Photocatalytic degradation of EU priority substances: A comparison between TiO$_2$ and Fenton plus photo-Fenton in a solar pilot plant

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Abstract

Titanium dioxide photocatalysis (200 mg/L) and photo-Fenton were applied to the treatment of several different pesticides considered priority substances (PS) by the European Commission dissolved in water at 50 mg/L or at maximum water solubility (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol) alone (20 mg/L of iron) and as a mixture (10 mg/L of iron). All tests were performed in new twin 75-L compound parabolic collector (CPC) pilot plants driven by solar energy. Total organic carbon (TOC) mineralisation, disappearance of the parent compound and inorganic ion release are discussed as a function of treatment time. Photo-Fenton treatment was found to be shorter than TiO$_2$ and more appropriate for these compounds and mixtures of them.
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1. Introduction

The increasing volume of wastewater containing non-biodegradable pollutants discharged into the environment demands the development of new powerful, clean and safe decontamination technologies. In this context, EU legislation is continually being adapted to protect and improve the quality of Europe's fresh water resources. The most recent update was the European Water Framework Directive (WFD), Directive 2000/60/EC, establishing a framework for Community action in the field of water policy. The WFD represents a breakthrough in EU water policy, not only in terms of the scope of water protection, but also its development and implementation. The WFD calls for conservation of aquatic ecosystems, sustainable use of water and preservation of water resources, such as groundwater. This is to be obtained by reducing emissions of environmental pollutants into bodies of water, improving water quality and controlling pollution at its source [1]. The WFD includes a list of 33 priority substances (PS) which represent a signifi-

cant risk to or through the European aquatic environment [2]. Cessation or phasing out of discharges, emissions and losses of these substances must follow an appropriate timetable not to exceed 20 years. The water-soluble pesticides, alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol, are included among these substances.

Several processes and technologies are available today for the treatment of wastewater [3,4]. The wastewater treatment techniques most frequently used can be classified as physical, biological and chemical. However, very often wastewater containing pesticides cannot be treated by biological techniques, since they are toxic to the microorganisms and therefore their biodegradation is impossible.

Advanced oxidation processes (AOP) may be used for decontamination of water containing these compounds and interesting reviews about them have recently been published [5–7]. Although there are different reaction systems, all of them are characterised by the production of OH radicals ($^\bullet$OH), which are able to oxidise and mineralise almost any organic molecule, yielding CO$_2$ and inorganic ions.

Methods based on H$_2$O$_2$/UV, O$_3$/UV and H$_2$O$_2$/O$_3$/UV combinations rely on photolysis of H$_2$O$_2$ and ozone to produce the hydroxyl radicals. Heterogeneous photocatalysis is based

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on the use of a wide-band-gap semiconductor, where photo-excitement of a valence band electron leads to several reactions and production of the desired hydroxyl radical [8]. The Fenton method applies the combination of H_2O_2 and Fe^{2+} salts. This reaction had already been described towards the end of the 19th century [9], but its application for wastewater treatment was not discussed until the second half of the last century [10]. If the Fenton reaction is irradiated with UV–vis light, it is called the photo-assisted Fenton, or more simply, photo-Fenton reaction. Irradiation is known to greatly enhance reaction rates by accelerating the regeneration of ferrous from ferric iron [11,12].

Heterogeneous photocatalysis (TiO_2) and photo-Fenton are of special interest since sunlight can be used for them [13,14], while AOP based on O_3 and H_2O_2 photolysis need short wavelength photons, which have to be generated by energy and cost-intensive UV-C lamps. Consequently, the use of solar energy can improve not only wastewater treatment costs, but also contribute to process sustainability by saving electricity.

Although the strong potential of AOPs for treating non-biodegradable compounds containing wastewater is widely recognized, it is also known that their operating costs for total oxidation of the hazardous organic compound remain relatively high compared to biological treatments. However, their use as a pre-treatment step for enhancement of the biodegradability of wastewater containing recalcitrant compounds can be justified if microorganisms in a biological treatment can readily degrade the intermediates resulting from the reaction.

In this context, under the "CADOX" project (http://www.psa.es/webeng/projects/cadox/index.html), financed by EC-DGXII (started in February 2003 and scheduled to last 42 months) an industrial consortium of nine public and private institutions has been formed for the development of a new technology based on integrating AOP and aerobic biological processes to improve the cost effectiveness of AOP for the remediation of industrial wastewater with non-biodegradable contaminants. In this study, preliminary experiments to achieve this goal were carried out in new twin solar reactors developed in the project work program and located at the Plataforma Solar de Almería, Tabernas, Spain (photo-Fenton experiments) and the INETI, Lisbon, Portugal (TiO_2 experiments).

2. Experimental

2.1. Chemicals

The pesticides used in the study were alachlor (95%, $C_{14}H_{20}ClNO_2$, Aragonesas Agro S.A. technical grade), atrazine (95%, $C_8H_{14}ClN_5$, Ciba-Geigy technical grade), chlorfenvinphos (93.2%, $C_{12}H_{14}Cl_3O_4P$, Aragonesas Agro S.A. technical grade), diuron (98.5%, $C_9H_{10}Cl_2N_2O$, Aragonesas Agro S.A. technical grade), isoproturon (98%, $C_{12}H_{18}N_2O$, Aragonesas Agro S.A. technical grade) and pentachlorophenol (98%, C_6HCl_5O, Aldrich Chemical analytical grade). Mixtures of these were also tested.

Titanium dioxide P25 was donated by Degussa Iberica, iron sulphate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (30% w/v) and sul-

phuric acid for pH adjustment were provided by Panreac (analytical grade).

2.2. Equipment and analytical methods

2.2.1. TOC

Mineralisation of the chemicals was monitored by measuring the total organic carbon (TOC) by direct injection of the filtered samples into a Shimadzu-5050A TOC analyzer provided with an NDIR detector.

2.2.2. HPLC

The amount of atrazine, alachlor, chlorfenvinphos, diuron, isoproturon, and pentachlorophenol in the samples was determined at the PSA by reverse-phase liquid chromatography with UV detection in an Agilent Series 1100 chromatograph equipped with a C-18 column (LUNA 5 µm, 3 mm × 150 mm from Phenomenex, flow rate 0.5 mL/min). Ultra pure distilled-deionized water obtained from a Milli-Q (Millipore Co.) system was used to prepare all solutions. At the INETI, compounds were determined by reverse-phase liquid chromatography with UV detection in a Hewlett-Packard series 1100 chromatograph equipped with a Waters µ-Bondapack C-18 column (10 µm; 4.6 mm × 250 mm, flow rate 1.5 mL/min). Ultra-pure water obtained from a Millipore Elix S device was used for the preparation of all standard and mobile-phase aqueous solutions. Table 1 shows the mobile-phase composition and wavelength in each case.

2.2.3. Ion concentrations

2.2.3.1. Photo-Fenton experiments. Cation concentrations were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4 mm × 250 mm column. Isocratic elution was done with H_2SO_4 (20 mN) at a flow rate of 1.3 mL/min. Anion concentrations were measured with a Dionex DX-600 ion chromatograph using a Dionex Ionpac AS11-HC 4 mm × 250 mm column. The flow rate was 1.5 mL/min and elution was done with NaOH gradient programmes. Finally, iron concentration was determined according to ISO 6332, and hydrogen peroxide by iodometric analysis.

2.2.3.2. TiO_2 experiments. The phosphate formed during destruction of chlorfenvinphos was assessed colorimetrically by the vanadomolybdophosphoric acid method and the amount of nitrogen liberated in the form of ammonium from photocatalytic degradation of pesticides was evaluated using the colorimetric phenate method [15]. Chloride ions in photocatalytically oxidised samples of pesticides were quantified using a WTW model CL801 selective combined electrode connected to a WTW Inolab pH level 1 device. Nitrate levels were estimated directly using analytical kits from Merck in the ranges of 0.5–20 mg N–NO_3/L.

2.3. Experimental set-up

2.3.1. Solar reactor

The reactor loop consists of a continuously stirred tank, a centrifugal recirculation pump (1.5 m³/h), a solar collector and

Table 1
HPLC methods for target compounds

Compound	Mobile phase (ratio)	Wavelength (nm)
Alachlor	H_2O/acetonitrile (ACN) (40/60)	225
Atrazine	H_2O/ACN (55/45)	240
Chlorfenvinphos	H_2O/ACN (40/60)	240
Diuron	H_2O/ACN (40/60)	254
Isoproturon	H_2O/ACN (55/45)	240
Pentachlorophenol	H_2O (pH 3)/methanol (10/90)	220
Mixture (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon)	H_2O/ACN (65/35), 0–12 min; H_2O/ACN (35/65), 12.1–25 min	220: alachlor; 240: chlorfenvinphos, isoproturon; 254: atrazine, diuron

connecting tubing and valves. Piping and valves are made of polypropylene. The total volume of the reactor is between 70 and 82 L (V_T), depending on the level of liquid in the tank. The solar collector is composed of four compound parabolic collector (CPC) units [16] (concentration factor = 1) with an area of 1.04 m^2 (total area 4.16 m^2), in an aluminium frame mounted on a fixed south-facing platform tilted 37° in Tabernas, Almería (Spain) and 40° in Lisbon (Portugal). Each unit has five borosilicate-glass tubes (OD 50 mm, transmissivity > 50% at $\lambda > 300$ nm; >75% at $\lambda > 320$ nm; >90% at $\lambda > 350$ nm) connected by plastic joints, and the total illuminated volume inside the absorber tubes is 44.6 L (V_i). To perform tests adequately (mixing in the dark, changing the illuminated area of the collector, etc.), the collector can be covered with special "hand-made" aluminium sheets. Flow diagram and isometric drawing are depicted in Fig. 1.

Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV3), mounted on a platform tilted 37° (the same angle as the CPC) in Tabernas, Almería and a global UV radiometer Ecosystem model ACADUS 85P tilted 40° in Lisbon, both of which provide data in terms of incident W_{UV} m^{-2}. This gives an idea of the energy reaching any surface in the same position with regard to the sun. Using Eq. (1), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible:

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

where t_n is the experimental time for each sample, UV the average solar ultraviolet radiation measured during Δt_n, and t_{30W} is a "normalized illumination time". In this case, time refers to a
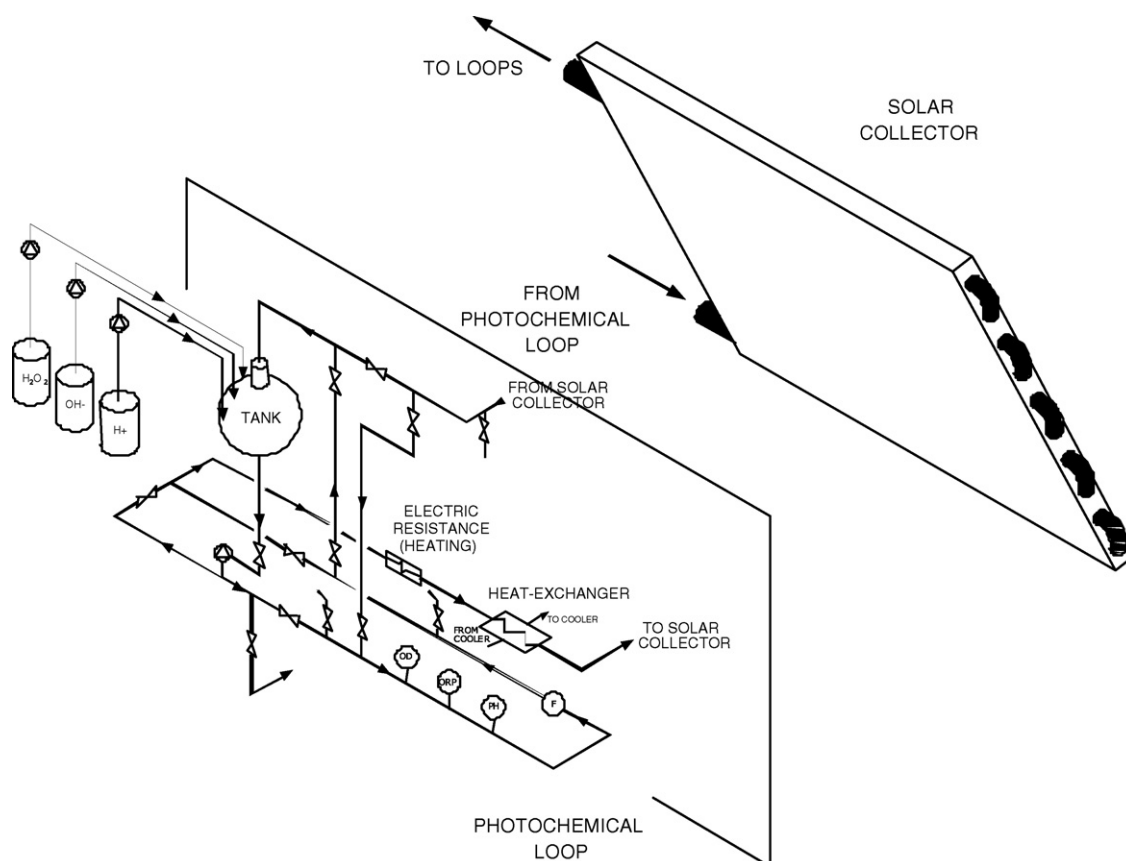

Fig. 1. Flow diagram and isometric drawing of the solar reactor.

constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon).

Eq. (2) has sometimes been used (mainly for comparison of collector efficiency) for data obtained from the experiments:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \, UV \frac{A_r}{V_T}, \quad \Delta t_n = t_n - t_{n-1} \tag{2}$$

where A_r is the illuminated collector surface (m^2) and $Q_{UV,n}$ is the accumulated energy per unit of volume (J/L) incident on the reactor for each sample taken during the experiment.

2.4. Procedures

For photo-Fenton tests, pH was adjusted to 2.7–2.9 (except pentachlorophenol, see Section 3 for details) with sulphuric acid to avoid iron hydroxide precipitation. The first dose of hydrogen peroxide was always added after pH adjustment and addition of Fe, and was usually 100 mL (reagent grade, 30% w/v). The concentration of peroxide in the reactor was determined by frequent analysis and controlled to avoid complete disappearance by adding small amounts as consumed. All the tests were begun the same way with the collectors covered to avoid illumination. It should be remarked that all single-substance experiments were performed at 50 mg/L or close to their water solubility limit. Once the pilot plant was filled with the "simulated wastewater", a sample was taken and sulphuric acid was added (Point 1 in the photo-Fenton figures). After 15 min, a sample was taken to confirm that the pH was around 2.8–2.9 (Point 2). Then, iron salt (FeSO$_4$·7H$_2$O) was added and mixed for 15 min until homogenous and another sample was taken. All experiments were carried out at 20 mg/L Fe concentration. Hydrogen peroxide was then added (Point 3) and after 15 and 30 min two samples were taken (these samples correspond to the Fenton reaction, from Point 3 until $t = 0$) and, finally, the collectors were uncovered, which is when photo-Fenton began.

The start-up procedure was shorter for TiO$_2$ tests. All the experiments were started by recirculating the solution with the collectors covered for about 15 min until a constant concentration was achieved throughout the system. After sampling, the catalyst, titanium dioxide, was added (concentration = 200 mg/L) and the mixture recirculated for 15 min more. Just before uncovering the CPC to start the photocatalytic process, another sample was collected to characterise the initial condition of the solution. Samples were also taken at different times to evaluate the progress of photocatalytic oxidation.

3. Results and discussion

First of all, it should be remarked that the catalyst concentration (200 mg/L of TiO$_2$ and 20 mg/L of Fe) is in the optimum range for 50-mm-OD solar photoreactors, as stated previously [16]. The complete mineralization of each chemical product is described by Eqs. (3)–(8). The decomposition of nitrogenated compounds gives rise to ammonia which, afterwards, is, in gen-
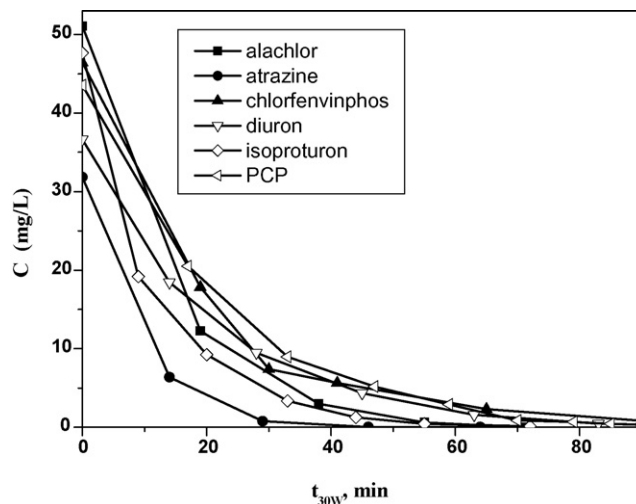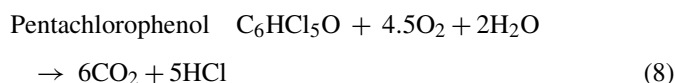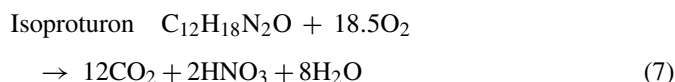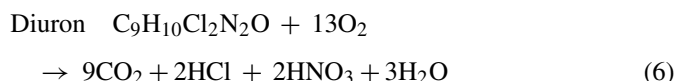

Fig. 2. Degradation of pesticides by TiO$_2$.

eral, oxidised to nitrate.

Alachlor $\quad$ C$_{14}$H$_{20}$ClNO$_2$ + 20O$_2$

$\quad \rightarrow 14CO_2 + HCl + HNO_3 + 9H_2O$ $\quad$ (3)

Atrazine $\quad$ C$_8$H$_{14}$ClN$_5$ + 12.5O$_2$

$\quad \rightarrow 8CO_2 + HCl + 5HNO_3 + 4H_2O$ $\quad$ (4)

Chlorfenvinphos $\quad$ C$_{12}$H$_{14}$Cl$_3$O$_4$P + 14.5O$_2$

$\quad \rightarrow 12CO_2 + HCl + H_3PO_4 + 4H_2O$ $\quad$ (5)

Diuron $\quad$ C$_9$H$_{10}$Cl$_2$N$_2$O + 13O$_2$

$\quad \rightarrow 9CO_2 + 2HCl + 2HNO_3 + 3H_2O$ $\quad$ (6)

Isoproturon $\quad$ C$_{12}$H$_{18}$N$_2$O + 18.5O$_2$

$\quad \rightarrow 12CO_2 + 2HNO_3 + 8H_2O$ $\quad$ (7)

Pentachlorophenol $\quad$ C$_6$HCl$_5$O + 4.5O$_2$ + 2H$_2$O

$\quad \rightarrow 6CO_2 + 5HCl$ $\quad$ (8)
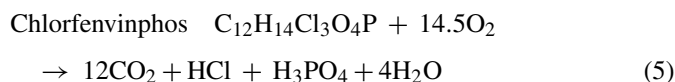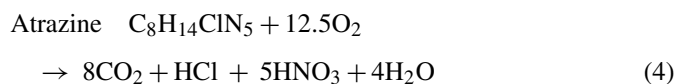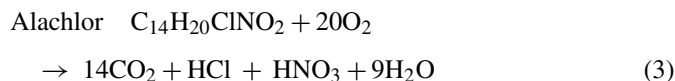
Figs. 2 and 3 show the degradation and mineralization of pesticides treated by TiO$_2$. It has been demonstrated that target compounds can be treated successfully by heterogeneous photocatalysis using titanium dioxide (200 mg/L). Alachlor was completely mineralized in 240 min, and the compound disappeared in less than 1 h. According to the process stoichiometry (Eq. (3)), chloride and nitrogen were completely released, although the latter appeared mainly in the form of ammonia. The chlorfenvinphos degradation profile shows mineralization occurring in about 320 min with overall disappearance of the compound in about 120 min. Stoichiometric release of phosphorus and chloride was complete (Eq. (5)) and concomitant with product removal. Pentachlorophenol was mineralised to
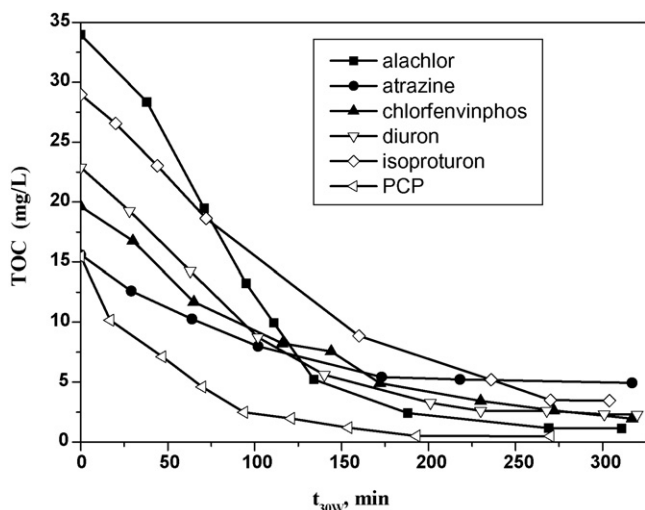
Fig. 3. Mineralization of pesticides by TiO$_2$.

Fig. 4. Evolution of pH (open symbols) and ammonium cation concentration (solid symbols) in TiO$_2$ experiments.

less than 1 mg/L of TOC in about 2.5 h, by which point the original compound had also been destroyed and all the chloride was present.

Atrazine completely disappeared in less than 1 h, yielding chlorinated and/or nitrogenated secondary products. As a matter of fact, several authors refer to the ultimate formation, in heterogeneous photocatalytic degradation of atrazine, of very recalcitrant compounds, bearing 3/8 of the organic carbon of the original molecule and the triazine ring [17,18]. As a consequence of the formation of such compounds, mineralisation is deficient, and nitrogen released from atrazine is incomplete, as observed in the experiment performed (final TOC = 5 mg/L = 3/8 initial TOC). As ammonia is a precursor of nitrate, its concentration in the solution is usually higher. However, in atrazine degradation, the inorganic nitrogen was almost completely oxidised to nitrate.

Complete mineralisation of diuron and isoproturon was also very difficult. Diuron concentration was reduced to less than 1 mg/L in 60 min, but final TOC (2.3 mg/L) was not mineralised, probably due to the formation of recalcitrant nitrogenated products containing 62% of total nitrogen and the rest of carbon. In contrast, dechlorination was faster and complete. In the case of isoproturon, 3 mg/L of organic carbon remained in the solution at the end. Reduction of TOC was initially faster, up to 85% in 4 h, but continued very slowly afterwards (from t = 200 min to the end of the test). Disappearance of the compound is complete in less than 1 h. Only 50% of the original amount of nitrogen was released from isoproturon, suggesting the formation of stable nitrogenated intermediates. N$_2$ formation seems not probable due to the absence of N–N bondings in the molecular structure [19].

Very slow degradation of TOC from phenylurea pesticides after 80–90% mineralisation [20,21] and very slow mineralisation of urea have been reported previously [22]. Urea could therefore be expected as an intermediate originating from phenylurea pesticides. Urea contains only one C atom and two N atoms, with the C atom being fully oxidised (oxidation state +IV). This impedes as well hydrogen abstraction as electrophilic
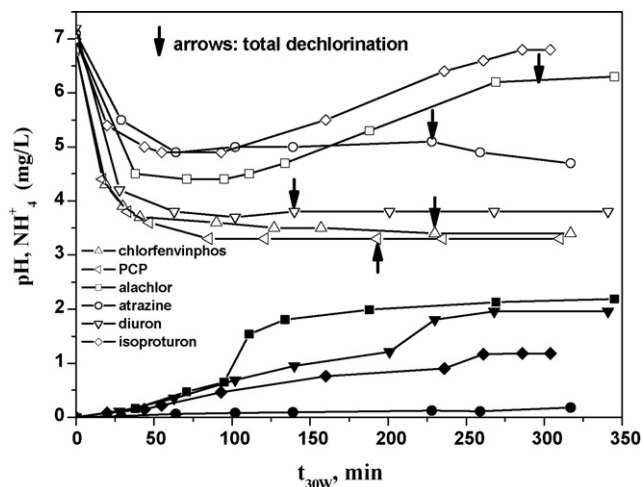
attack by hydroxyl radicals at the carbon atom. Furthermore, several resonance structures are possible making the molecule very stable and the oxidative attack on the amine groups very slow. Hydroxylamine could be an intermediate product leading to the formation of nitrate [19]. Mainly, the formation of urea could justify not only the remaining TOC, but also the incomplete release of N as NH$_4^+$ or NO$_3^-$.

Fig. 4 shows evolution of pH and ammonium cation concentration, arrows show the point of total dechlorination. Alachlor and isoproturon behave the same way. Both molecules are destroyed with an initial decrease in pH because of Cl$^-$ release (alachlor) and/or formation of carboxylic acids (in both cases) followed by an increase up to 6.3–6.8, as a result of the increase in ammonium cations. Diuron, chlorfenvinphos and PCP show an initial decrease in pH in the solution and a constant value thereafter. In this group only diuron has nitrogen in the molecular structure, so the increase in the concentration of ammonium cations could compensate for the formation of short-chain carboxylic acids [19,23]. However, as also observed in Fig. 4, there is a less pronounced decrease in pH during the first stages of treatment of isoproturon and alachlor, as diuron has two Cl atoms. On the other hand, behaviour of atrazine is different from the rest of the compounds. An initial decrease in pH (chloride release), soon became constant (formation of ammonia and carboxylic acids) and afterwards decreased slightly, probably as a consequence of inorganic nitrogen oxidation to nitrate [24]. Such different behaviour of pH with each pesticide could be used to predict the treatment stage in industrial treatment plants by measuring pH on-line, as pH is an easy, reliable and cheap analytical method. By this procedure, more sophisticated and slower analytical methods (HPLC, TOC, COD) would only have to be used to confirm the wastewater treatment stage. It should also be remarked that this is valid only for TiO$_2$ treatment, not for photo-Fenton.

Figs. 5 and 6 show the degradation and mineralisation of pesticides treated by Fenton plus photo-Fenton. It can be observed that only Fenton degradation is able to degrade the pesticide in almost all cases into intermediates.
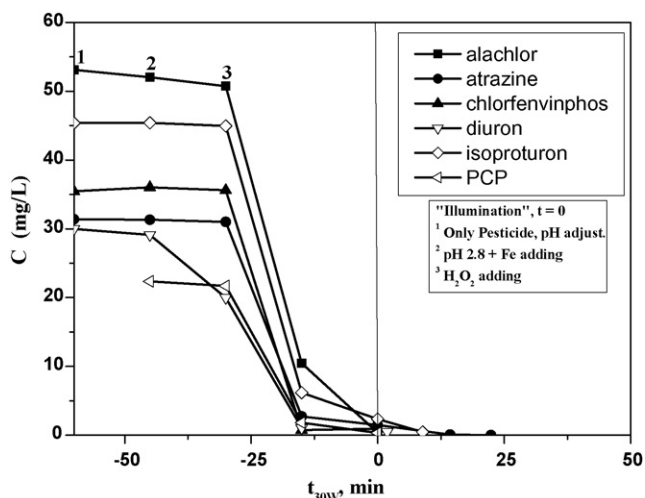
Fig. 5. Degradation of pesticides by photo-Fenton.

Alachlor was successfully degraded by Fenton plus photo-Fenton at 20 mg/L (see Fig. 5). The Fenton reaction (from "3" to $t = 0$) produced slight mineralisation of the pesticide (Fig. 6) before illumination and complete disappearance of the pesticide. Nevertheless, total mineralisation (i.e., disappearance of TOC) can be attained only after a very short period of irradiation (less than 15 min).

The Fenton (from "3" to $t = 0$) reaction did not produced any mineralisation of atrazine before illumination. Nevertheless, mineralisation (i.e., disappearance of TOC) can be attained after irradiation. Residual atrazine TOC was also confirmed to be 3/8 of the initial, because of the stability of the triazine ring, as mentioned above.

The Fenton reaction (from "3" to $t = 0$) mineralised some chlorfenvinphos before illumination, although, it is substantial only after irradiation. Chloride evolves very quickly (even in the Fenton process) and total dechlorination is confirmed, suggesting a very fast degradation/dechlorination stage compared
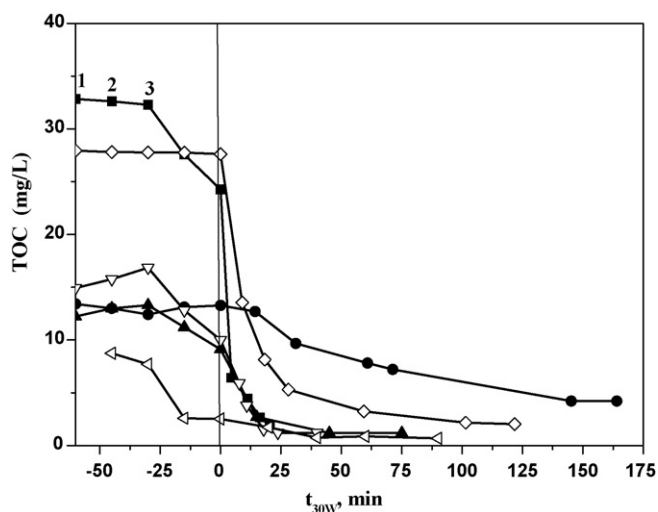
to disappearance of TOC. This means that the residual TOC at the end of the experiment did not correspond to any chlorinated compound. Phosphate release was also complete during Fenton, and afterwards, dissolved phosphate (and Fe) concentration decreased due to the formation of $FePO_4$. During Fenton plus photo-Fenton treatment of organophosphorus contaminants, the formation of $FePO_4$ lowered process efficacy and, therefore, more Fe could be necessary to reach the desired treatment level.

The Fenton reaction (from "3" to $t = 0$) produced considerable mineralisation of diuron. Nevertheless, 90% mineralisation is attained only after irradiation. Less than 10% of initial TOC seems to be difficult to degrade. This must be from aliphatic compounds, as the HPLC diode array detector scans did not show any signal above 210 nm.

The Fenton reaction (from "3" to $t = 0$) did not mineralise any isoproturon, which is attained only after irradiation. Around 15% of the initial TOC seems to be difficult to degrade (see Fig. 6, $t_{30\,W} > 30$ min). As discussed for diuron, TOC after $t_{30\,W} > 30$ min must be from aliphatic compounds, as there was no signal above 210 nm on the HPLC diode array detector scans. The same reasoning concerning the presence of urea in intermediate degradation of TiO_2 treatment could be valid for Fenton plus photo-Fenton treatment of diuron and isoproturon.

In the case of PCP degradation experiment, since PCP solubility is very low at acid pH ($pK_a = 4.7$), it was decided not to reduce the pH at the beginning of experiment adding sulphuric acid, as hydrochloric acid (Cl^- ions release from PCP molecules) would be produced during degradation anyway. This achieved two things: (i) pH did not have to be reduced at the beginning, while PCP in solution was maintained and (ii) pH was reduced to the desired value, avoiding excessive iron hydroxide precipitation during degradation. Part of dissolved iron was lost at the beginning due to the high pH (around pH 5, $t_{30\,W} < -30$ min), but dropped very quickly (pH 3) right after addition of hydrogen peroxide ($t_{30\,W} > -30$ min), and the remaining iron was enough to mineralise PCP. The Fenton reaction (from "3" to $t = 0$) produced complete disappearance of PCP and significant mineralisation before illumination. Total dechlorination was confirmed, suggesting very fast dechlorination in the dark.

In view of the results obtained, less than 20 mg/L of Fe could be enough for wastewater containing tens of mg/L of contaminants, except for treatment of chlorfenvinphos. In this case, the reason could be related to phosphate. As mentioned above, release of phosphate was complete during Fenton reaction, and afterwards, dissolved phosphate concentration (and also Fe) decreased due to the formation of $FePO_4$. Fe concentration dropped to 7–8 mg/L. Therefore, it has been demonstrated that, as general rule, using low Fe concentrations (2 mg/L of Fe) in photoreactors with a long enough light path length, excellent efficiency can be obtained in a short time (tens of minutes) [25]. Under these conditions Fe need not be removed at the end of the treatment if water is disposed of into a conventional biological wastewater treatment plant. However, special care should be taken with the Fe dose when wastewater contains organophosphorus compounds.

On the other hand, the proper way to compare solar photocatalytic collector efficiency is using "accumulated energy" (Eq.

Fig. 6. Mineralisation of pesticides by photo-Fenton. Legend and comments (1–3) as in Fig. 5.

Table 2
Accumulated energy Q (kJ/L) for disappearance of the original compound, mineralisation of 90% ($TOC_{90\%}$) and first-order rate constants during titanium dioxide and photo-Fenton (ph-F) treatment

Target compounds	$TOC_{90\%}$		Compound $= 0$		k (min^{-1})	
	TiO_2 Q_{UV} (kJ/L)	ph-F Q_{UV} (kJ/L)	TiO_2 Q_{UV} (kJ/L)	ph-F Q_{UV} (kJ/L)	TiO_2	ph-F
Alachlor	26.3	2.2	11.9	0	0.080	0.17
Atrazine[a]	29.0	24.4	10.8	4.4	0.130	0.10
Chlorfenvinphos	54.7	7.3	30.2	2.3	0.054	0.26
Diuron	50.6	3.0	41.1	0	0.047	0.20
Isoproturon	68.1	10.0	12.1	1.9	0.080	0.13
Pentachlorophenol	20.1	1.1	20.1	0	0.046	0.14

[a] 3/8 of TOC_0 remained in the solution.

(2)), which takes total volume and solar collector surface into account, enabling the efficiency of a solar photocatalytic reactor to be estimated for a specific purpose (Table 2). First-order rate constants for the six compounds are also shown.

As seen in Table 2, compound photoreactivity with TiO_2 can then be ranked in the following order: Atrazine > isoproturon ≈ alachlor > chlorfenvinphos ≈ PCP ≈ diuron. The differences in photoreactivity suggest that k is directly related to whether the various substituents in the aromatic ring are electron-donors or acceptors, which would activate or deactivate the ring under electrophilic attack of the $^\bullet OH$ radical. Atrazine, isoproturon and alachlor were the most reactive compounds. In the case of atrazine, this was probably due to fast loss of lateral chains located in Positions 3 and 5 (see Fig. 7) [26]. Isoproturon and alachlor, are the next most active due to the presence of $CH(CH_3)_2$ and CH_2CH_3, which are benzene-ring activating, and the absence of halogen substituents [21]. The other three compounds contain deactivating halogen groups.

The photoreactivity of compounds by Fenton plus photo-Fenton (with most of the degradation in the dark) was in the following order: Chlorfenvinphos > diuron > alachlor > pentachlorophenol > isoproturon > atrazine. The degradation pathway of aromatic rings begins with attack by $^\bullet OH$ radical leading to formation of phenol moiety and subsequently to hydroquinone moiety. The hydroquinone moiety reduces Fe^{3+}

to Fe^{2+} which serves as an electron-transfer catalyst between the dihydroxycyclohexadienyl radical (the $^\bullet OH$ adduct of phenol) and Fe^{3+} by way of a semiquinone radical [27]. This process considerably improves the Fenton and photo-Fenton reaction rate [28] and can explain the last position of atrazine in the photoreactivity ranking shown above, because atrazine is the only compound that cannot form the hydroquinone moiety. Therefore, photo-Fenton could be an especially suitable treatment for wastewater containing phenolic compounds.

3.1. Pesticide mixture experiments

After testing single compounds, mixtures of them simulating a more realistic effluent were tested to determine any constraints related to the simultaneous presence of different pesticides.

The mixture tested in TiO_2 degradation experiments (Figs. 8 and 9) contained 30 mg/L each of six pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol) ($TiO_2 = 200$ mg/L). Fenton plus photo-Fenton degradation experiments (Fig. 10) did not include PCP because it precipitates at acidic pH. Indeed, as it is mineralised so quickly, its presence is not considered relevant to consistent results. At the same time, Fe concentration was reduced to 10 mg/L to find out whether this concentration is low enough
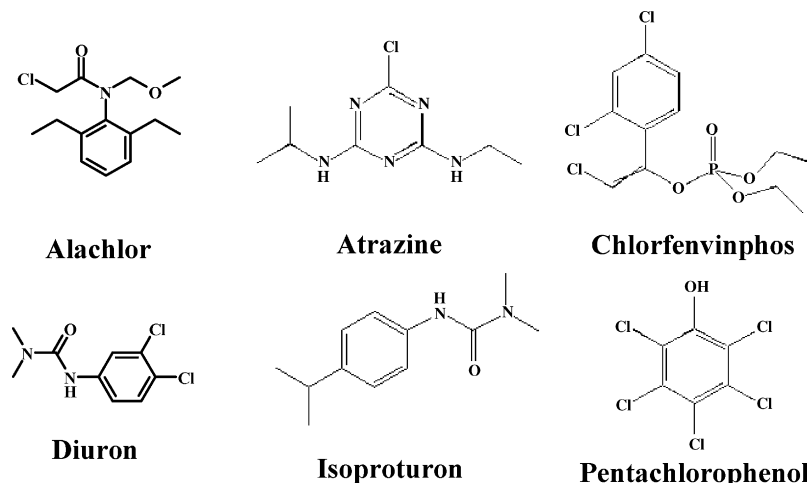

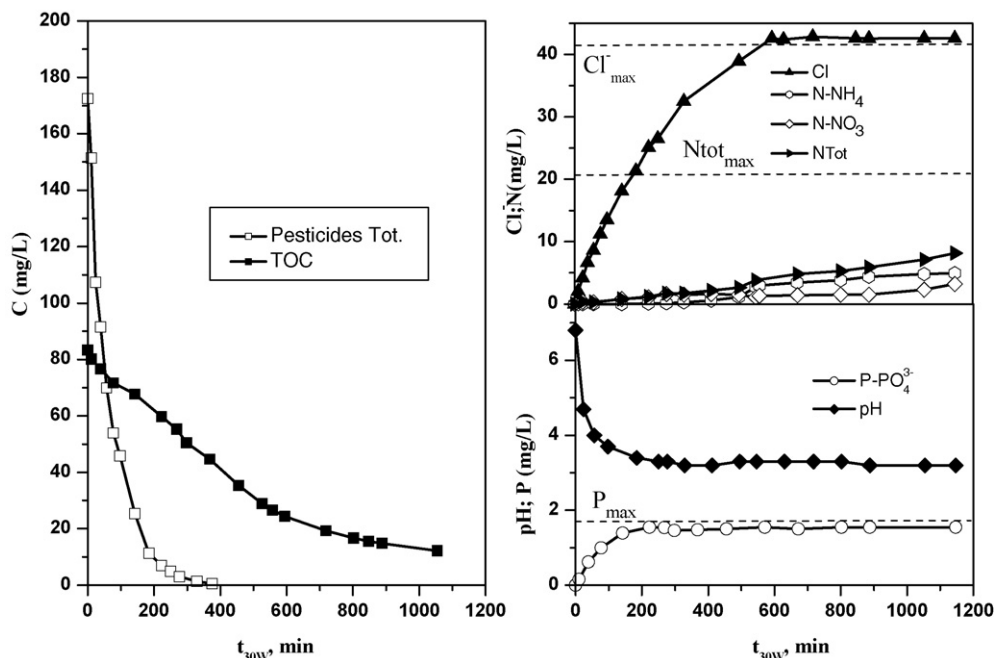Fig. 7. Chemical structure of the six compounds studied.

Fig. 8. Evolution of main parameters during titanium dioxide photocatalytic degradation of a mixture of six pesticides (30 mg/L) (TiO$_2$ = 200 mg/L).
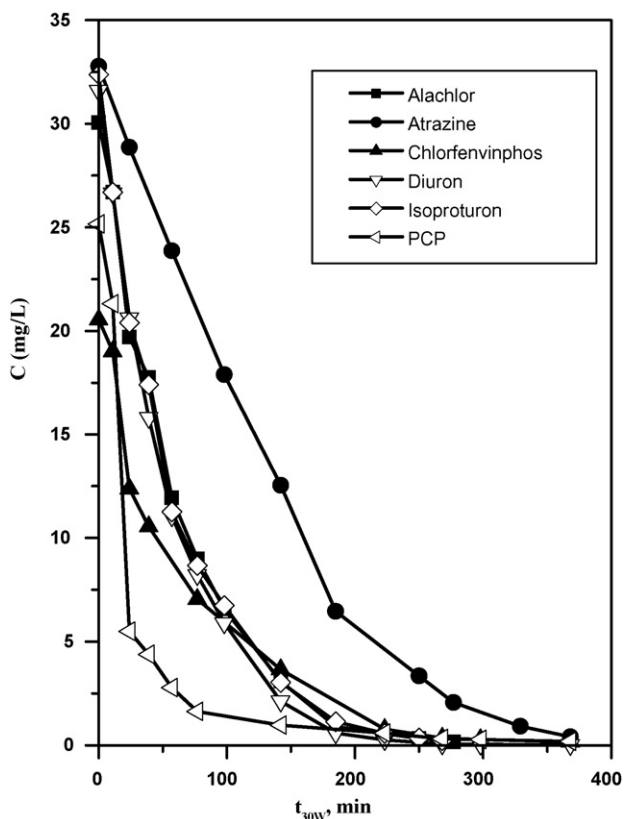

Fig. 9. Evolution of compound concentration during titanium dioxide photocatalytic degradation of a mixture of six pesticides (30 mg/L) (TiO$_2$ = 200 mg/L).

to dispose of the water into a bio-treatment plant, as mentioned above.

The mixture degradation profile presented in Figs. 8 and 9, shows the destruction of the original compounds in about 6 h, while only 85% of TOC mineralisation was possible. As expected, the increase in concentration to 180 mg/L also substantially increased length of treatment. According to the stoichiometric ratios, dechlorination and phosphorus release were complete. However, at least some of the remaining recalcitrant intermediates are nitrogenated, as only 40% of the nitrogen originally present in the pesticide molecules was detected in the solution in inorganic form. This observation agrees with results previously reported for the photocatalytic treatment of single-compound solutions of diuron, isoproturon and atrazine, probably related to the formation of cyanuric acid and urea products. A sharply drop in pH at the beginning was due to the rapid release of Cl and P atoms, but after a certain time NH$_4^+$ formation compensated anion (Cl$^-$, NO$_3^-$, carboxylates) formation and it became almost constant around pH 3.

Isoproturon was the first compound to completely disappear, dropping to undetectable levels in the HPLC analysis. However, these results do not reflect the destruction rate, which was the fastest for diuron and the slowest for atrazine as can be seen from Table 3. The photoreactivity of compounds in this case was diuron > isoproturon > alachlor > PCP > chlorfenvinphos > atrazine. Atrazine degradation in the mixture was exactly the opposite of single-compound experiments (Table 2). However, the presence of different compounds may interfere in the oxidation process, either hindering or improving, as titanium dioxide photocatalysis depends strongly on adsorption phenomena [29].
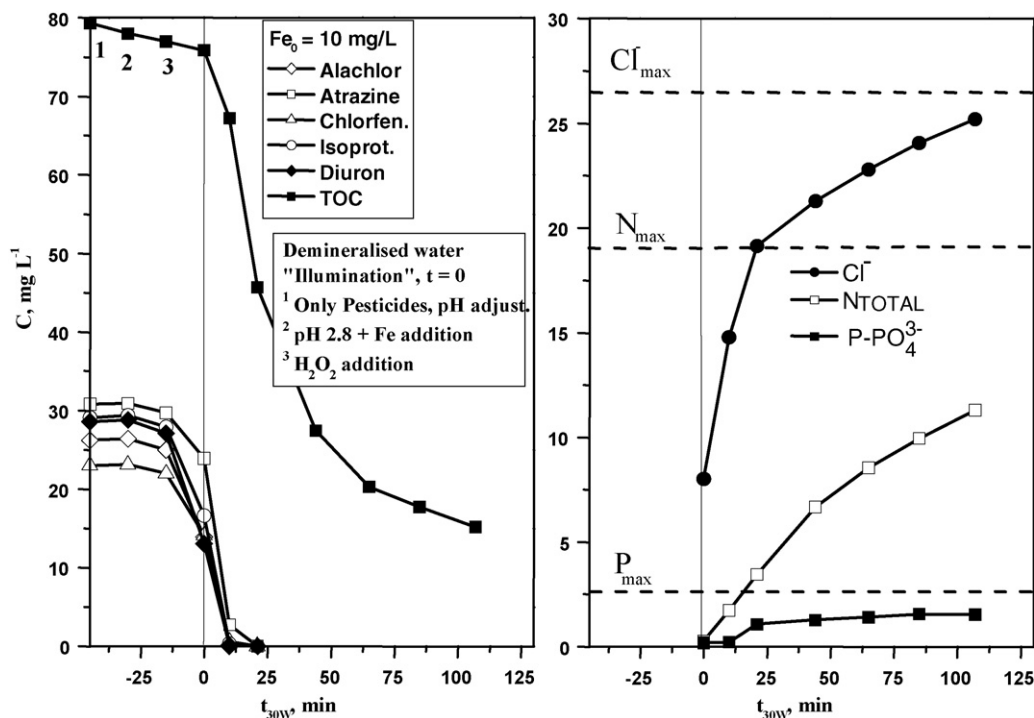
Fig. 10. Pesticide mixture (30 mg/L each) degradation by photo-Fenton (Fe = 10 mg/L). Main parameters.

Indeed, their kinetic constants are more similar than in single compound experiments.

Results presented in Fig. 10 show that Fenton plus photo-Fenton at low Fe concentrations is also effective for treating these compounds. Complete disappearance and total dechlorination of all pesticides was very easily attained at the initial test concentration.

Release of phosphate was incomplete during treatment, and Fe concentration decreased to 5 mg/L after 100 min due to the formation of $FePO_4$. The TOC mineralisation rate decreased at the end of the treatment (after $t > 60$ min) due to the decrease in dissolved Fe.

The order of photoreactivity observed in this treatment was diuron > alachlor > isoproturon > chlorfenvinphos > atrazine (see Table 3). The behaviour of the compounds in the mixture was basically the same as in the individual treatments, with the exception of chlorfenvinphos, and also similar to the TiO_2 pesticide mixture experiments.

Table 3
First-order rate constants during titanium dioxide and photo-Fenton (ph-F) treatment of pesticide mixture and accumulated energy Q (kJ/L) for disappearance of the original compound

Target compounds	k (min^{-1})		Compound = 0	
	TiO_2	ph-F	TiO_2 Q_{UV} (kJ/L)	ph-F Q_{UV} (kJ/L)
Alachlor	0.016	0.039	46.4	1.8
Atrazine	0.010	0.015	61.7	3.9
Chlorfenvinphos	0.014	0.030	61.7	3.9
Diuron	0.018	0.049	50.0	3.9
Isoproturon	0.017	0.035	44.9	3.9
Pentachlorophenol	0.015	–	61.7	–

4. Conclusions

It has been demonstrated that Fenton plus photo-Fenton is more efficient than TiO_2, not only for pesticide degradation but also for TOC mineralisation, Fenton very often being sufficient for pesticide abatement. Behaviour was similar with single compounds and mixtures of all of them up to more than 100 mg/L.

Compounds that form hydroquinone moieties are favoured during Fenton plus photo-Fenton treatment while the presence of alkyl chains favours TiO_2 degradation.

Iron at very low concentrations could be enough for treating wastewater containing pesticides. This would be very helpful because removal of iron at this concentration would not be necessary before disposal, but special care should be taken with wastewater containing organophosphorus compounds, as an important part of Fe could be precipitated as $FePO_4$.

From an industrial operation point of view, pH measurement could very often be used to determine degradation (with TiO_2) stage, as this measurement is easy, fast, cheap and reliable; but not when contaminants contain N, as there is then simultaneous generation of NH_4^+ and anions.

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