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Applicability of the Photo-Fenton method for treating water containing pesticides

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Abstract

The Photo-Fenton process, i.e., the system Fe^{2+}/H_2O_2/UV-Vis, was successfully applied to a mixture of ten commercially available pesticides that served as a model for a proposed recycling plant for pesticide bottles. Experiments with single pesticides revealed that although all of them were degradable, there were remarkable differences concerning the reaction rate. Sunlight driven pilot scale experiments with the complete mixture were conducted. For the pesticide mixture the initial pollutant concentration and the amount of iron was varied. The addition of oxalate and different modes of oxidant addition were tested in order to improve the process. Thereby, the reaction rate was increased, while the final degree of TOC reduction was affected only slightly. All the experiments carried out were considerably faster than the previously published results of degradation tests that applied solar driven TiO_2/UV and $TiO_2/Na_2S_2O_8$/UV photocatalysis. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Wastewater treatment; Pesticides; Photocatalysis; Solar light; Photo-Fenton reaction; Pilot scale study

1. Introduction

In Almería, a province located in the south-east of Spain, agriculture is very intense. About 35 000 ha of greenhouses have been erected, about 50% of them placed around the municipality of El Ejido. The most urgent issue related to this area is the extensive use of pesticides. According to the 1995 data 5200 tonnes of pesticides were applied in this region, which are sold in around 1.5 million bottles and containers per year [1]. Consumed bottles, containing small quantities of pesticide residue, are lacking an organised disposal. Usually most of them are mixed with conventional agricultural wastes or just dumped without control. On the long term, soil and groundwater of the region are in danger of contamination by these residues. In order to cope with this growing problem, a recycling process for the plastic of these bottles was designed, which leaves water from washing of the plastic containers, contaminated with some hundred ppm of total organic carbon (TOC) of toxic and persistent compounds. For detoxification of this water the application of a photocatalytic process was proposed [2], because conventional biological water treatment is more suitable for high concentrations of biodegradable substances, while photocatalysis is able to deal with effluents containing a low level of highly persistent pollutants. Therefore, photocatalysis appears to be very promising, even more as strong sunlight is available as a cheap energy source all over the year in this region. By application of sunlight the common drawback of relatively high costs for UV-lamps

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and electrical energy can be overcome. Thus, the high availability of sunlight and the lack of alternatives justify the application of a new technology. Previous studies were carried out with the aim to evaluate the feasibility of such a process for a pilot plant ($1500\,m^3$ wastewater per year) that is to be erected in the near future. Most of the previous work was dealing with the widely known TiO_2/persulphate reaction [2], and a cost estimation for this study, comparing TiO_2/persulphate with Photo-Fenton, has already been published [4,5]. The work presented here is dedicated to a more detailed study of the pesticide degradation by the Photo-Fenton process using otherwise the same conditions as during previous experiments.

Like other AOPs (advanced oxidation processes) [6], the Photo-Fenton reaction has been developed to detoxify non-biodegradable wastewater. The mechanism of the Fenton reaction has been known for a long time [7–11]. The most important improvement, the additional application of light, was based on discoveries in atmospheric chemistry, where ferric complexes play a key role in the degradation of organic substances [12–14]. Accordingly the so-called Photo-Fenton reaction was introduced as a very promising water treatment method [15–17]. Recently new questions concerning the mechanism of the reaction occurred, whether Fe^{+IV} species are involved in the reaction [18], but since products of both pathways cannot be distinguished [19], the question is rather of academic interest, and here only the 'classical interpretation' is used.

In the key reaction of the Photo-Fenton process Fe^{2+} ions are oxidized by H_2O_2 while one equivalent $OH^\bullet$ is produced ('Dark-Fenton reaction', (1)). The obtained Fe^{3+} or its complexes subsequently act as the light absorbing species that produce another radical while the initial Fe^{2+} is regained (2, 3).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad (1)$$

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

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

Note that reaction (3), which involves organic ligands L (e.g. $RCOO^-$, RO^-, RNH^+ etc.), is more efficient than the oxidation of organic substrates via $OH^\bullet$. Therefore, usually TOC degradation is getting faster during the reaction since the more inert hydrocarbons are first oxidised by $OH^\bullet$ to yield substances containing several hydroxyl or carboxyl groups that are able to participate in reaction (3) thereafter [17,20]. As a consequence the overall TOC degradation curves often exhibit a quasi autocatalytic behaviour during part of the reaction. As this leads to the impossibility of calculating rate constants according to simple rate equations, besides the TOC half-times a second, new parameter is introduced during this paper to compare various results, namely the maximum rate (r_{max}) that is reached during one experiment.

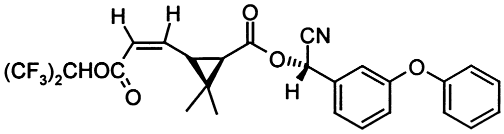
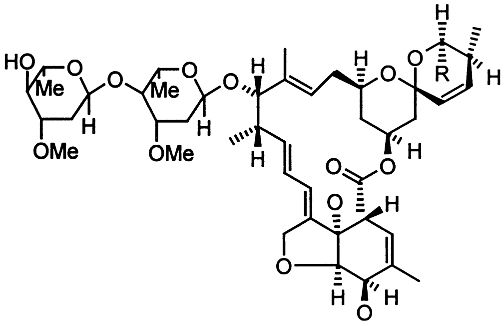
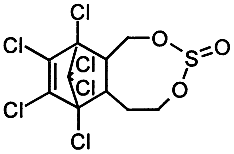
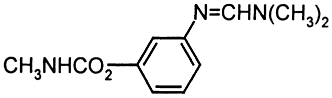
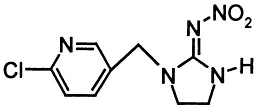
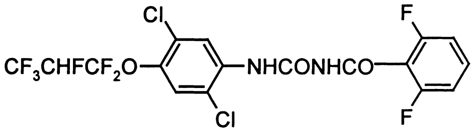
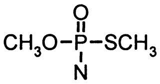
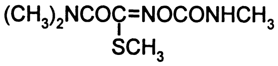
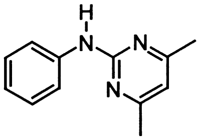
The main advantage of the Photo-Fenton process is the light sensitivity up to a wavelength of 600 nm (35% of the solar irradiation). The depth of light penetration is high and the contact between pollutant and oxidising agent is close, since a homogenous solution is used. Disadvantages are the low pH values required (usually below pH 4) and the necessity of iron removal after the reaction, but these problems could be circumvented by immobilisation of iron, e.g., on membranes [21,22].

The efficiency of Photo-Fenton treatment compared to other advanced oxidation processes has already been proved in laboratory experiments [23,24], but few large scale studies are available up to the present [3,25,26], while various publications have described pilot scale experiments with the TiO_2 system [27–29]. This paper deals with Photo-Fenton laboratory experiments as well as with pilot scale studies with the application of sunlight.

2. Experimental

Ferrous sulphate $FeSO_4 \cdot 7H_2O$ and sulphuric acid were of analytical grade (Merck). Hydrogen peroxide (30% wt.) was analytical grade (Merck) for laboratory purposes and technical grade for the pilot plant experiments. For the degradation experiments ten commercial pesticides were selected, which are presented in Table 1 [2]. They were used without purification, i.e. all impurities and additives contributed to the total organic carbon (TOC) content. For the cases in which mixtures of all the 10 pesticides were used, equal TOC quantities (e.g. 10 ppm) of each pesticide were added. For each pesticide the amount needed for achieving 100 ppm TOC in solution was determined by pre-experiments. Unfortunately this could not be done exactly, as some of the pesticide usually adhered

Table 1
Model pesticides used for this study

Active ingredient	Name of commercial product	Producer	Structure
Acrinatrin	Rufast	Rhône-Poulenc	
Abamectin	Vertimec	Merck	
Endosulfan	Thiodan	AgrEvo	
Formetanate	Dicorzol	AgrEvo	
Imidacloprid	Confidor	Bayer	
Lufenuron	Match	Ciba-Geigy	
Methamidofos	Tamaron 50	Bayer	 $\mathrm{CH_3O-\underset{N}{\overset{O}{P}}-SCH_3}$
Oxamyl	Vydate	DuPont	 $\mathrm{(CH_3)_2NCO\underset{SCH_3}{C}=NOCONHCH_3}$
Pyrimethanil	Scala	AgrEvo	
Propamocarb	Previcur	AgrEvo	$\mathrm{(CH_3)_2NCH_2CH_2CH_2\text{-}NHCO_2NHCO_2CH_2CH_2CH_3}$

to the reactor walls due to some hydrophobic ingredients. As a consequence, the measured TOC was usually too low at the beginning of treatment but reached a maximum as the solubility of intermediates grew and the emulsion became clear. Therefore, in this work the maximum TOC of each experiment has been used for calculations instead of the starting level.

Total organic carbon (TOC) was measured by means of a Shimadzu TOC 5000 analyser with an ASI 5000 auto sampler (laboratory experiments, Vienna) and Hereaus-Foss TOC-2001 analyzer (solar pilot experiments, PSA, Spain), respectively. H_2O_2 in solution was determined by iodometric titration, pH was measured with a pH-glass electrode. Iron concentrations were obtained by photometric measurement with 1,10-phenanthroline (following ISO 6332) using a Shimadzu UV160A spectrophotometer. Chemical oxygen demand (COD) was determined by Spectroquant® cuvette tests from Merck. For the solar plant global UV (300–400 nm) irradiance was recorded by a Kipp and Zonen CUV3 detector, inclined 37° like the reactor modules, permitting the evaluation of incident radiation dependent on hour of the day, clouds and other environmental variations.

Laboratory experiments (in Vienna) were carried out in a prototype reactor fitted for a volume of 8–15 l wastewater (Fig. 1). The irradiated core consists of two coaxial hollow glass cylinders (Duran glass, 400 mm length, wall thickness 8 mm, outer diameters 215 and 270 mm, irradiated area is $0.27\,m^2$, illuminated volume $V_{ill} = 5.75\,l$). The wastewater was continuously pumped through the gap between the two cylinders with a flow rate of 300 l/h. In the centre of the inner cylinder a medium pressure Hg lamp (Osram Ultra-Tech, electrical power 400 W, main output between 300 and 450 nm) was adjusted. The illumination time was calculated as $t_{ill} = V_{ill} \cdot t_T \cdot V_T{}^{-1} = 0.575\,t_T$, where t_T is the total time elapsed and V_T is the total volume (usually 10 l). For further details of the pilot plant refer to [30].

Solar driven experiments were carried out at the Plataforma Solar de Almería (PSA), southern Spain, an ideal place for installing solar plants, as more than 300 days per year can be expected to be sunny, with an average of much more than 3000 sunny hours per year. Furthermore the weather conditions are quite comparable to El Ejido, where the proposed pilot plant will be built later. Compound parabolic collectors (CPCs, Fig. 1) manufactured by Industrial Solar Technology Corporation, Denver, were used for the solar experiments. Three modules, each $2.44 \times 1.22\,m^2$ in size, are connected in series and are mounted on a fixed platform orientated south and inclined 37° to maximise performance (the PSA is located at +37° latitude). Each module consists of 16 parallel CPC reflectors (152 mm wide) with an acceptance angle of 60° on each side. As the concentration of this reflector is about one sun and diffuse light is utilised efficiently, the CPC can also be operated under moderate cloudy conditions. The absorber tubes (I.D. 48 mm) are made of fluoropolymer (transmissivity in the UV range between 0.73 and 0.86) which provides excellent stability against chemicals and light. The reflectors are made of polished aluminium (reflectivity in the UV range about 0.81–0.86). Total efficiency has been estimated to be 72% [29]. Total wastewater volume was $V_T = 250\,l$, while the illuminated volume was $V_{ill} = 108\,l$, as usually all the three modules were used. Therefore, in this case illumination time was calculated as $t_{ill} = 0.43\,t_T$. The wastewater was recirculated at a flow rate of 4000 l/h.

The model wastewater was prepared by adding the appropriate pesticide amount to distilled water. Mixing was done by recirculating the water directly within the apparatus. $FeSO_4 \cdot 7H_2O$ was added as well (usually 0.25 mM), and the solution was acidified using sulphuric acid (initial pH was 2.8 in all the cases), leaving a homogenisation period of 30 min. Degradation was started by addition of the oxidant (H_2O_2), leaving the first five minutes for the dark reaction to take place before light was switched on or the cover of the solar collectors was removed. Samples were taken at regular intervals, and when necessary, further H_2O_2 was added immediately after a sample was taken.

3. Results and discussion

3.1. Laboratory experiments

The 10 commercially available pesticides under investigation were chosen to reflect as many different chemical properties as possible, and to cover a wide range of functional groups. Therefore, the first experiments were targeted on the degradability of each

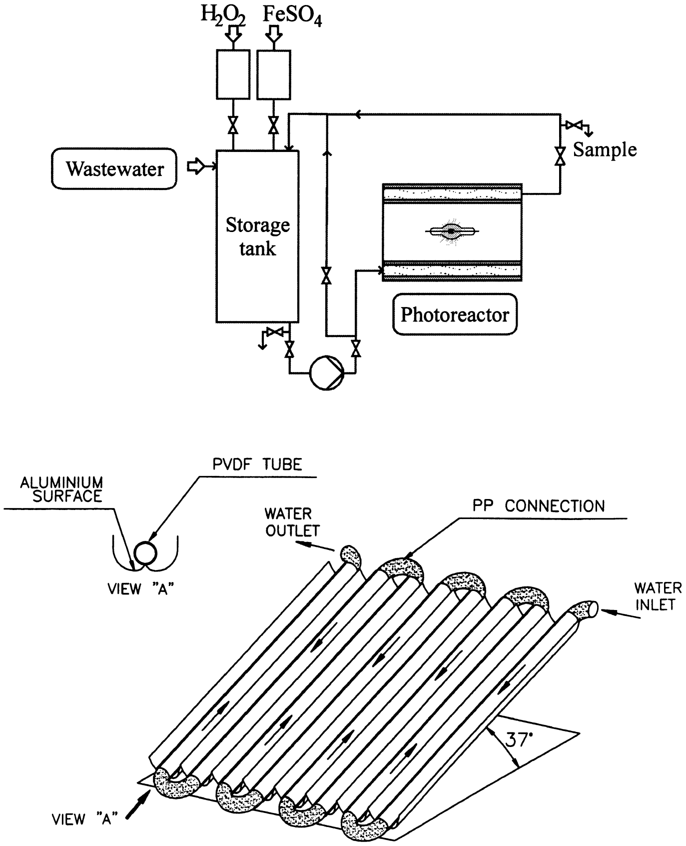


Fig. 1. Upper picture: scheme of the photoreactor used for laboratory experiments. Below: principle of the CPC reactor used at the Plataforma Solar de Almería.

pesticide. For this reason 10 l of model wastewater containing approximately 100 ppm of TOC (total organic carbon) of the chosen pesticide were treated in the laboratory reactor. Fig. 2 illustrates the corresponding results. As already mentioned, it was not possible to start the experiments with exactly the desired TOC concentration, as most of the pesticides showed poor solubility, and part of the emulsion adhered on the walls of the reactor. During the treatment the solubility of the organic substrates rises, so an increase of TOC is observed. For the convenience of the spectator and for better comparability, for the diagrams the TOC values have been normalised by dividing by the maximum TOC reached during the experiment. Neglecting the first increase of organic substrate, the picture is nearly the same for all substances investigated. First higher oxidised intermediates are produced, which does hardly decrease TOC values. Only later a fast decrease of the organic constituents is monitored. Finally, in some cases the last few ppm of TOC seem to be persistent, a phenomenon still lacking a satisfying explanation. A simple theory would either include some hardly degradable products, like aliphatic hydrocarbons [31], perhalogenated carbons [32] or electron-deficient rings (like s-triazines [33,34]), or the formation of stable ferric complexes exhibiting a high catalytic activity for the disproportionation of hydrogen peroxide [35].

As the reaction does not follow simple models like first or zero order kinetics, overall reaction rate constants cannot be calculated. The complexity of the results, of course, is caused by the fact that TOC is a sum parameter often including several hundreds of products that undergo a manifold of reactions. In order to obtain a practical handle for the comparison of various experiments, two different parameters have been

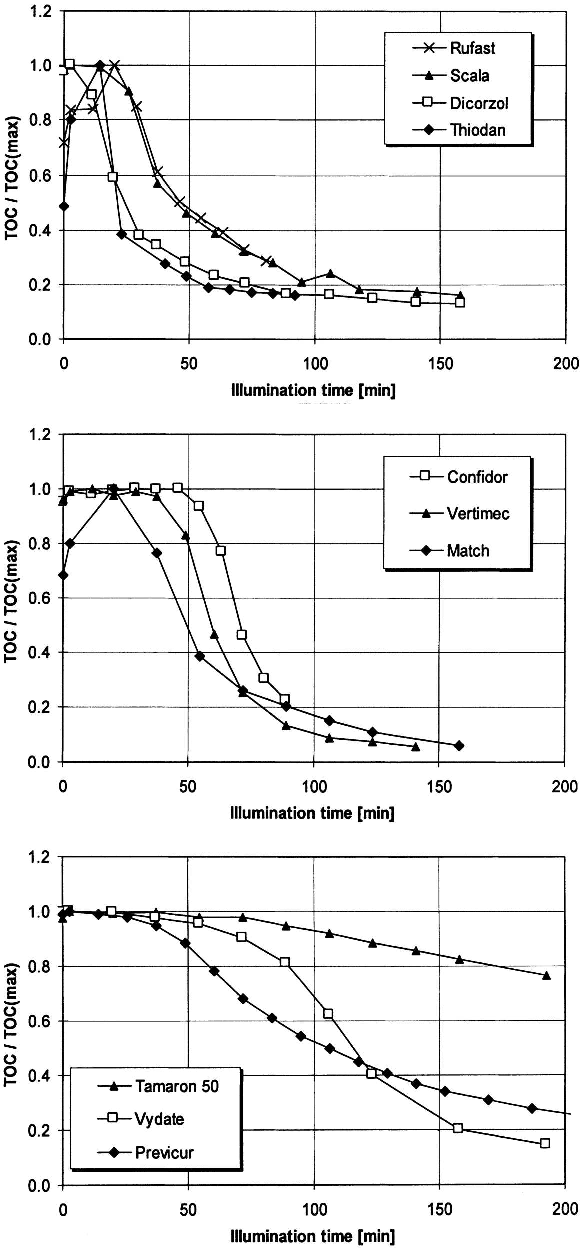


Fig. 2. Degradation of single pesticides in the laboratory reactor. Total volume was 10 l. $TOC_{max} \approx 100$ ppm, c(Fe) = 0.25 mM, $c_0(H_2O_2) = 20$ mM, $pH_0 = 2.8$. Temperature usually increased from 20°C to about 55°C. Pesticides are sorted by degradability.

Table 2
Kinetic parameters for degradation of the single pesticides in the laboratory plant. For experimental conditions see Fig. 2. $t_{50\%}$ refers to TOC half-life, $t_{80\%}$ is the time necessary for degradation of 80% of TOC, and r_{max} is the inflection gradient as defined in the text

Pesticide (commercial name)	$t_{50\%}$ (min)	$t_{80\%}$ (min)	r_{max} (ppm/min)
Thiodan	21.4	55.4	7.9
Dicorzol	24.5	72.5	4.3
Scala	44.9	116.2	2.8
Rufast	46.0	> 80	2.3
Match	49.5	89.1	2.3
Vertimec	59.3	79.6	2.7
Confidor	70.8	> 90	3.5
Vydate	98.7	158.1	1.3
Previcur	105.9	> 200	0.8
Tamaron 50	> 200	–	0.2

chosen: on the one hand the half-time, or more often the time necessary for a certain degree of degradation (like 80% or 90% of the initial/maximum TOC), on the other hand the maximum gradient of the degradation curve, which is formally the gradient of the tangent at the inflection point. It has the unit of a zero-order rate constant (i.e. ppm/min) and, therefore, appears to be easy to handle. Furthermore this gradient can be roughly considered as the initial rate of a reaction, which is a common method in kinetics [36], because it is preceded by a period of nearly constant TOC level. This parameter r_{max} is refered to as ‘maximum rate’ or ‘inflection gradient’ throughout this paper. The calculated values for the experiments of Fig. 2 are listed in Table 2. Pesticides are sorted by TOC half-life. But as can bee seen from the 80% degradation times, it depends on the target value of degradation in order to define ‘well degradable’, as e.g., Scala is a well degradable substrate according to half-life and inflection gradient, but the target of 80% TOC reduction is reached much later than in the case of Vertimec, which in turn shows a similar gradient but a longer half-life. But for the most part a combination of these parameters seems to be a practical criterion of assessment.

Thereafter, mixtures of all ten pesticides have been investigated. The crosshair curve in Fig. 3 depicts a standard experiment in the laboratory reactor. In this case the initial chemical oxigen demand (COD) was measured and the whole calculated H_2O_2 demand (23 ml) was added at the start of the test run. When the peroxide was consumed after 124 min, about 72% of the TOC were degraded. Further two additions of the initial H_2O_2 amount led to only 82% degradation after a total of 190 min. In another experiment (data not shown) 1 ml of hydrogen peroxide (30% wt.) was

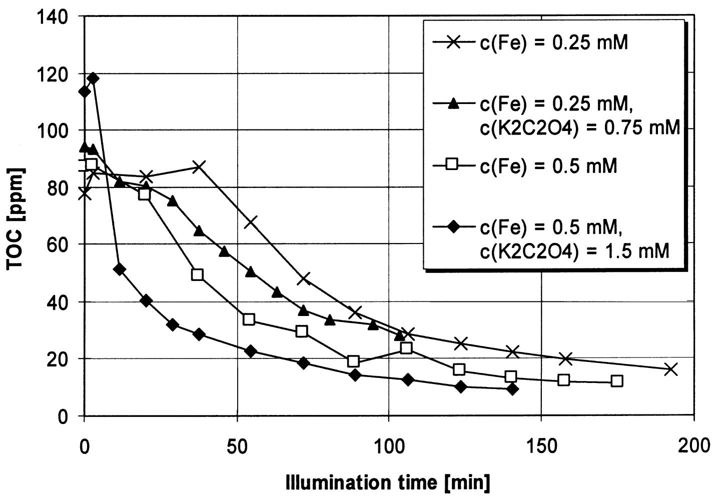


Fig. 3. Effect of iron concentration and oxalate addition on the degradation of a mixture of all 10 pesticides in the laboratory reactor. Initial concentration of the pesticides was 10 ppm TOC each, hydrogen peroxide was added in several portions. Crosshairs: Standard experiment (0.25 mM Fe, no oxalate added). Triangles: Same, but 0.75 mM $K_2C_2O_4$ added. Open squares: c(Fe) = 0.5 mM, no oxalate. Diamonds: Same, with 1.5 mM potassium oxalate.

added after every sample (i.e. every 15 min). Degradation rate was approximately the same as before, but for the first 50% of TOC about 60% less H_2O_2 than in the first case were consumed. Towards the end of reaction the differences grew less. The final degree of TOC degradation did not vary significantly. Furthermore the concentration of the iron salt was increased. As shown in Fig. 3, this leads to a significantly faster reaction and a slightly better final degree of TOC degradation.

Since addition of oxalate is claimed to be able to improve the Photo-Fenton reaction [14,32,37], this option was also investigated. The reported improvement affects two issues: The high quantum efficiency of reaction (4) increases the degradation rate, while the intermediate radical $CO_2^{\bullet -}$ should be able to attack persistent species like CCl_4 (6), that are not affected by $OH^{\bullet}$ radicals [32]. Therefore, adding oxalate could lead to an improved final degradation, since halogenated hydrocarbons could be one of the reasons for the delay in the final degradation.

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

$$C_2O_4^{\bullet -} \rightarrow CO_2 + CO_2^{\bullet -} \quad (5)$$

$$CO_2^{\bullet -} + CCl_4 \rightarrow CO_2 + CCl_3^{\bullet -} + Cl^- \quad (6)$$

The results of the conducted experiments shown in Fig. 3 support this thesis. In case of the pesticide mixture with c(Fe) = 0.25 mM and initial addition of $K_2(COO)_2$ the degradation of TOC started immediately. This indicates that the reaction mechanism must have changed. However, the final degradation was reached nearly within the same time interval as without oxalate, as the oxalate was consumed during the first stage. In the second test run (with c(Fe) = 0.5 mM) the improvement of reaction rate is even more obvious, and the final degradation again corresponds to that of the experiment without oxalate. Note also the increased initial TOC caused by the oxalate. Finally, in the same experiment oxalate was added a second time near the end, but this did not show any effect, but the added oxalate was degraded practically immediately. This contradicts the theory, that halogenated alkanes are responsible for the persistent TOC residue, because the ferrioxalate/H_2O_2/UV was reported to be able to degrade these moieties [32].

3.2. Pilot plant experiments

After these investigations further research was focused on pilot scale experiments with application of solar light. Previous studies [2,5] have already dealt with the same mixture of pesticides, but there the TiO_2/persulphate system was applied. In order to obtain results comparable to that study, experimental

Table 3
Influence of iron concentration on the degradation of a mixture of 10 pesticides in the CPC reactor at the PSA (Spain). Total volume was 250 l, initial TOC about 100 ppm, H_2O_2 was added in 3 aliquots of 30% of the stoichiometric amount during the first hour of the experiments. Further $H_2O_2$was added after the previous amount had been consumed. Weather was mostly sunny with rare occasions of small clouds. $t_{50\%}$ refers to TOC half-life, r_{max} is the inflection gradient as defined in the text

c(Fe)	r_{max} (ppm/min)	$t_{50\%}$ (min)
0.25	4.65	20.0
0.5	5.74	32.9
1.0	6.57	20.6
2.0	8.75	16.6

conditions were chosen as close to the TiO_2 study as possible. The influence of iron catalyst concentration on degradation of the pesticide mixture was studied first (see Table 3). The inflection gradient r_{max} is growing with catalyst concentration, but the trend of half-times is not that clear. An explanation for the weak dependency on iron concentration may be the fact, that usually the reaction rate increases with the catalyst amount, but reaches a plateau at a certain threshold iron concentration. This threshold is dependent on the light source, the thickness of the irradiated layer and the type of wastewater, because internal light filtering may occur. In case of the CPC reactors and the pesticide mixture, the plateau seems already reached at 0.5 mM Fe, while in experiments with 4-chlorophenol the optimum iron concentration is higher than 1 mM [26]. Anyway, compared to degradation by TiO_2 methods, the Photo-Fenton reaction is much faster in all cases investigated. The half-time in the Photo-Fenton experiments ranged between 17 and 24 min illumination time, while it was 130 min in the case TiO_2/persulphate and over 10 h, when TiO_2 was used without persulphate [4,5]. However, the slow-down at the end is not that significant in the TiO_2 cases, i.e., 90% degradation of TOC are reached after 214 min in the TiO_2/persulphate system, which is less then twice the half-life, whereas it needs 125 min (more than five times the half-life) in the Photo-Fenton case. Still, the latter is considerably faster than application of TiO_2 photocatalysis.

One of the advantages of the Photo-Fenton process is the ability of treating very high sewage concentrations. For the pesticide bottle washing plant proposed for the El Ejido project, the freshwater consumption can be chosen freely according to boundary conditions of the succeeding water detoxification process. This means that initial organic concentration is a subject of optimisation for the photocatalytic process. Experiments were carried out accordingly, and again half-times and maximum rates were calculated for discussion. As can be seen in Fig. 4, half-times are linearly dependent on the initial concentration (in this work the maximum concentration reached during the first reaction period). This usually indicates, that the reaction is zero order, but in this case such a conclusion seems uncertain, since the times necessary for 80% degradation should also be linearly dependent on concentration. This seems to be doubtful in the case of the pesticides (Fig. 4). Furthermore the figure shows the dependency of the inflection gradient on pollutant concentration. In case of a zero order reaction the gradient has to be constant.

In order to find out the economically optimal starting concentration of the pollutant, various parameters have to be considered: As the mass of pesticide degraded is $V_{water} \cdot c_0$, higher TOC concentrations require less water and iron consumption per mass pesticide, and less installed electrical power for pumps. Furthermore, since the plant should be operated only with sunlight, a tank is to be installed, in which the polluted water is collected during night or during dark and rainy days. If high TOC values are tolerable, a smaller storage tank may be installed. On the other hand, high initial concentrations may be a drawback, if conflicts with legal limits occur, as the remaining TOC level will be higher when 90% degradation are reached. High starting concentrations would be favourable if the half-time increased less than direct proportional with rising concentration, which is the case for reaction orders greater zero.

Concerning the pesticide mixture, the half-time is increasing linearly. Thus, (τ/c_0) is constant and, therefore, $\tau \cdot V$ is constant, which means that for a given time limit (the sunny hours per year) the reactor volume is also constant. This in turn predicts, that higher initial concentrations do not lead to a significant cost reduction of the process. In fact actual costing for different pesticide levels was found to be nearly constant.

Finally the fate of the hydrogen peroxide was monitored, which is especially interesting, as H_2O_2 is responsible for 80–90% of the chemical costs. Fig. 5 depicts a typical degradation of the pesticide mixture

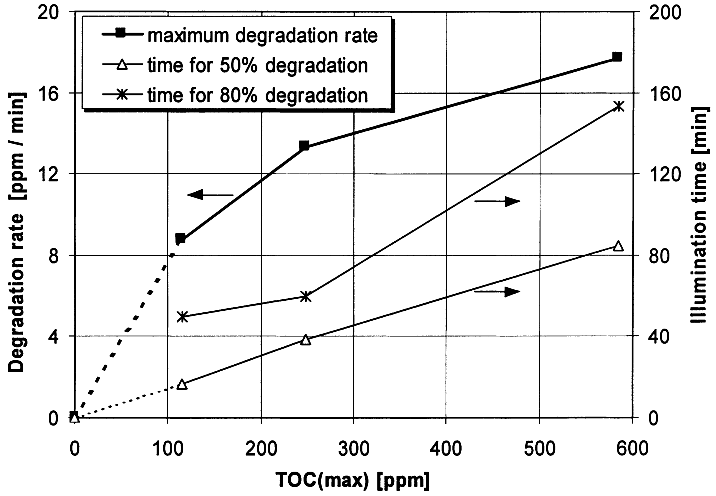


Fig. 4. Variation of initial concentration of pesticides in the CPC reactor. Squares (left scale): Degradation rate at the inflection point (i.e. maximum slope of the TOC degradation curve), triangles (right scale): Half-time of TOC, asterisks: Illumination time required for 80% TOC reduction.

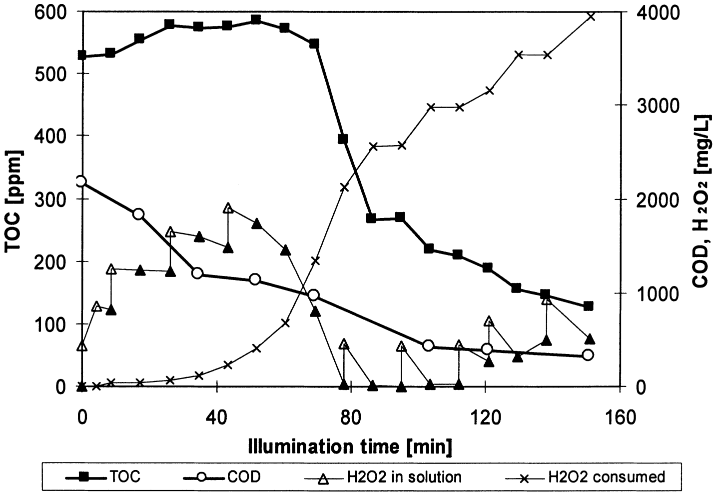


Fig. 5. Typical degradation of a highly loaded pesticidal wastewater in the CPC at the Plataforma Solar de Almería. Iron concentration is 2 mM, weather was sunny. Squares (left scale): TOC, circles (right scale): COD. The triangles indicate the hydrogen peroxide in solution. Filled triangles are measured values, open triangles indicate calculated values immediately at the time of addition. The crosshairs (right scale) depict the accumulated H_2O_2 consumption.

in the CPC reactor. Again, the TOC slightly increases during the first minutes, but the chemical oxygen demand (COD) is already lowered by 50%. Surprisingly, at this stage only 3.5% of the theoretical H_2O_2 demand are consumed. This clearly indicates that ambient oxygen significantly contributes to degradation (7) [17].

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \rightarrow\rightarrow \text{products}(CO_2) \quad (7)$$

As a consequence, aerating the wastewater seems to be a promising option in order to reduce chemical costs. When TOC starts to decrease, the situation is changing significantly. The H_2O_2 consumption per COD grows continuously until in the end peroxide is degraded by the iron catalyst, hardly affecting the remaining organic carbon. In turn, this means that for reaching the desired 90% TOC degradation, much more than the stoichiometric amount of H_2O_2 is consumed. This clarifies that the desired final TOC greatly influences the peroxide consumption and total process costs.

After the investigations presented within this paper, the total costs of a large scale plant were estimated [4,5] and compared to the corresponding results on the TiO_2/UV and TiO_2/UV/persulphate systems. As the necessary chemicals of the Photo-Fenton system are cheaper, and as the faster reaction leads to smaller solar collectors, the Photo-Fenton option is 30% cheaper than the TiO_2 system, and neglecting the personnel costs even 50%.

4. Conclusions

During this work the Photo-Fenton process proved to be very powerful in destroying persistent pesticides in the wastewater of a pesticide bottle recycling plant. Even though all the substances could be degraded, some reacted rather slowly, and often a few ppm remained almost inert. Minimising the H_2O_2 amount in solution has a positive effect on oxidant consumption. Addition of oxalate quickens the reaction, but enhances final degradation only slightly. Also an increase of iron concentration proved useful, while rising the initial pollutant concentration did not affect the overall efficiency of the process. Summing up, the efficiency of all the sunlight driven Photo-Fenton experiments carried out exceeded the results of the previous TiO_2 study. Further investigations are needed concerning the toxicity and biodegradability of intermediates and final products, since these parameters highly affect the feasibility of the photocatalytic (Photo-Fenton as well as TiO_2) water treatment.

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