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Degradation of emerging contaminants at low concentrations in MWTPs effluents with mild solar photo-Fenton and TiO_2

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ABSTRACT

The purpose of this study was to propose a municipal wastewater treatment method based on solar Advanced Oxidation Processes (AOPs) permitting reuse of the treated wastewater. Experiments were performed in a pilot compound parabolic collector (CPC) solar plant at the Plataforma Solar de Almería. Mineralisation was monitored by measuring the dissolved organic carbon (DOC), and the concentration profile of each compound during degradation was determined by HPLC–UV. Two different approaches, photo-Fenton (pH = 2.8) and TiO_2 were tested with 9 different emerging contaminants at 100 $\mu g\ L^{-1}$ each (acetaminophen, antipyrine, atrazine, caffeine, diclofenac, isoproturon, progesterone, sulfamethoxazole, and triclosan) at low iron and TiO_2 concentrations. Photo-Fenton was by far more effective than TiO_2 for degrading these contaminants, and was therefore selected for further study. The 9 contaminants were tested under the following conditions without pH adjustment: (i) Fe = 5 $mg\ L^{-1}$, D.I. water; (ii) Fe = 5, 15 and 55 $mg\ L^{-1}$, standard fresh water; (iii) Fe = 5 $mg\ L^{-1}$, standard fresh water without $NaHCO_3$. Initial amount of hydrogen peroxide was 50 $mg\ L^{-1}$, frequently analysed and added to maintain this concentration. It was demonstrated that low efficiency in some cases is mainly due to bicarbonates, and it is therefore proposed that the process be improved, either by increasing the iron concentration, or eliminating bicarbonates.

1. Introduction

Spain has the highest water deficit in Europe, with water exploitation rates (annual consumption/resources) of over 20%, which is generating serious social concern. Approximately 65% of this consumption is for agriculture, 20% for industry and 15% is domestic. Although possible methods for mitigating the scarcity of water are widely discussed in the media (e.g., desalination and inter-basin water transfer), and although they may be cost-effective, they are not the best options due to high environmental costs, energy consumption and/or specific infrastructures. Therefore, economically competitive reuse of water is a necessary environmental alternative to avoid the aforementioned energy consumption and direct environmental impact. Spain is also one of the countries with the highest water reuse, but still in small quantities; only 5% of wastewater is reused, whilst its potential for water reuse is 1300 Mm^3, one order of magnitude more than at present [1].

One of the main sources of water for potential reuse comes from municipal wastewater treatment plants (MWTPs). However, quality demands for reusable water [2–4] are that it do not contain any toxic, endocrine-disrupting compounds or nonbiodegradable substances, such as pesticides, pharmaceuticals, hormones, synthetic fragrances, and others which escape conventional wastewater treatment [5,6]. Special attention has recently been given to what are called "emerging contaminants", mostly unregulated compounds that may be candidates for future regulation depending on research on their potential effects on health, and monitoring data regarding their occurrence. Particularly relevant examples of such emerging compounds are those which do not need to persist in the environment to cause a detrimental effect, because their high transformation/removal rates are compensated by their continuous introduction into the environment [7]. Concern about the growing problem of the continuously rising concentrations of these compounds must be emphasized [8–10]. These hardly biodegradable products, which resist treatment by conventional sewage plants, have been found in their effluents at mean concentrations ranging from 0.1 to 20.0 $\mu g\ L^{-1}$ [11,12]. Consequently, the application of more exhaustive wastewater treatment protocols, including the use of new and improved technologies, is a necessary task.

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Oxidation technologies [13], among them AOPs (Advanced Oxidation Processes), are recently considered an interesting option to solve this problem, mainly because of their versatility [14,15]. AOPs, generally defined as oxidation processes generating hydroxyl radicals, are responsible for organic degradation due to their strong oxidising power. They are therefore able to oxidise and mineralise almost every organic molecule yielding CO_2 and inorganic ions. Most of the systems classified as AOPs make use of a combination of either oxidants and irradiation (O_3/H_2O_2/UV), or a catalyst and irradiation (Fe^{2+}/H_2O_2; UV/TiO_2). The common drawback of such systems is the high demand of electrical energy for devices such as ozonators, UV lamps, etc., very often making such treatments economically disadvantageous. This is why, although AOPs are well known for their capacity for oxidising and mineralising almost any organic contaminant, commercial applications are still scarce. Future applications of these processes could be improved through the use of catalysis and solar energy. Therefore, investigation is focusing increasingly [16] on the two AOPs, which can be powered by solar radiation, i.e., light with a wavelength over 300 nm, homogeneous catalysis by the photo-Fenton reaction and heterogeneous catalysis by UV/TiO_2.

Photo-Fenton and TiO_2 treatments have been reported as effective methods for eliminating these compounds [17], but their main drawback is their relatively high operating cost. As the concentrations of these substances in reusable MWTP water effluents are normally below 20 $\mu g\,L^{-1}$, conventional treatment with TiO_2 slurries (hundreds of mg L^{-1}, or more) [18], high iron concentrations (mM range), excessive amounts of H_2O_2 and a pH around 3 [19] would be unnecessary. Therefore, a very mild treatment with photo-Fenton (at an extremely low iron concentration and H_2O_2 dose, and no pH adjustment) or with highly diluted TiO_2 slurries could be of interest for study.

The purpose of this paper is therefore technical evaluation of mild solar TiO_2 and photo-Fenton as tertiary treatments in MWTPs. The contaminated water tested in this paper was a mixture of emerging contaminants at low concentrations (such as pharmaceuticals, pesticides and personal care products) selected from 56 compounds found in MWTP effluents in previous studies [12]. This research, the first results of which are included in this paper, is part of an ambitious programme (Treatment and Reuse of Waste Waters for Sustainable Management "TRAGUA", http://www.consolider-tragua.com) financed by the Spanish Government, and involving the participation of a multidisciplinary team of 24 research groups tackling the different aspects involved in the reuse of wastewater coming from MWTPs.

2. Experimental

2.1. Reagents

All reagents used for chromatographic analyses, acetonitrile, methanol, and ultrapure (MilliQ) water, were HPLC grade. Analytical standards for chromatography analyses were purchased from Sigma–Aldrich. Table 1 lists the 9 compounds used. The heterogeneous photocatalytic degradation tests were carried out using a slurry suspension (5 mg L^{-1}) of Degussa (Frankfurt, Germany) P-25 titanium dioxide (surface area 51–55 $m^2\,g^{-1}$). Photo-Fenton experiments were performed using iron sulphate ($FeSO_4{\cdot}7H_2O$), reagent-grade hydrogen peroxide (30%, w/v) and

Table 1

List of the 9 model compounds used in this study, including the limits of detection (LODs) and limits of quantification (LOQs).

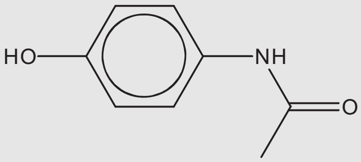
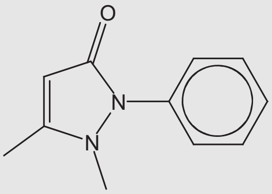
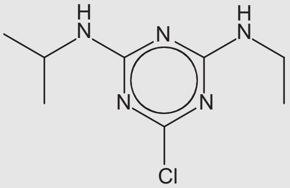
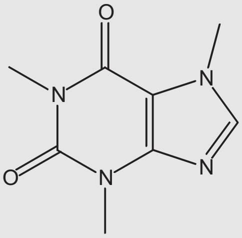
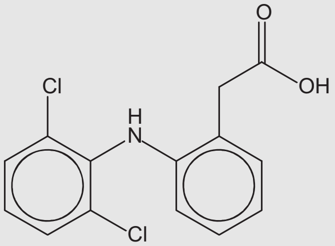
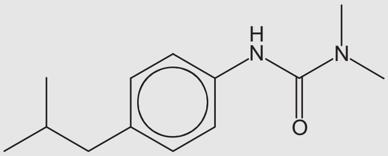
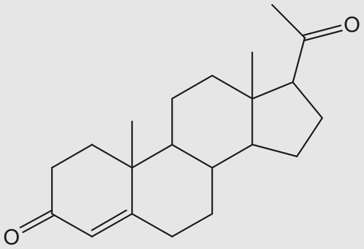
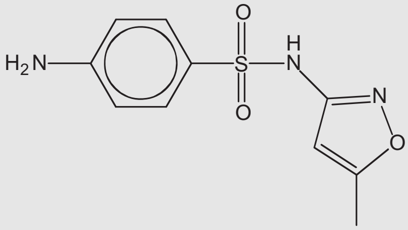
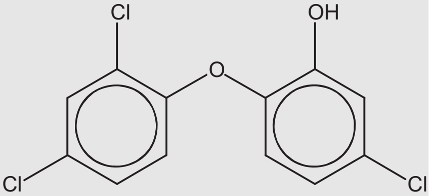
Name	Used as	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)	Structure
Acetaminophen	Analgesic/antipyretic	3	6	
Antipyrine	Analgesic	5	9	
Atrazine	Herbicide	2	4	
Caffeine	Stimulant	2	4	

Table 1 (*Continued*)

Name	Used as	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)	Structure
Dichlofenac	Non-steroidal anti-inflammatory	10	20	
Isoproturon	Phenylurea herbicides	2	4	
Progesterone	Steroid hormone	5	10	
Sulfamethoxazole	Bacteriostatic antibiotic	3	6	
Triclosan	Antibacterial and antifungal agent	12	25	

sulphuric acid for pH adjustment (around 2.7–2.9) only when necessary, all provided by Panreac. $NaHCO_3$ ($96\,mg\,L^{-1}$), $CaSO_4{\cdot}2H_2O$ ($60\,mg\,L^{-1}$), $MgSO_4$ ($60\,mg\,L^{-1}$), and KCl ($4\,mg\,L^{-1}$) for preparing standard moderately hard fresh water [20] were all analytical grade and supplied by Panreac. Demineralised water used in the pilot plant was supplied by the Plataforma Solar de Almería (PSA) distillation plant (conductivity $<10\,\mu S\,cm^{-1}$, $Cl^- = 0.7–0.8\,mg\,L^{-1}$, $NO_3^- = 0.5\,mg\,L^{-1}$, organic carbon $<0.5\,mg\,L^{-1}$).

2.2. Analytical equipment and methods

Photo-Fenton and TiO_2 slurry experiments were performed in a pilot compound parabolic collector (CPC) solar plant designed at the Plataforma Solar de Almería for solar photocatalytic applications. This reactor is composed of two modules (11 L each) with twelve Pyrex glass tubes (30 mm O.D.) 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 reservoir tank (10 L). The piping and valves (3 L) between the reactor and the tank are black HDPE, material chosen because it is highly resistant to chemicals, weather-proof and opaque to avoid any photochemical effect outside the collectors. The total illuminated area is $3\,m^2$, the total volume (two modules + reservoir 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). The temperature inside the reactor was continuously recorded by a PT-100 inserted in the piping. A plant diagram has been published elsewhere [21]. With Eq. (1), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible, 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 W m^{-2} (typical solar UV power on a perfectly sunny day around noon).

$$t_{30\,\mathrm{W},n} = t_{30\,\mathrm{W},n-1} + \Delta t_n \frac{\mathrm{UV}}{30} \frac{V_\mathrm{i}}{V_\mathrm{T}}; \quad \Delta t_n = t_n - t_{n-1}; \quad t_0 = 0 \ (n = 1) \tag{1}$$

The mixture of the 9 compounds (100 μg L^{-1} each) previously dissolved in methanol at 2.5 g L^{-1} each (mother solution) was added directly (1.4 mL of mother solution) into the pilot plant and properly homogenised by turbulent recirculation for 15 min. Methanol was used to dissolve the contaminants and also to attain background organic content similar to MWTP effluents. Indeed, original Total Organic Carbon (TOC) provided by methanol was 12 mg L^{-1}. At the beginning of the process, the collectors were covered, the pH was adjusted (only in those experiments with pH adjustment) and ferrous iron salt was added. After each addition of reagents, the plant was well homogenised by recirculation. Finally, an initial amount of hydrogen peroxide was added (50 mg L^{-1}). Then the collectors were uncovered and photo-Fenton began. Hydrogen peroxide was measured frequently. The TiO_2 experiments were performed similar to the photo-Fenton experiments at a concentration of 5 mg L^{-1}. As in the photo-Fenton experiments, 1.4 mL of the concentrated mother solution was added to the reactor. After homogenisation, the TiO_2 was added, homogenised for 15 min and illuminated.

Mineralisation was monitored by measuring the Dissolved organic carbon (DOC) by direct injection of filtered samples into a Shimadzu-5050A TOC analyser calibrated with standard solutions of potassium phthalate and provided with an NDIR detector. Colorimetric determination of total iron concentration with 1,10-phenantroline was used according to ISO 6332. Hydrogen peroxide was analysed by a fast, simple spectrophotometric method using ammonium metavanadate, which allows the H_2O_2 concentration to be determined immediately based on a red-orange peroxovanadium cation formed during the reaction of H_2O_2 with metavanadate, with a maximum absorption at 450 nm. The peroxide concentrations are calculated from absorption measurements by a ratio found by Nogueira et al. [22].

The concentration profile of each compound during degradation was determined by an HPLC–UV method specially developed for this application [12]. Analytes were separated using an HPLC (series 1100, Agilent Technologies, Palo Alto, CA) equipped with a reversed-phase C-18 analytical column (phenomenex Gemini 5 μm C18, 150 mm × 3.0 mm). The compounds were separated using acetonitrile (mobile phase A) and ultrapure water (25 mM formic acid, mobile phase B) at a flow rate of 0.2 mL min^{-1}. A linear gradient progressed from 10% A (initial conditions) to 100% A in 40 min. Re-equilibration time was 15 min. 25 mL of sample was filtered through a 0.2-μm syringe-driven filter, and to get any adsorbed amounts of compounds, the filter was washed with 3 mL acetonitrile. The two solutions were mixed and a 50-μL aliquot was injected into the HPLC. The UV signal was recorded at different wavelengths according to the wavelength of maximum light absorption of each compound as follows: 205 nm (caffeine and isoproturon), 223 nm (atrazine), 243 nm (antipyrine), 245 nm (acetaminophen), 248 nm (progesterone), 267 nm (sulfamethoxazole), 277 nm (diclofenac) and 280 nm (triclosan). Under these conditions, the limits of detection (LODs) and limits of quantification (LOQs) were those shown in Table 1.

3. Results and discussion

As the scope of this study was to propose a solar AOP treatment permitting reuse of MWTP effluents, the first step was to compare two different approaches, photo-Fenton and TiO_2. In both cases tests were done under mild conditions (low iron and TiO_2 concentration). Taking into consideration, as commented in the introduction, that typical concentrations are in the 0.1–20.0 μg L^{-1} range, it was decided to work at 100 μg L^{-1}. It was also decided not to work (at least during the first stages of the studies presented in this paper) with real effluents from MWTP due to the difficulties in acquiring representative samples and preserving them in steady conditions for a long enough time to perform the tests. Indeed, these results could be considered unadventurous compared to a real-life situation, as all the tests were done at a higher-than-typical concentration (100 μg L^{-1}) of emerging contaminants, with organic carbon in the same range of concentration (around 15 mg L^{-1}) found in the effluents and the key experiments in reconstituted fresh water.

3.1. Comparison of TiO_2/photo-Fenton

The main purpose of the first set of experiments was to find out which one of the reactions (TiO_2 or photo-Fenton) is best suited for the degradation of emerging contaminants. According to the previous results with other compounds [23] small amounts of iron could well be enough to provide satisfactory reaction rates. Kinetics would be slow with TiO_2 at 5 mg L^{-1}, as only around 50% of the photons could be absorbed in a 30-mm photoreactor [24], but it would enough to degrade such a low concentration of contaminants. The TiO_2 experiment showed almost complete degradation of the 9 compounds except atrazine after 200 min under illumination, as shown in Fig. 1. Degradation by TiO_2 presented typical first-order kinetics (data not shown). It was not possible to calculate first-order constants during the photo-Fenton experiments (accurately enough) due to the rapid evolution of all the contaminants, therefore the two treatments were not compared by first-order kinetics, but by other empirical kinetics results as shown in Table 2.

The irradiation time ($t_{30\,\mathrm{W}}$) necessary for TiO_2 to achieve degradation below the LOQ is around 60 min for diclofenac and triclosan, 113 min for triclosan and caffeine, and 145 min for sulfamethoxazole, progesterone and acetaminophen. Atrazine and antipyrine were still present after 196 min of irradiation, but only the atrazine concentration was significant (20 μg L^{-1}). Fig. 2 shows the degradation of the 9 compounds by photo-Fenton (5 mg L^{-1} Fe

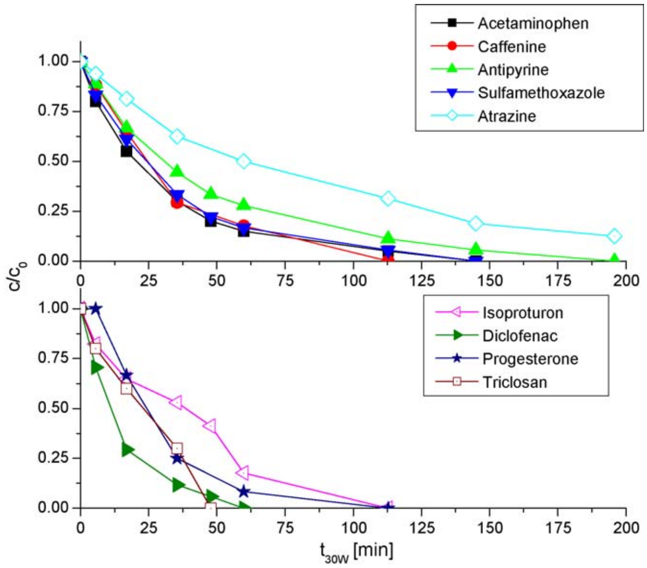


Fig. 1. Degradation of 9 emerging contaminants (0.1 mg L^{-1} each) with TiO_2 at 5 mg L^{-1} in demineralised water.

Table 2
Initial reaction rates (r_0) and $t_{30\ \mathrm{W,LOQ}}$ for TiO_2 and photo-Fenton experiments.

Compound	TiO_2		Photo-Fenton	
	r_0 (μg L^{-1} min^{-1})	$t_{30\ \mathrm{W,LOQ}}$ (min)	r_0 (μg L^{-1} min^{-1})	$t_{30\ \mathrm{W,LOQ}}$ (min)
Acetaminophen	5.3	145	>10.7	10
Caffeine	3.4	113	>11.3	10
Antipyrine	3.6	>196	>10.8	10
Sulfamethoxazole	4.1	145	>11.0	10
Atrazine	1.7	>196	9.2	20
Isoproturon	3.6	113	10.9	33
Diclofenac	7.1	60	>10.5	10
Progesterone	2.5	145	9.9	20
Triclosan	2.0	60	8.8	20

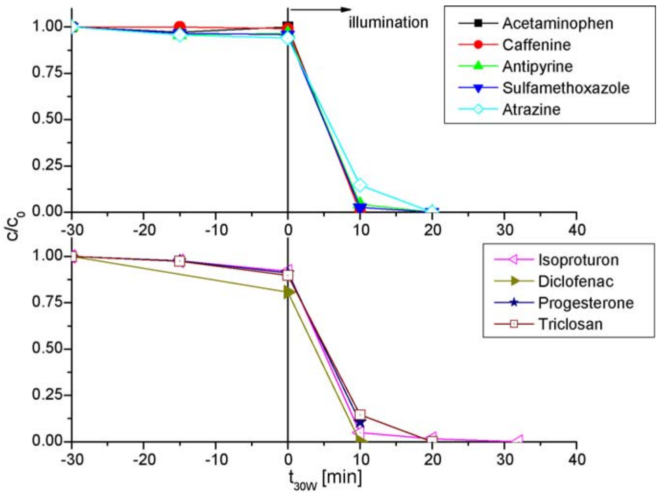


Fig. 2. Degradation of 9 emerging contaminants (0.1 mg L^{-1} each) by photo-Fenton with 5 mg L^{-1} Fe and pH = 2.8 in demineralised water.

and pH = 2). Almost no degradation of any compound was detected before illuminating the photoreactor. The degradation of most compounds was (below the LOQ) achieved within the first 10 min of illumination, atrazine, triclosan and progesterone were degraded after 20 min of irradiation and isoproturon was still detected at 38 min. All compounds were below the LOD after 33 min. Table 2 shows the initial reaction rates and illumination time to LOQ of the 9 model compounds for the experiments with TiO_2 and photo-Fenton. With photo-Fenton, the initial reaction rates (r_0) were calculated using only two experimental points and so Table 2 does not show an exact value of r_0 (r_0 could be higher). It could therefore be argued that the results are imprecise, but the sampling periods were selected for the characteristics of the photoreactor (see next paragraph). In this case, due to the rapid evolution of the compounds during the photo-Fenton treatment only two experimental points were possible.

More experimental points were not possible during the photo-Fenton experiment, as the pilot plant used in this work is a 3-L recirculation loop in a 22-L plug flow photoreactor with a well-stirred, 10-L non-reacting mixing tank. Since it is a dynamic system, the photoreactor outlet concentration (C_1) is not exactly the same as the mixing tank outlet concentration (C_2). Thus, unless properly accounted for, the presence of the tank can alter the perceived photoreactor performance. To solve this problem, a very high flow rate (20 L min^{-1}) was set in the photoreactor and so conversion would be low each time through (1.25 min) and sampling periods would be long enough (≥15 min). As pointed out by Wolfrum and Turchi [25], one must only account precisely for mixing in the dark tank if there is substantial conversion per pass ($C_2 > C_1$).

3.2. Photo-Fenton tests under different conditions without pH adjustment

As shown in Figs. 1 and 2 and in Table 2, photo-Fenton was by far more effective than TiO_2 for degrading the emerging contaminants. It has therefore been selected for further study. As mentioned in the introduction, it was intended to apply photo-Fenton under mild conditions (low iron concentration and without acidifying the wastewater). Tests were therefore done with the following conditions without pH adjustment for this purpose: (i) Fe = 5 mg L^{-1}, D.I. water; (ii) Fe = 5, 15 and 55 mg L^{-1}, standard fresh water; (iii) Fe = 5 mg L^{-1}, standard fresh water without $NaHCO_3$.

The main goal was to determine the effect of different Fe concentrations without modifying the pH of the wastewater, as treating reusable water with a large amount of acid is costly, so treatment of water without changing the pH is preferred. In these experiments, it was also decided to exploit the Fenton process during mixing and circulation of the water with iron and H_2O_2 by adding H_2O_2 to the reactor at $t = -30$ min, adding Fe at $t = -15$ min and starting illumination at $t = 0$. The idea behind this approach is to avoid precipitation of Fe as iron hydroxide (as pH was not adjusted to 2.8) due to remaining too long in the water without Fenton taking place. Indeed, with this procedure, Fe concentration in solution after the treatment was always over 2.5 mg L^{-1}. This procedure, which was used in all the experiments described below, leads to a 20–50% degradation of compounds and in some extreme cases up to 80% during the first step in the dark (Fenton process). Fig. 3 shows the degradation of the 9 compounds in D.I. water without pH adjustment. The degradation of all compounds but atrazine is achieved within 20 min illumination time. Atrazine is totally degraded after 35 min. The pH changes from pH = 6.8 at $t_{30\ \mathrm{W}} = 0$ min to pH = 3.8 at $t_{30\ \mathrm{W}} = 40$ min, demonstrating that the photo-Fenton process is efficient enough to degrade emerging contaminants at low concentrations without adjusting pH to the optimum pH = 2.8 and at low iron concentrations in demineralised water.

The next step was to simulate the behaviour of the 9 compounds with an iron concentration of 5 mg L^{-1} Fe in a moderately hard simulated fresh water (see Section 2.1) as shown in Fig. 4. Although some of the compounds (acetaminophen,

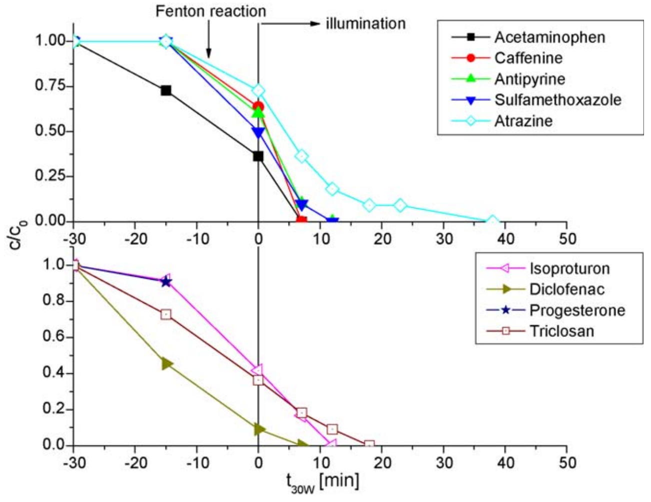


Fig. 3. Degradation of 9 emerging contaminants (0.1 mg L^{-1} each) by photo-Fenton with 5 mg L^{-1} Fe without pH adjustment in demineralised water.

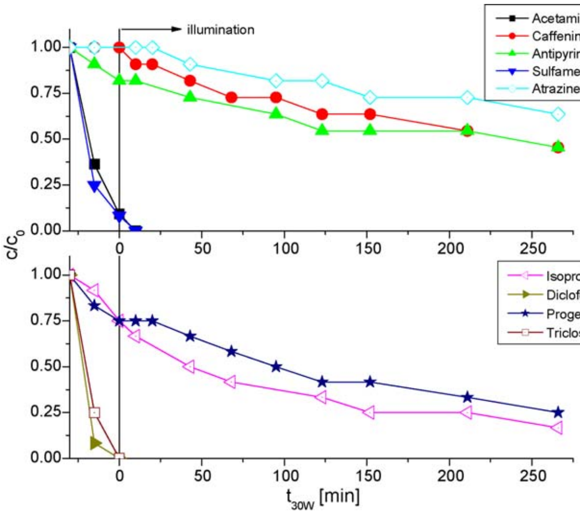


Fig. 4. Degradation of 9 emerging contaminants (0.1 mg L^{-1} each) by photo-Fenton with 5 mg L^{-1} Fe without pH adjustment in simulated fresh water.

sulfamethoxazole, triclosan and diclofenac) are degraded in the dark by Fenton, the other compounds (atrazine, caffeine, antipyrine, isoproturon and progesterone) are still present after 270 min of illumination at a relatively high concentrations (between 25% and 75% of the initial concentration).

It is well known that inorganic species (chloride, sulphate, phosphates, etc.) are usually detrimental to the photo-Fenton reaction rate [19], but radical scavengers such as carbonate species ($CO_3{}^{2-}$ and $HCO_3{}^{-}$) especially compete with organic contaminants for hydroxyl radical reactions, and significantly decrease the degradation efficiencies of organics through reactions (2) and (3). The carbonate ion is over 40 times as kinetically effective as the bicarbonate ion in scavenging hydroxyl radicals [26], as indicated by the rate constants for reactions ($2, k_{\mathrm{OH^{\cdot}HCO_3}} = 8.5 \times 10^6\,\mathrm{M^{-1}\,s^{-1}}$) and ($3, k_{\mathrm{OH^{\cdot}HCO_3}} = 3.9 \times 10^8\,\mathrm{M^{-1}\,s^{-1}}$). The simulated fresh water pH of 8.2 was lowered slightly during treatment to 7.9, which favoured the bicarbonate ions.

$$^{\bullet}OH + HCO_3{}^{-} \rightarrow H_2O + CO_3{}^{-\bullet} \tag{2}$$

$$^{\bullet}OH + CO_3{}^{2-} \rightarrow OH^{-} + CO_3{}^{-\bullet} \tag{3}$$

It was predicted that bicarbonates would be mainly responsible for the low process efficiency, as the concentration of other ionic species was not high enough to critically reduce photo-Fenton. As stated before, only acetaminophen, sulfamethoxazole, triclosan and diclofenac were easily degraded by $^{\bullet}$OH due to its aromatic substituted structure (OH–, Cl–, NH_2–) and therefore radical scavengers did not change substantially their degradation rate at low initial concentration (100 μg L^{-1}).

Therefore, one way to solve the problem could be to increase the iron concentration and thereby raise the concentration of $^{\bullet}$OH. Nevertheless, raising the iron concentration in this way to 15 mg L^{-1} did not enhance degradation. Degradation of the 9 emerging contaminants was quite similar to that shown in Fig. 4. Further increasing the iron concentration to 55 mg L^{-1} Fe, however, does have a significant effect on degradation of the compounds. Most of them were degraded after 30 min of illumination and only caffeine (8% of original) and atrazine (12% of original) were still present after 30 min. No Fe precipitation was detected as Fe was still in solution after 30 min. Caffeine and atrazine were degraded (below LOQ) after 45 and 75 min illumination time, respectively. This leads to the conclusion that increased $^{\bullet}$OH radical concentration (by increasing the photocatalyst concentration) could overcome the detrimental effect of radical scavengers.

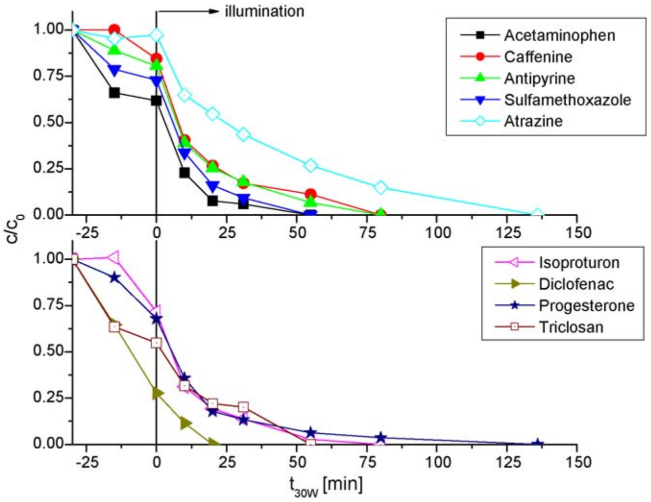


Fig. 5. Degradation of the 9 emerging contaminants (0.1 mg L^{-1} each) by photo-Fenton with 5 mg L^{-1} Fe without pH adjustment in simulated fresh water without $HCO_3{}^{-}$.

To confirm the effect of bicarbonates, another experiment was performed with simulated fresh water containing 81 mg L^{-1} Na_2SO_4 instead of 96 mg L^{-1} $NaHCO_3$ in order to maintain the concentration of the counter ion (Na) and the ionic strength. Fig. 5 shows the results. Although degradation is slower than in demineralised water (Fig. 3), it is far faster than degradation with 5 and 15 mg L^{-1} Fe. All of the compounds are degraded after 55 min illumination with the exception of atrazine which is degraded to below the LOQ after 130 min (Fig. 6).

3.3. Mineralisation and hydrogen peroxide consumption

Mineralisation measured during all tests was congruent with the results found with the 9 emerging contaminants. The more efficient process for eliminating the 9 parent compounds was, the more efficient overall mineralisation of the organic content was. Photo-Fenton in D.I. water at pH = 2.8 and unadjusted pH was able to substantially mineralise the organic content of the water, and both were very efficient. TiO_2 was also able to reduce

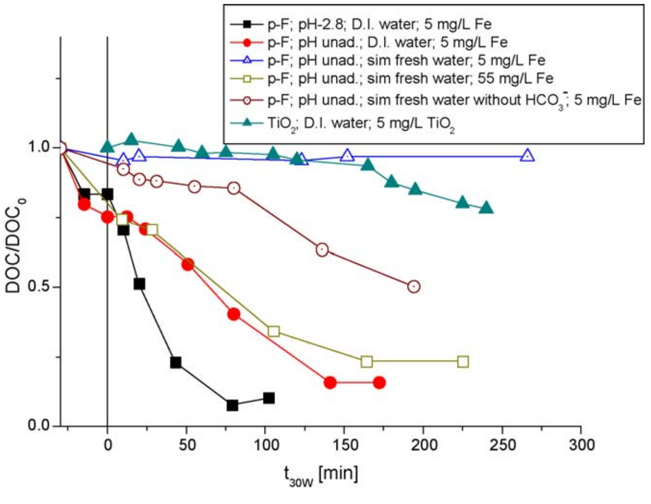


Fig. 6. DOC mineralisation during all tests shown in Figs. 1–5.

the organic content, but only by 20%. In the case of simulated fresh water treated using Fe = 55 mg L^{-1}, mineralisation was 75%, and only 50% when 5 mg L^{-1} of iron were used in the absence of bicarbonates. The processes (Fe 5 and 15 mg L^{-1} in simulated fresh water) which were inefficient for degrading the emerging contaminants were not efficient for reducing DOC either. H_2O_2 consumption for attaining complete degradation of the 9 emerging contaminants to the LOQ was higher when the pH was not optimum: 55 and 81 mg L^{-1} with 5 mg L^{-1} of Fe at pH = 2.8 and without pH adjustment, respectively. Very high (>250 mg L^{-1}) measured consumption with 5 and 15 mg L^{-1} in standard fresh water still did not reach the LOQ of all emerging contaminants. 148 mg L^{-1} were consumed with 55 mg L^{-1} of iron and only 92 mg L^{-1} when photo-Fenton was run with 5 mg L^{-1} but without bicarbonates. This reinforces the importance of bicarbonates as $^{\bullet}OH$ scavengers, as hydrogen peroxide required to reach LOQ was lower when no bicarbonates were present. It also reinforces the importance of removing CO_3^{2-} and HCO_3^- when using low iron concentration and low hydrogen peroxide with photo-Fenton.

4. Conclusions

The experiments showed that emerging contaminants at low concentrations can be successfully degraded to negligible concentrations (a few μg L^{-1}) with photo-Fenton at low iron concentration (5 mg L^{-1}) and low initial H_2O_2. pH below 3 is not, in fact, a limiting factor for photo-Fenton to work properly, nor is the precipitation of iron. The main limitation to be overcome is the presence of CO_3^{2-} and HCO_3^-, which are very efficient $^{\bullet}OH$ radical scavengers. The problems encountered with the scavenging of $^{\bullet}OH$ radicals can be avoided either by using higher amounts of iron, or by removing CO_3^{2-} and HCO_3^- before beginning photo-Fenton. The latter is more desirable, as less hydrogen peroxide is consumed for degradation. Extrapolation of the results obtained has to be carefully interpreted as in real effluents from municipal wastewaters other compounds could be also detrimental for the process. The results presented are really important for interpreting adequately the results obtained with real waters.

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