Catalysis Today 161 (2011) 241–246

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Modified photo-Fenton for degradation of emerging contaminants in municipal wastewater effluents

N. Klamerth[a,c], S. Malato[a,c,*], M.I. Maldonado[a,c], A. Agüera[b], A. Fernández-Alba[b,c]

[a] *Plataforma Solar de Almería-CIEMAT, Carretera de Senés km 4, 04200 Tabernas, Spain*
[b] *Pesticide Residue Research Group, University of Almería, 04120 Almeria, Spain*
[c] *CIESOL, Joint Centre University of Almeria-CIEMAT, 04120 Almeria, Spain*

ARTICLE INFO

Article history:
Received 8 June 2010
Received in revised form 13 October 2010
Accepted 20 October 2010
Available online 26 November 2010

Keywords:
Advanced oxidation process
Solar photocatalysis
Wastewater reuse

ABSTRACT

As normal municipal wastewater treatment plants (MWTP) are not able to entirely degrade xenobiotic substances, this study focuses on modified solar photo-Fenton treatment (5 mg L^{-1} Fe, initial pH ≈ 7) of a municipal wastewater treatment plant (MWTP) effluent. However, effluents do not contain compounds which could form photoactive Fe^{3+} complexes. The use of ferrioxalate, humic substances (HA) and mixing the MWTP effluent with small amounts of influent could be justified to form photoactive Fe^{3+} complexes. All experiments were done in MWTP effluent spiked (5 or 100 μg/L) with 15 emerging contaminants (ECs) using a pilot compound parabolic collector (CPC) solar plant designed for solar photocatalytic applications. Dissolved organic carbon and UPLC–UV (with prior solid phase extraction) were applied for evaluating the results. The oxalate-enhanced process provided satisfactory EC degradation results but low residual pH of the treated water. HA (10 mg L^{-1}) enhanced the process, balancing degradation time and residual pH. Mixing of MWTP influent and effluent delivered rather disappointing results, as EC degradation was unsuccessful in all cases tested.

1. Introduction

Growing use of xenobiotic substances like pharmaceuticals, synthetic fragrances, pesticides, drugs and other contaminants is leading to increasing concentrations of these substances in waste water [1–4]. As normal municipal wastewater treatment plants (MWTP) are not able to entirely degrade these contaminants, present in μg-ng L^{-1} concentration levels, they end up in the aquatic environment and may cause ecological problems, such as feminization of higher organisms, microbiological resistance and accumulation of these substances in soil, plants and animals [5–7]. It is therefore important to degrade these emerging contaminants (ECs) prior to their release into the environment, and even more so if the water is reused for irrigation. If treated water is reused for irrigating crops, golf courses, public gardens and so forth, they not only have to be disinfected (free of pathogens), but entirely free of these ECs as well.

Among the advanced treatment technologies for degrading ECs in waste water, advanced oxidation processes (AOPs) present a particularly attractive option, as they produce OH radicals, which are capable of oxidizing almost any organic molecule, yielding short-chain organic acids, inorganic ions and CO_2 as final products. The usual drawback of AOPs are their high electricity demand for devices such as UV lamps and ozonators, and large amounts of oxidants and catalysts, as well as low pH operating conditions (for Fenton and photo-Fenton) [8,9], which is why commercial applications are still scarce. Processes like photo-Fenton can be made feasible for commercial applications by using solar energy, and optimizing the pH and amounts of iron and oxidant [10].

This study focuses on modified solar photo-Fenton treatment (5 mg L^{-1} Fe, initial pH ≈ 7, 50 mg L^{-1} initial H_2O_2) of an MWTP effluent in which the pH is far from the optimum of 2.8 for photo-Fenton treatment [11,12]. At this pH, there is still no precipitation and the dominant iron species in solution is $[Fe(OH)]^{2+}$, the most photoactive ferric iron–water complex (Eqs. (2) and (3)). A pH far from 2.8 is detrimental to the process, as the concentration of $[Fe(OH)]^{2+}$ is low, thereby justifying the use of oxalic acid, humic acid or a mixture of secondary MWTP effluents with influent wastewater, which could compensate for the disadvantage of the lack of $[Fe(OH)]^{2+}$ by forming ferric iron complexes ($Fe^{3+}L$) from other compounds (Eq. (1)). This study focuses in all these matters. However, effluents from MWTPs do not contain compounds, such as oxalic acid, lactic acid, quinolinic acid, fusaric acid or pinolenic acid, to name only a few [11] which could form photoactive $Fe^{3+}L$, as they are usually highly biodegradable.

$$[Fe^{3+}L] + h\nu \rightarrow [Fe^{3+}L]^{*} \rightarrow Fe^{2+} + L^{\bullet} \quad (1)$$

---

[*] Corresponding author at: Plataforma Solar de Almería-CIEMAT, Carretera de Senés km 4, 04200 Tabernas, Spain.
E-mail address: sixto.malato@psa.es (S. Malato).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.10.074

$$[Fe(H_2O)]^{3+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} + H^+ \quad (2)$$

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \quad (3)$$

The use of ferrioxalate has certain advantages: it is a photosensitive complex, which allows the solar spectrum up to 450 nm to be used, thus improving solar photo-Fenton oxidation efficiency, and complexation of iron with oxalate widens the pH operating range to near neutrality. Apart from that, its chemistry provides additional sources of oxidant H_2O_2 and catalyst Fe^{2+} for the Fenton reaction, thus yielding more OH radicals according to the following reactions (Eqs. (4)–(9)) [13,14]:

$$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4{}^{2-} + C_2O_4{}^{\bullet -} \quad (4)$$

$$C_2O_4{}^{\bullet -} + [Fe(C_2O_4)_3]^{3-} \rightarrow Fe^{2+} + 3C_2O_4{}^{2-} + 2CO_2 \quad (5)$$

$$C_2O_4{}^{\bullet -} + O_2 \rightarrow 2CO_2 + O_2{}^{-} \quad (6)$$

$$O_2{}^{-} + H^+ \rightarrow HO_2{}^{\bullet} \quad (7)$$

$$2HO_2{}^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \quad (9)$$

Humic substances (HS) are naturally occurring organic substances resulting from microbiological and chemical transformation of organic debris. Although there are differences in HS from different sources, some general properties are similar. They are the largest fraction of dissolved organic matter in natural water and are categorized as humic acid (HA), fulvic acid and humin (according to their solubility). They strongly absorb sunlight and generate exited triplet states ($^3HS^*$), various reactive oxygen species, hydroxyl radicals, singlet oxygen ($^1O_2$) and hydrogen peroxide, and may therefore photoinduce the transformation of non-absorbing organic chemicals. They behave like colloids and have absorptive qualities. They contain carboxylic acids, phenolic, alcoholic quinine, and amino and amido groups which enable them to support ion exchange and redox processes, and to form complexes. They contain also large numbers of stable free radicals which can react with various substances [15–18].

Finally, as a way to avoid adding other chemicals to the treatment, mixing the MWTP effluent with small amounts of influent wastewater could be justified, as influent wastewater could contain substances that form photoactive ferric iron complexes ($Fe^{3+}L$), which, as mentioned above, are very unusual in effluents because, as they are so biodegradable, they are eliminated during the MWTP treatment.

2. Materials and methods

2.1. Reagents

All reagents used for chromatographic analyses, acetonitrile, methanol and ultrapure water (Milli-Q) were HPLC grade. Analytical standards for chromatography analyses were purchased from Sigma–Aldrich. The 15 compounds selected were: acetaminophen, antipyrine, atrazine, caffeine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole and triclosan. Photo-Fenton experiments were performed using iron sulfate ($FeSO_4{\cdot}7H_2O$), reagent grade hydrogen peroxide (30%, w/v), sulfuric acid (98%) for carbonate stripping, oxalic acid ($C_2H_2O_4{\cdot}2H_2O$) and HA, all provided by Panreac. The filters used were Millipore Millex syringe driven 0.2 μm (pore size) nylon membrane filters.

2.1.1. MWTP effluent and influent

All experiments were done in MWTP effluent spiked with ECs. The treated waste water was taken downstream of the MWTP secondary biological treatment in El Ejido (province of Almería, Spain) and used as received within the next 3 days. Initial COD (chemical oxygen demand), DOC (dissolved organic carbon) and TIC (total inorganic carbon) were between: 26 and 63, 10 and 24 and 91 and 120 mg L^{-1} respectively. The main characteristics of the MWTP influent were COD between 250 and 300, DOC between 97 and 120 and TIC 95 and 120 mg L^{-1}.

2.2. Solar photo-Fenton pilot plant

Photo-Fenton experiments were performed at the Plataforma Solar de Almería in a pilot compound parabolic collector (CPC) solar plant designed for solar photocatalytic applications [19]. This batch reactor is composed of two 11 L modules (CPC) with 12 pyrex glass tubes (30 mm O.D.) operated in series mounted on a fixed platform tilted 37° (local latitude). The water flows (20 L min^{-1}) directly from one module to the other and finally to a 10 L tank. From the tank it is pumped again to the solar collectors. The piping and valves (3 L) between the reactor and the tank are black HDPE, which is highly resistant to chemicals, weatherproof and opaque, preventing any photochemical effect from outside the collectors. The total illuminated area is 3 m^2, the total volume (two modules + tank + piping and valves) is 35 L (V_T) and the irradiated volume is 22 L (V_i). Solar ultraviolet radiation (UV) was measured by a global UV radiometer (Kipp & Zonen, model CUV 3) mounted on a platform tilted 37° (the same as the CPCs) and connected to a computer for continuous recording (data every 1 s). The temperature inside the reactor was continuously recorded by a temperature probe (Crioterm PT-100 3H) inserted in the piping. With Eq. (10), combination of the data from several days of experiments and their comparison with other photocatalytic experiments is possible,

$$t_{30\,W,n} = t_{30\,W,n-1} + \Delta t_n \frac{UV}{30}\frac{V_i}{V_T}; \quad \Delta t_n = t_n - t_{n-1}; \quad t_0 = 0\,(n = 1) \quad (10)$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation ($\lambda < 400$ nm) measured between t_{n-1} and t_n, and $t_{30\,W}$ is a “normalized illumination time”. In this case, time refers to a constant solar UV power of 30 Wm^{-2} (typical solar UV power on a perfectly sunny day around noon).

2.3. Experimental setup

The MWTP effluent was stripped of carbonates with H_2SO_4 (98%), as it is a well known fact that $CO_3{}^{2-}$ and $HCO_3{}^{-}$ are efficient radical scavengers [20–22], and spiked with 15 ECs at 100 μg L^{-1} each, selected from those often found in MWTP effluents [23]. Although the concentration of 100 μg L^{-1} for each compound is quite high compared to the real concentration of these ECs in the μg L^{-1} range [1,4], it is still low enough to simulate real conditions and compare the different approaches. In any case, the approach considered most suitable was tested under realistic conditions, spiking MWTP effluent with 5 μg L^{-1} of each EC. Samples were concentrated 50 times for analysis by SPE, as mentioned below.

Between 0.4 and 0.5 g of acid per liter effluent water was used to lower the TIC below 1 mg L^{-1}. After the stripping of CO_2, 1.4 mL of a solution containing the 15 compounds (2.5 g L^{-1} of each compound in MeOH, DOC from methanol was 12 mg L^{-1} or 0.6 mg L^{-1} for 100 μg L^{-1} and 5 μg L^{-1} experiments, respectively) was added directly into the reactor containing the effluent water. After homogenization, three different approaches were used:

(a) Adding peroxide, then after homogenization, 5 mg L^{-1} Fe and 35 mg L^{-1} oxalic acid which ads up to a molar ratio of 1:3.6 (ratio derived from Eq. (4)). Some excess oxalic acid was added, as it is consumed throughout the process.

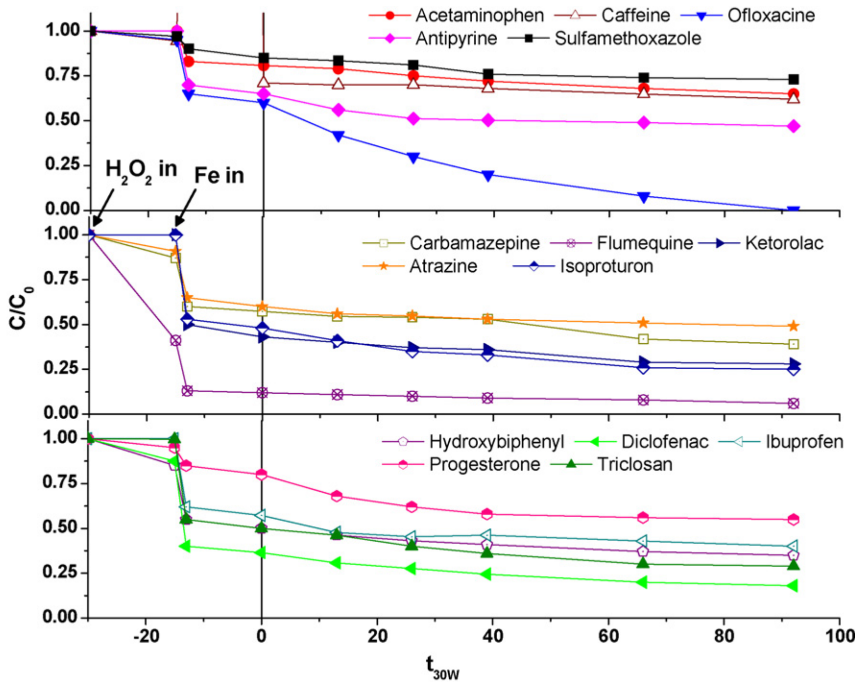

Fig. 1. Degradation profile of the 15 ECs (100 $\mu g\,L^{-1}$ of each) treated by photo-Fenton with 5 $mg\,L^{-1}$ Fe, 50 $mg\,L^{-1}$ H_2O_2 and neutral pH.

(b) Adding HA in the reactor, then 50 $mg\,L^{-1}$ H_2O_2 and after homogenization 5 $mg\,L^{-1}$ Fe as $FeSO_4{\cdot}7H_2O$.
(c) Mixing 11 L (31%) MWTP influent and 24 L (69%) effluent before adding peroxide and iron into the reactor, 50 $mg\,L^{-1}$ H_2O_2 and 5 $mg\,L^{-1}$ Fe, respectively.

After recirculation for 15 min, during which the Fenton reaction took place in the dark, the collectors were uncovered and the photo-Fenton reaction started. Iron, temperature, pH and hydrogen peroxide were measured in every sample taken, and if needed, additional peroxide was added to the reactor as consumed.

2.4. Analytical setup

Dissolved organic carbon (DOC) was measured immediately after taking the sample with a Shimadzu 5050A TOC analyzer. Total iron concentration (filtered and unfiltered) was determined with 1,10-phenantroline according to ISO 6332. Hydrogen peroxide was determined using titanium (IV) oxysulfate according to DIN 38402H15. The concentration profile of each compound was determined by UPLC–UV (Series 1200, Agilent Technologies, Palo Alto, CA). 25 mL samples were filtered through 0.2 μm syringe driven filters, the filters were washed (to avoid adsorption of any extraneous substance on it) with 3 mL acetonitrile, and then the two solutions were mixed, and an aliquot was injected into the UPLC–UV system. Analytes were separated using a reversed-phase C-18 analytical column (Agilent XDB-C18 1.8 μm, 4.6 × 50 mm) using acetonitrile (mobile phase A) and ultra pure water (25 mM formic acid, mobile phase B) at a flow rate of 1 $mL\,min^{-1}$. A linear gradient progressed from 10% A (original conditions) to 82% A in 12 min. Re-equilibration time was 3 min. The UV signal for each compound was recorded according to the wavelength of maximum light absorption, with the response limits of detection (LODs) and limits of quantification (LOQs) as shown elsewhere [23]. The limit of quantification was 1.5–10.0 $\mu g\,L^{-1}$, depending on the EC, and the concentrations were calculated using a linear 5-point calibration curve (100, 50, 25 10 and 5 $\mu g\,L^{-1}$). Calibration curves had an R^2 of 0.9998 (sulfamethoxazole) to 0.9653 (triclosan). For the experiment with 5 $\mu g\,L^{-1}$ of each EC, solid phase extraction (SPE) was applied using an extraction vacuum chamber (Supelco Visiprep) and 6 cm^3 Oasis HLB cartridges. The cartridges were conditioned with 5 mL MeOH and 5 mL H_2O (pH 8). 100 mL of sample was adjusted to pH 8 and extracted at 10 $mL\,min^{-1}$, the cartridges were washed with 4 mL H_2O (pH 8), dried with N_2 for 10 min and eluted with 2 × 4 mL MeOH, evaporated to dryness with N_2 and recovered in 2 mL of ACN/H_2O (1:9), filtered through a 0.2-μm syringe driven filter and injected into the UPLC–UV described above. Under these conditions the recovery of ECs during the SPE was >90% and the LOD was approximately 0.5–0.1 $\mu g\,L^{-1}$.

3. Results

As mentioned above, in all cases, it was necessary to remove the carbonates from the MWTP effluent, as preliminary experiments had shown that degradation of the ECs in water containing carbonates is very slow and in some cases virtually inexistent. It is obvious as well that the buffer capacity of the CO_2-stripped MWTP effluent without any $CO_3{}^{2-}/HCO_3{}^{-}$ is very low, and that addition of any substance changes the pH significantly. Experiments with stripped wastewater (see Fig. 1), 100 $\mu g\,L^{-1}$ of each EC, 50 $mg\,L^{-1}$ H_2O_2 and 5 $mg\,L^{-1}$ Fe and neutral pH (6.5–7.5) showed partial degradation of the ECs in the first 15 min (Fenton reaction). Fenton degradation was very quick after adding just 5 $mg\,L^{-1}$ of Fe^{2+} but it did not proceed further until the reactor was uncovered ($t_{30\,W} > 0$), as Fe^{3+} reduction to Fe^{2+} was inefficient without illumination. The same behavior was observed during the different tests performed for this work. After illumination though, the reaction stopped due to the inhibition of Fe^{2+} regeneration by Reactions (1)–(3) as no photoactive ferric iron complexes were available. Experiments with an initial peroxide concentration of 200 $mg\,L^{-1}$ showed an enhanced, but still unsatisfactory degradation of the ECs, in a $t_{30\,W}$ of 110 min, but with a residual H_2O_2 concentration of 150 $mg\,L^{-1}$ and a final pH of 4.3. All in all, these results were unsatisfactory and favored the three approaches for promoting Reaction (1), and making it available for photochemical reactions and Fe^{2+} regeneration.

Table 1
Summary of EC (100 $\mu g\,L^{-1}$ of each) degradation under different experimental conditions.

EC	Oxalic acid C/Co [%] at $t_{30\,W}$ > 50 min	HA 50 $mg\,L^{-1}$ C/Co [%] at $t_{30\,W}$ > 150 min	HA 25 $mg\,L^{-1}$ C/Co [%] at $t_{30\,W}$ > 150 min	HA 10 $mg\,L^{-1}$ C/Co [%] at $t_{30\,W}$ > 150 min	Influent:effluent = 1:3 C/Co [%] at $t_{30\,W}$ > 200 min
Acetaminophen	<LOD	27%	<LOD	<LOD	65%
Caffeine	<LOD	10%	11%	4%	82%
Ofloxazine	<LOD	<LOD	<LOD	<LOD	2%
Antipyrine	<LOD	52%	12%	1%	83%
Sulfamethoxazole	<LOD	21%	7%	3%	75%
Carbamazepine	<LOD	24%	1%	<LOD	76%
Flumequine	<LOD	<LOD	<LOD	<LOD	<LOD
Ketorolac	<LOD	6%	1%	<LOD	38%
Atrazine	2%	70%	43%	24%	94%
Isoproturon	<LOD	22%	6%	<LOD	73%
Hydroxybiphenyl	<LOD	28%	8%	2%	60%
Diclofenac	<LOD	6%	<LOD	<LOD	11%
Ibuprofen	<LOD	26%	<LOD	<LOD	76%
Progesterone	<LOD	25%	10%	6%	65%
Triclosan	<LOD	20%	26%	11%	44%
H_2O_2 consumption [$mg\,L^{-1}$]	48	70	50	58	57
DOC initial [$mg\,L^{-1}$]	22	32	28	26	39
DOC final [$mg\,L^{-1}$]	15.4	30	24	25	38
pH initial	6.1	6.8	7.2	6.7	6.9
pH final	4.0	6.0	4.6	4.2	6.8

The experiments with the addition of 35 $mg\,L^{-1}$ of oxalic acid showed promising degradation, but lowered the pH significantly. Most of the ECs were degraded in $t_{30\,W}$ = 46 min (see Table 1). Only atrazine at a very low concentration remained after this time. Figs. 2 and 3 show the degradation profile of the 15 compounds and the development of DOC, pH, and peroxide consumption. It may clearly be seen that oxalic acid lowers the pH to 3.3, which is in the range of a normal photo-Fenton treatment. After a certain treatment time, pH rose again (without any detrimental effect on EC degradation) due to oxalic acid mineralization. So the effectiveness of this experiment could well be due to the low pH, but previous experiments [23] showed, that the degradation of the 15 compounds was slower in a simple photo-Fenton system at pH 3. In that experiment, total degradation of ECs was achieved after $t_{30\,W}$ = 160 min (a few $\mu g\,L^{-1}$ of atrazine and triclosan were still present at that time). These results confirm that the main difficulty in running photo-Fenton (at low iron concentration) far from the optimum pH is related to the absence of photoactive $[Fe(OH)]^{2+}$.The presence of other substances is therefore necessary for Fe^{2+} regeneration, but the use of oxalic acid was excluded from further development because the results were not as promising as simple photo-Fenton and it would not be consistent to add other organics at high concentration to MWTP effluent to promote EC degradation. Low pH (around pH 4) at the end of the treatment was another drawback of this procedure (Table 2).

To simplify presentation of the results, all the following figures were drawn for the sum of all ECs (ΣECs) instead of including the detailed concentration of each EC. In any case, EC details are included in the text. For experiments with the second option, three different concentrations of HA were used: 50 $mg\,L^{-1}$, 25 $mg\,L^{-1}$ and 10 $mg\,L^{-1}$, which accounts for a mass ratio to iron of 1:10, 1:5 and 1:2 respectively. All experiments conducted with HA showed

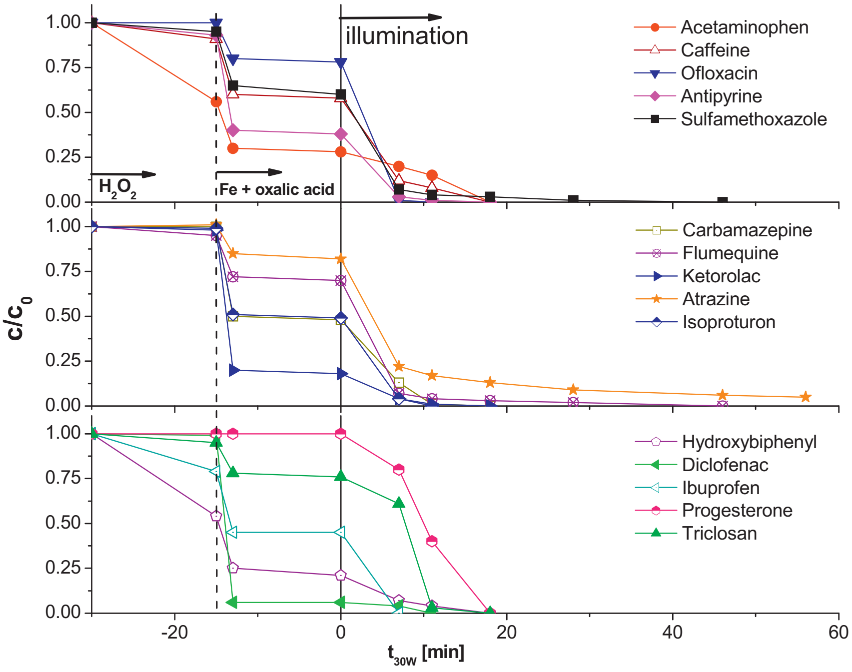

Fig. 2. Degradation profile of the 15 ECs (100 $\mu g\,L^{-1}$ of each) treated with photo-Fenton and oxalic acid. Procedure: Adding peroxide, 15 min homogenization, adding Fe + oxalic, 15 min homogenization and illumination.

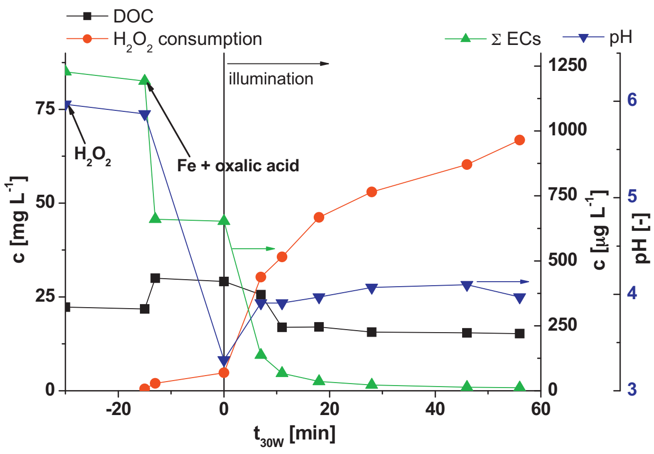

Fig. 3. DOC evolution, H_2O_2 consumption, pH value and sum of all ECs as a function of t_{30W}.

slower degradation of the ECs (see Fig. 4) than the experiments conducted with oxalic acid (see Table 1), and the higher the HA concentration, the slower their degradation, but the pH was more stable. The slower EC degradation rate with higher HA concentration could be due to the fact that HA was also degraded during the process, thus competing with the ECs for the HO radicals [18]. Wastewater background DOC was in the range of tens of mg/L, and all 15 compounds together at concentrations of 100 µg L^{-1} produce no more than 1 mg/L of DOC. Therefore, results of DOC degradation with EC mineralization would be meaningless. These results also demonstrated that ECs were degraded without a substantial mineralization of DOC, which also led to less consumption of H_2O_2 (Fig. 5).

The idea behind the experiments with a mixture of treated and untreated waste water in a 1–3 ratio was to make use of substances occurring naturally in waste water which could form photoactive $Fe^{3+}L$ and avoid adding them. The results of this experiment were rather disappointing, as degradation of the ECs was very slow. Reasons for that could be a lack of L in the particular waste water used or substances in it which either scavenge the radicals and/or peroxide. As a mixture of MWTP influent and effluent was used, the reason is difficult to imagine, but what was very clear was that any possible beneficial effect of L content of the influent was balanced by its higher organic content. Therefore, the next step was to determine whether the conditions tested (photo-Fenton at neutral pH with 10 mg L^{-1} HA) were suitable for treating effluent from a MWTP. For this purpose, MWTP effluent was spiked with 5 µg L^{-1} of each EC. Samples were analyzed after applying SPE as described in Section 2.4.

Table 2
Summary of EC (5 µg L^{-1} of each) degradation at neutral pH with and without 10 mg L^{-1} HA.

EC	Photo-Fenton pH 6.5 C/C$_0$ [%] at t_{30W} > 147 min	Photo-Fenton pH 6.5 10 mg L^{-1} HA C/C$_0$ [%] at t_{30W} > 147 min
Acetaminophen	53%	n.q.
Caffeine	n.q.	10%
Ofloxazine	<LOD	<LOD
Antipyrine	56%	<LOD
Sulfamethoxazole	62%	2%
Carbamazepine	23%	2%
Flumequine	n.q.	1%
Ketorolac	12%	<LOD
Atrazine	56%	31%
Isoproturon	29%	<LOD
Hydroxybiphenyl	42%	n.q.
Diclofenac	8%	<LOD
Ibuprofen	20%	<LOD
Progesterone	n.q.	<LOD
Triclosan	n.q.	8%
H_2O_2 consumption [mg L^{-1}]	38	37
DOC initial [mg L^{-1}]	21	18
DOC final [mg L^{-1}]	17.5	17.5
pH initial	6.2	6.4
pH final	6.5	4.9

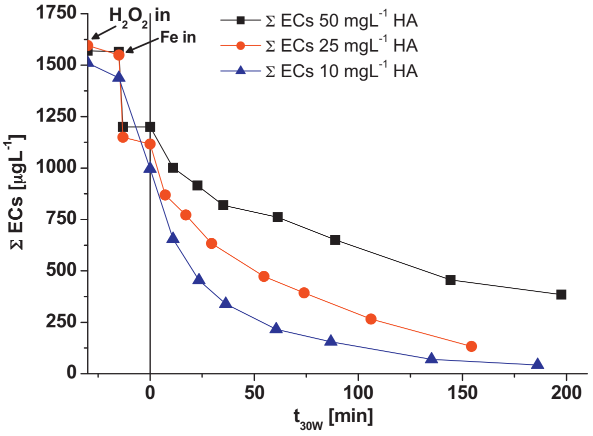

Fig. 4. Degradation profile for the sum of the ECs (100 µg L^{-1} of each) treated with photo-Fenton and different HA concentrations.

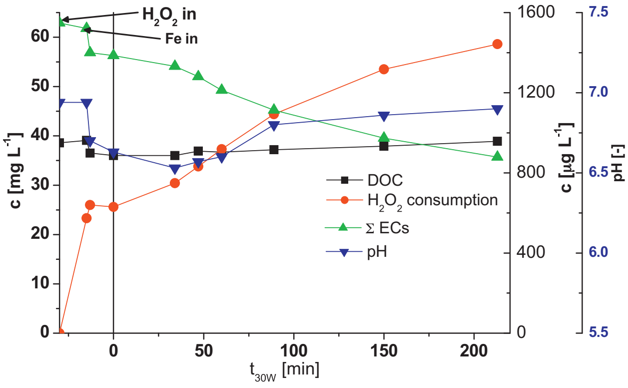

Fig. 5. DOC, H_2O_2 consumption, pH value and sum of all EC degradation as a function of t_{30W} in a mixture of 31% influent water and 69% effluent water.

Photo-Fenton experiments with an initial concentration of 5 µg L^{-1} ECs were carried out at neutral pH with and without addition of 10 mg L^{-1} HA to see if a lower concentration of ECs behaved the same as the higher concentration of 100 µg L^{-1}. As seen in Fig. 6, EC degradation was very slow at pH 6.5 without HA. H_2O_2 consumption in the two different experiments was quite similar taking into account the illumination time, as well as the decrease in DOC. pH dropped from 6.4 to 4.9 in the experiment with HA, while pH rose slightly (6.2–6.5) in the experiment without HA. Degradation, on the other hand, increased drastically with HA, confirming the results found with 100 µg L^{-1} of each EC. It should be mentioned that the LOD in this case was between 0.5 and 0.1 µg L^{-1} as SPE with an average recovery rate of >90% was applied.

4. Conclusions

The oxalate-enhanced process provided satisfactory EC degradation results, which were complete within a reasonable time. The only drawback of this process is the low residual pH of the treated water, which must be raised again to at least 6.5 for reuse. This may

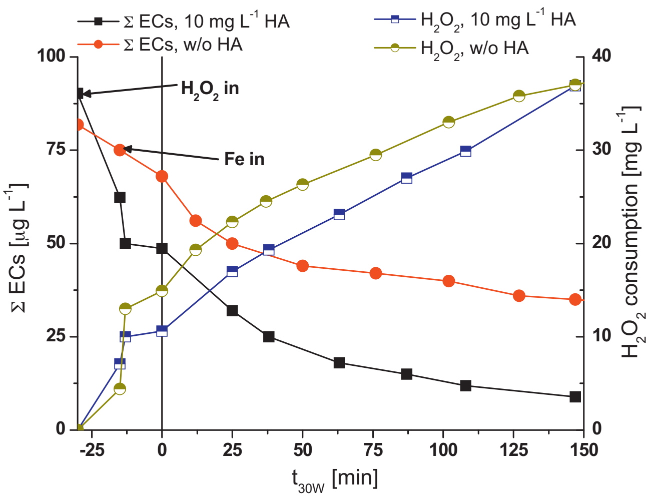

Fig. 6. EC (5 μg L^{-1} of each) degradation in real waste water at pH = 6.5, 5 mg L^{-1} Fe and H_2O_2 peroxide consumption with 10 mg L^{-1} HA (■) and without HA (●).

pose a problem, as the salinity of the water is also raised and thus may not be suitable for all plants.

EC degradation with the HA-enhanced process was fast and nearly complete. 50 mg L^{-1} HA is too slow and can be discarded. 10 mg L^{-1} HA was a good option, balancing degradation time and residual pH, which was close to 5. This means that the ECs can be degraded in a reasonable time while much less base would be needed to neutralize the water than for oxalic acid.

Mixing of MWTP influent and effluent delivered rather disappointing results, as EC degradation was unsuccessful in all cases tested. This option has to be reviewed, to see if degradation behavior varies with influents from different MWTPs or with samples taken from different sections of the MWTPs prior to the biotreatment (secondary treatment). This procedure would offer a new and promising way of degrading ECs in MWTP effluents without adding any other substances.

Acknowledgements

Funding for this work was provided by the Spanish Ministry of Science and Innovation under the Consolider-Ingenio 2010 programme (project CSD2006-00044 Tragua; http://www.consolider-tragua.com) and by the Andalusia Regional Government (project no. P06-TEP-02329). Nick Klamerth would to thank the University of Almería and CIEMAT for his Ph. D. research grant.

References

[1] J.B. Baugros, B. Giroud, G. Dessalces, M.F. Grenier-Loustalot, C. Cren-Oliv, Analytica Chimica Acta 607 (2008) 191–203.
[2] M.J. Gómez, M.M. Gómez-Ramos, A. Agüera, M. Mezcua, S. Herrera, A.R. Fernández-Alba, Journal of Chromatography A 1216 (2009) 4071–4082.
[3] K. Kümmerer, Antibiotics in the aquatic environment – a review – part I, Chemosphere 75 (2009) 417–434;
K. Kümmerer, Antibiotics in the aquatic environment – a review – part II, Chemosphere 75 (2009) 435–441.
[4] N. Unceta, M.C. Sampedro, N. Kartini, A. Bakar, A. Gómez-Caballero, M.A. Goicolea, R.J. Barrio, Journal of Chromatography A 1217 (2010) 3392–3399.
[5] N. Bolong, A.F. Ismail, M.R. Salim, T. Matsuura, Desalination 239 (2009) 229–246.
[6] M.D. Camacho-Muñoz, J.L. Santos, I. Aparicio, E. Alonso, Journal of Hazardous Materials 177 (2010) 1159–2116.
[7] D. Fatta-Kassinos, I.K. Kalavrouziotis, P.H. Koukoulakis, M.I. Vasquez. Science of the Total Environment, doi:10.1016/j.scitotenv.2010.03.036, in press, Available online 1 May 2010.
[8] O.K. Dalrymple, D.H. Yeh, M.A. Trotz, Journal of Chemical Technology and Biotechnology 82 (2007) 121–134.
[9] S. Malato, P. Fernandez-Ibañez, M.I. Maldonado, J. Blanco, W. Gernjak, Catalysis Today 147 (2009) 1–59.
[10] N. Klamerth, L. Rizzo, S. Malato, M.I. Maldonado, A. Agüera, A.R. Fernández-Alba, Water Research 44 (2010) 545–554.
[11] J.J. Pignatello, E. Oliveros, A. MacKay, Critical Reviews in Environmental Science and Technology 36 (2006) 1–84.
[12] A. Safarzadeh-Amiri, J.R. Bolton, S.R. Carter, Journal of Advanced Oxidation Technologies 1 (1996) 18–26.
[13] D. Prato-Garcia, R. Vasquez-Medrano, M. Hernandez-Esparza, Solar Energy 83 (2009) 306–315.
[14] J.M. Monteagudo, A. Duran, I. San Martin, M. Aguirre, Applied Catalysis B: Environmental 96 (2010) 486–495.
[15] J.P. Auger, C. Richard, Journal of Photochemistry & Photobiology A: Chemistry 93 (1996) 193–198.
[16] M. Kepczynski, A. Czosnyka, M. Nowakowska, Journal of Photochemistry & Photobiology A: Chemistry 185 (2007) 198–205.
[17] M.J. Farré, X. Doménech, J. Peral, Journal of Hazardous Materials 147 (2007) 167–174.
[18] E. Lipczynska-Kochany, J. Kocjany, Chemosphere 73 (2008) 745–750.
[19] M. Kositzi, I. Poulios, S. Malato, J. Cáceres, A. Campos, Water Research 38 (2004) 1147–1154.
[20] G.V. Buxton, A.J. Elliot, Radiation Physics and Chemistry 27 (1986) 241–243.
[21] N. Klamerth, N. Miranda, S. Malato, A. Agüera, A.R. Fernandez-Alba, M.I. Maldonado, J.M. Coronado, Catalysis Today 144 (2009) 124–130.
[22] D. Vione, S. Khanra, S. Cucu Man, P.R. Maddigapu, R. Das, C. Arsene, R.I. Olariu, V. Maurino, C. Minero, Water Research 43 (2009) 4718–4728.
[23] N. Klamerth, S. Malato, M.I. Maldonado, A. Agüera, A.R. Fernández-Alba, Environmental Science and Technology 44 (2010) 1792–1798.