effluents

In the five effluents studied, a range from 18 to 45 compounds were identified by LC–MS/MS. These compounds were mainly pharmaceuticals, some pesticides, antibiotics and opioids were also found. The degradation profiles of all compounds over time and the removal percentages in each effluent are shown in Tables S1-S5. Fig. 3 shows the degradation profiles of the six most abundant compounds in each effluent (eleven different CECs). In all cases, the sum of the non-biodegradable metabolites of dipyrone [48] (4-aminoantipyrine,4-acetylaminoantipyrine, 4-formylaminoantipyrine, 4-methylaminoantipyrine), named as DPR-M, represented the highest concentration of CECs (between 33% and 55% of the total load of CECs). Gabapentin, *O*-desmethylvenlafaxine (metabolite of venlafaxine), tramadol and its metabolite *O*-desmethyltramadol were also found with the highest initial concentrations in most wastewaters. DPR-M and tramadol are low-cost analgesics, which can be consumed without medical prescription, and gabapentin and venlafaxine are pharmaceuticals commonly used as anticonvulsant and antidepressant, respectively. Therefore, it is usual to find all these compounds or their metabolites at high concentrations in MWWTP effluents [49,50]. In the case of the high-level effluent, naproxen (anti-inflamatory) was found among the compounds in the highest concentrations. This could be due to the localization of the MWWTP near a hospital. Moreover, theophylline and cotinine, two alkaloids related to the consumption of tea and tobacco, were also often detected.

Despite DPR-M representing the highest load, around 80-100% was removed after a t_{30W} of 15 min in all effluents, except in medium-level A, in which DPR-M was removed 60%. The other five pollutants with the highest initial concentration were removed between 70 and 100% after a t_{30W} of 15 min in all effluents, except in medium-level A, where the percentages were lower again, between 30 and 90%. Therefore, the low percentage of degradation achieved in medium-level A (in comparison with the other effluents) was not due to the degree of recalcitrance of the CECs, since CECs found in the highest concentrations in this effluent were also found and rapidly degraded in other wastewaters. It reinforces the proposed statement that composition of the organic matter present in MWWTP effluents is the key point that governs kinetics under the same treatment conditions.

It is worth mentioning that 88% of the total initial load was removed in the high-level effluent at t_{30W}= 11 min, with a ratio Fe^{3+}-EDDS 1:1 and 0.88 mM H_2O_2 in an RPR. This agrees with the 88% reported at t_{30W}= 8 min for an effluent from the same MWWTP, with a ratio Fe^{3+}-EDDS 1:2 and 1.47 mM H_2O_2 in a CPC reactor [32]. Thus, the results obtained show the similar removal rate in the low-cost RPRs for the treatment of municipal wastewater in comparison with the CPCs.

The average removal of CECs in the five effluents was 83% at a t_{30W} of 15 min. The new Swiss water protection act entered into force on January 2016 and requires WWTPs upgrade within the next twenty years [51]. According to that, CECs need to be removed by 80% relative to the raw wastewater. The treatment target is defined by the elimination of a selection of CECs from a list of twelve defined compounds [52]. So far, few plants are in full-scale operation in Switzerland, either with ozonation or activated carbon treatment and less than 50% CEC removal is expected from the advanced tertiary treatment. But, to date, results about CEC removal are scarce in full-scale. Therefore, even the lowest percentage of removal attained in this work would fulfill these rules.

3.3. Economic assessment

Once the technical feasibility of the process has been demonstrated, an estimation of the treatment cost gives insight of the potential applicability of the treatment. Nonetheless, to carry out a rigorous economic assessment data from demonstration plants are needed. Due to the high percentages of CEC removal achieved at short reaction time, the process should be operated in continuous flow mode at large scale [53]. In this work, only the order of magnitude of the cost was estimated considering the operation of an RPR in continuous flow mode at a hydraulic residence time of 15 min, being long enough to achieve more than 80% CEC removal. The treatment capacity would be 1600 L m^{-2} d^{-1} for the continuous flow operation of a 5-cm deep RPR with 0.1 mM Fe^{3+}-EDDS and 0.88 mM H_2O_2 at 15 min of hydraulic residence time (HRT) for 8 hour a day, the annual average sun hours per day in Almería (Spain) [54]. This estimated treatment capacity is 77% higher than the value reported at acidic pH with 20 min HRT [53]. With these data, the estimated area of the RPR was 250 m^2 to treat 400 m^3 d^{-1}, resulting in an amortization cost of 188 € y^{-1}.

Concerning operating costs, the reactant cost, mainly affected by the high cost of EDDS, represented 94% of the total value (67492 € y^{-1}). Energy cost, mainly affected by wastewater pumping, represented 6%. Maintenance cost was less than 0.1%, thus it could be considered negligible.

Finally, unitary total cost of the treatment was estimated to be 0.46 € m^{-3}. This value is in the reported range for AOPs [55]. Furthermore, it is competitive with the reported costs for the operation of a CPC solar pilot plant at neutral pH with Fe^{3+}-EDDS (in the range 0.71 - 1.31 € m^{-3} for the treatment of 500 m^3 d^{-1}) [56].

This economic assessment is only a rough estimation, based on the scaling of the results obtained in a 19L-RPR operated in batch mode. In future works, the technical feasibility of the process in continuous flow must be demonstrated. Then, from the results obtained on a larger scale, the economic feasibility could be evaluated. Furthermore, operating cost could be strongly reduced by using chelating agents cheaper than EDDS, such as natural complexing agents, which encourages to continue the study of the process at neutral pH.

4. Conclusions

As far as authors known, the efficiency of the photo-Fenton process for treating MWWTP effluents of very different composition has been demonstrated for the first time. Using a low-cost RPR, more than 80% removal of total load of contaminants of emerging concern was achieved regardless the origin of the secondary effluent in less than 15 min of treatment. No dependence of the photo-Fenton process with the inorganic components of secondary effluents was found, but results show that effluents with high load of chloride or sulfate can contribute to the improvement of the process efficiency. The nature (and not the load, at least until 20 mg L^{-1}) of the organic matter has a great effect on CEC degradation. Composition of the organic matter present in MWWTP effluents is the key point that governs kinetics under given treatment conditions (iron and EDDS concentration, H_2O_2 dose, photoreactor design). It should be highlighted that the results obtained in different real MWWTP effluents can be explained based on reaction mechanisms developed under controlled conditions with synthetic effluents. Finally, the short reaction time to reach substantial removal of CECs and the estimated cost in the range reported for AOPs encourage the study of the process in continuous flow.

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Table 1

Table 1. Characterization of MWWTP effluents, mean value ± standard deviation (n.d. = not detected).

	High-level	Medium-level A	Medium-level B	Low-level A	Low-level B
NO_2^- (mg L^{-1})	n.d.	4.2 ± 0.1	n.d.	2.1 ± 0.3	1.6 ± 0.1
Br^- (mg L^{-1})	3.8 ± 1.4	2.8 ± 0.1	3.0 ± 0.2	n.d.	n.d.
NO_3^- (mg L^{-1})	n.d.	17.7 ± 6.6	4.6 ± 3.3	15.3 ± 0.3	4.2 ± 0.1
PO_4^{3-} (mg L^{-1})	5.5 ± 1.6	4.5 ± 3.0	9.3± 3.6	n.d.	4.2 ± 0.1
SO_4^{2-} (mg L^{-1})	641 ± 12	238 ± 23	292 ± 33	161 ± 2	231 ± 2
Cl^- (mg L^{-1})	538 ± 3	386 ± 10	481 ± 18	133± 1	248 ± 3
DOC (mg L^{-1})	19.7 ± 5.7	16.2 ± 2.3	10.8 ± 0.1	9.8 ± 0.1	16.4 ± 0.4
COD (mg L^{-1})	58.3 ± 9.5	51.6 ± 4.7	32.5 ± 3.1	29.8 ± 1.8	44.9 ± 2.0
IC (mg L^{-1})	125 ± 2	47.0 ± 5.5	44.4 ± 4.5	47.6 ± 1.0	56.7 ± 1.0
IC* (mg L^{-1})	11.9 ± 1.0	11.3 ± 1.2	15.3 ± 4.4	10.4 ± 0.4	15.3 ± 0.4
pH	7.4 ± 0.1	7.9 ± 0.1	7.8 ± 0.1	7.2 ± 0.1	7.6 ± 0.2
Conductivity (mS cm^{-1})	2.2 ± 0.1	1.6 ± 0.1	1.8 ± 0.1	0.9 ±0.1	1.2 ± 0.1
Turbidity (NTU)	43.8 ± 12.9	9 ± 0.8	4.6 ± 2.8	1.9 ± 0.3	6.9 ±2.1
Population equivalents	108000	315000	52000	206250	121000

*Inorganic carbon (IC) pretreated until IC around 15 mg L^{-1}.

Table 2

Table 2. Initial concentrations (ng L^{-1}) of the most relevant CECs detected in each MWWTP effluent.

CEC	High-level	Medium-level A	Medium-level B	Low-level A	Low-level B
Antipyrine	n.d.	838	141	n.d.	39
Atenolol	391	642	95	287	672
Ciprofloxacin	976	1573	618	n.d.	n.d.
Cotinine	6015	n.d.	n.d.	n.d.	n.d.
DPR-M[a]	28919	16911	9073	2014	5741
Gabapentin	7863	1950	1309	943	1711
Lidocaine	244	283	124	n.d.	253
Naproxen	1207	647	56	n.d.	233
O-Desmethyltramadol	740	1916	871	319	590
Ofloxacin	965	792	541	105	311
O-Desmethylvenlafaxine	724	1324	1075	683	774
Ranitidine	881	1597	125	255	n.d.
Sulfametoxazol	798	n.d.	195	128	114
Sulfapyridine	90	201	161	n.d.	35
Theophylline	5041	n.d.	n.d.	n.d.	n.d.
Tramadol	756	n.d.	1170	905	928
Venlafaxine	176	420	177	198	179
Other CECs[b]	4609	3057	1451	336	1018
Total load (μg L^{-1})	58	31	17	6.2	12

[a] Sum of the non-biodegradable metabolites of dipyrone (4-aminoantipyrine, 4-acetylaminoantipyrine, 4-formylaminoantipyrine, 4-methylaminoantipyrine).

[b] Sum of the concentrations of the rest of detected CECs.

Table 3. Pseudo-first order rate constant of total load of CEC removal calculated over t_{30W}.

MWWTP effluent	k (min^{-1})	r^2
High-level	0.26	0.99
Medium-level A	0.10	0.95
Medium-level B	0.38	0.99
Low-level A	0.16	0.99
Low-level B	0.16	0.99

Figure 1

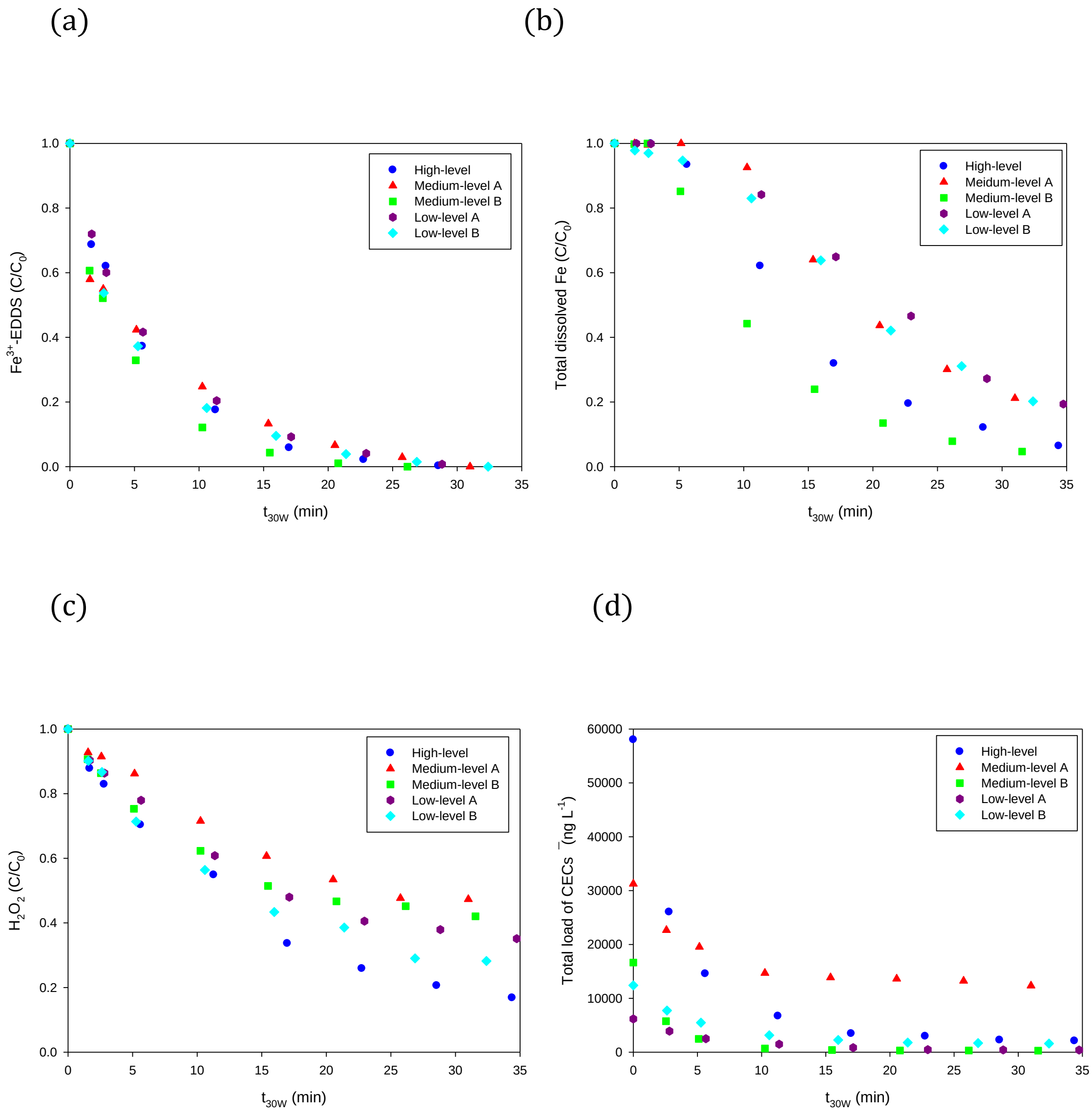


Fig. 1. Fe^{3+}-EDDS complex (a), total dissolved iron (b), H_2O_2 (c) and total load of CECs (d) profiles in the different MWWTP effluents.

Figure 2

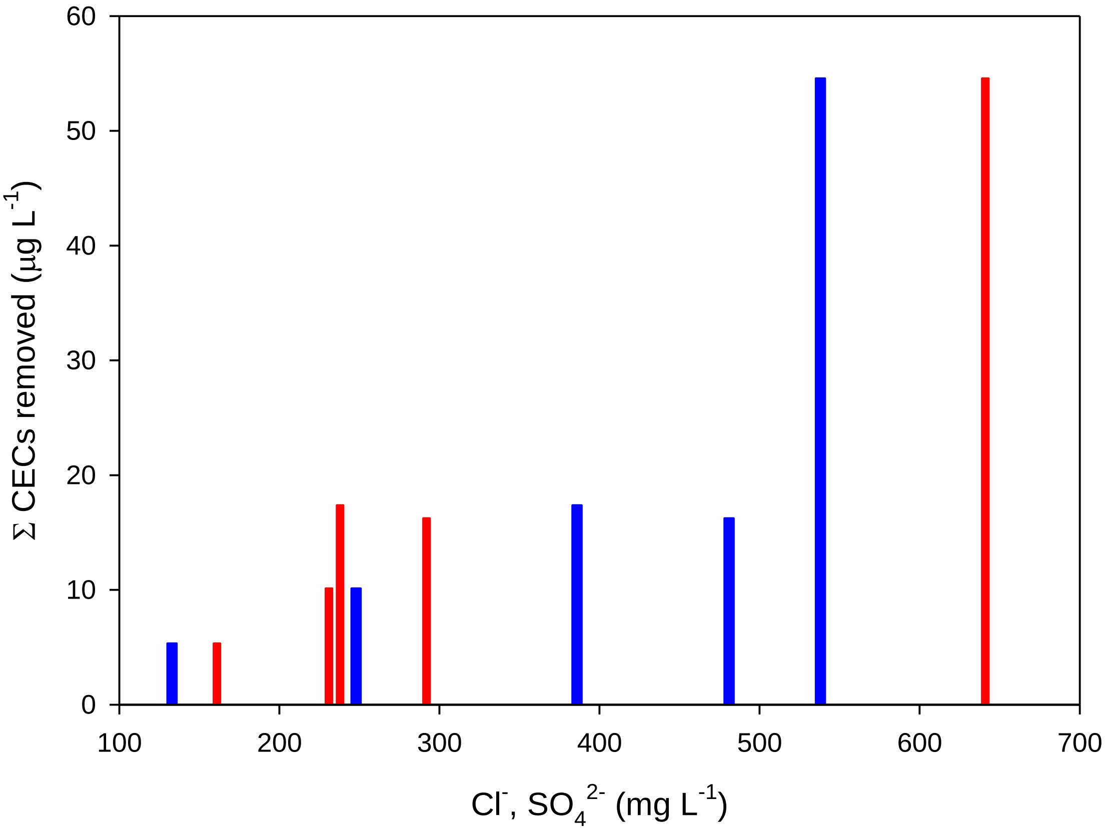
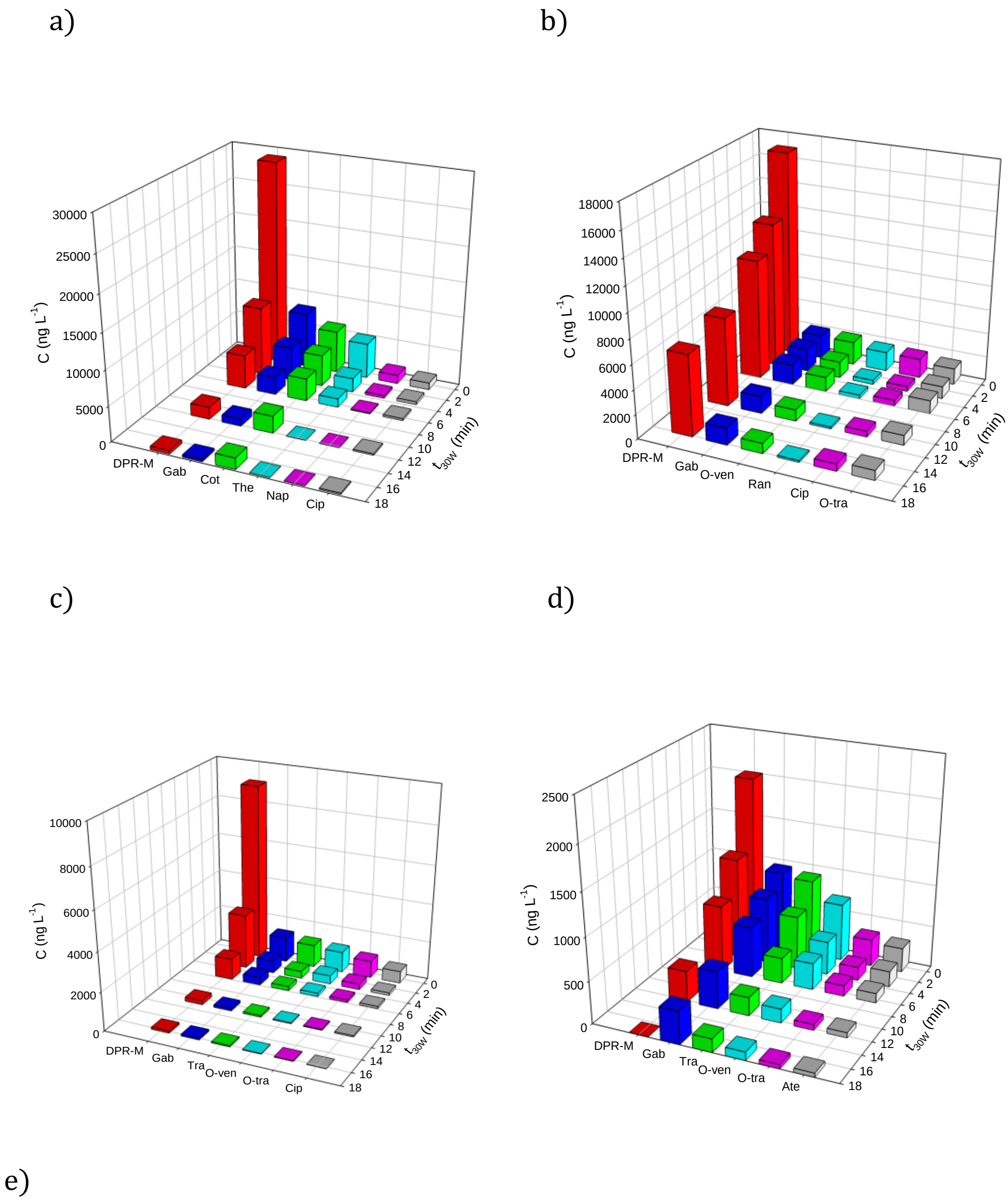


Fig. 2. Effect of chlorides (blue), sulfates (red) concentration on the sum of CECs removed after 15 min of t_{30W}.

Figure 3


a)
C (ng L-1)
0
5000
10000
15000
20000
25000
30000
DPR-M
Gab
Cot
The
Nap
Cip
t30W (min)
0
2
4
6
8
10
12
14
16
18
b)
C (ng L-1)
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
DPR-M
Gab
O-ven
Ran
Cip
O-tra
t30W (min)
0
2
4
6
8
10
12
14
16
18
c)
C (ng L-1)
0
2000
4000
6000
8000
10000
DPR-M
Gab
Tra
O-ven
O-tra
Cip
t30W (min)
0
2
4
6
8
10
12
14
16
18
d)
C (ng L-1)
0
500
1000
1500
2000
2500
DPR-M
Gab
Tra
O-ven
O-tra
Ate
t30W (min)
0
2
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e)

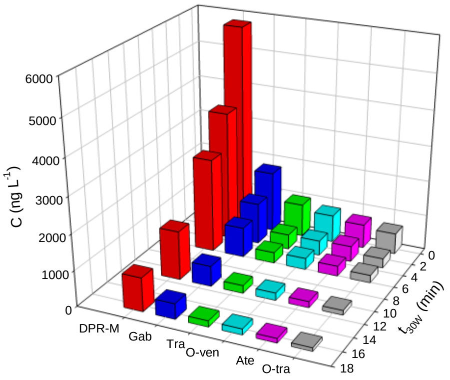

Fig. 3. Degradation of the six CECs with the highest initial concentration in each effluent: high-level (a), medium-level A (b), medium-level B (c), low-level A (d), low-level B (e) effluents (DPR-M= the sum of the non-biodegradable metabolites of dipyrone, Gab=gabapentin, Tra=tramadol, O-ven=*O*-desmethylvenlafaxine, O-tra=*O*-desmethyltramadol, Ate=atenolol, Ran=ranitidine, Cot=cotinine, The=theophylline, Nap=naproxen, Cip=ciprofloxacin).

Supplementary Material