Comparison of different TiO$_2$ samples as photocatalyst for the degradation of a mixture of four commercial pesticides

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Abstract

BACKGROUND: The presence of pesticides in surface and ground waters can trigger serious environmental problems, particularly in those areas where agriculture is the major economic activity. In this respect, photochemical advanced oxidation processes may be employed to decontaminate such matrices.

RESULTS: Semiconductor photocatalysis was employed to treat a mixture of four commercial pesticides (oxydemethon-methyl, methidathion, carbaryl and dimethoate at 25 mg/L each). Laboratory scale experiments under UV-A irradiation were performed to evaluate the relative activity of six commercially available titania samples at 0.5 g/L concentration with Evonik P25 (a 75:25 mixture of anatase:rutile) being the most...
effective one in terms of pesticides degradation. Experiments were then performed in a pilot plant reactor under natural sunlight leading to quantitative removal of pesticides in less than 300 min; this was accompanied by a substantial reduction of acute toxicity to *Vibrio fischeri* (i.e. from an initial value of 50% to 15%), as well as moderate mineralization, i.e. 40% COD and 25% DOC removal.

CONCLUSIONS: The use of sunlight, a renewable energy source, alongside a commercially available, inexpensive and active titania photocatalyst may offer a sustainable treatment option to detoxify this type of wastewaters.

**Keywords:** titanium dioxide, pesticides, photocatalysis, detoxification, sunlight

1. Introduction

Solar-based photochemical processes for wastewater treatment have been demonstrated as a promising alternative to deal with aqueous effluents which cannot be treated by conventional means, in particular those containing highly toxic chemicals, such as pesticides.¹ These methods are based on the photochemical generation of highly reactive species, such as hydroxyl radicals, singlet oxygen, or excited states of some molecules. Among the systems which can be used under sunlight irradiation are photocatalysis with semiconductors (mainly TiO₂),² the photo-Fenton process³ or organic sensitizers.⁴

Titanium dioxide is a photochemically active solid semiconductor which can be employed for different purposes, among them, in wastewater treatment.⁵⁻⁷ It has been demonstrated to promote the oxidation of a wide number of pollutants; in particular, its application to detoxify solutions containing pesticides has deserved attention from researchers,⁸ because of the important environmental concern associated with the high toxicity of these chemicals. Regarding the use of sunlight in photochemical processes to
remove pesticides, TiO$_2$, as well as photo-Fenton have deserved attention from different research groups. The use of solar photo-Fenton process is gaining momentum in recent years,\textsuperscript{9-13} and even experiments at industrial plant scale have been performed.\textsuperscript{14} However, TiO$_2$ has also been studied and it has been demonstrated to remove efficiently pesticides under solar irradiation;\textsuperscript{15} complete detoxification of the solution has also been reported in some cases.\textsuperscript{16,17}

The structure of TiO$_2$ has a remarkable influence on its photocatalytic properties and several titania catalysts are commercially available. Hence, comparing the performance of different commercial types of titanium dioxide in the detoxification of solutions containing pesticides seems meaningful. For this purpose the photodegradation of a mixture of four commercial pesticides, namely oxydemeton-methyl, methidathion, carbaryl and dimethoate (structures are shown in Figure 1) has been studied in the presence of different TiO$_2$ samples; this mixture of pesticides has been chosen since the photodegradation of the individual components using titania under sunlight has already been reported.\textsuperscript{16-18} Preliminary experiments employing several titania samples were performed at laboratory scale under artificial UV-A irradiation, while selected reactions were then scaled-up to pilot plant under natural sunlight. Furthermore, bioassays were employed in order to follow the changes in the biocompatibility of the mixture. Finally, results were compared with those obtained with solar photo-Fenton with the same mixture of pollutants.

2. Materials and methods

2.1 Reagents

Four commercial pesticides, based on oxydemeton-methyl, methidathion, carbaryl dimethoate were used for the photodegradation experiments: commercial name, purity
and main excipients are shown in Table 1. Pure ingredients were also employed as standards.

The employed TiO$_2$ were Evonik P25, Hombikat, Millennium PC50, Millennium PC100, Millennium PC105 and Kronos 7101; their main characteristics are summarized in Table 2.

2.2. Reactions

Preliminary experiments were conducted at laboratory scale with the mixture of pesticides (25 mg/L of each active ingredient) and 0.5 g/L of titanium dioxide. Irradiation took place in an immersion well, laboratory scale photoreactor, purchased from Ace Glass (Vineland, NJ, USA). It consists of an inner, double-walled, borosilicate glass housing the lamp (390 mm length, 53 mm outer diameter) and an external cylindrical reaction vessel (310 mm length, 73 mm internal diameter, 350 mL capacity) joined together with an internally threaded connection with the aid of a nylon bushing connector and an O-ring. UV-A irradiation was provided by a 400 W, high-pressure mercury lamp (Osram, HQL, MBF-U), which was placed inside the inner borosilicate glass and was cooled by a water jacket to maintain during photocatalytic experiments a constant temperature of 32 ± 2 °C. The reaction vessel was covered with aluminum foil. The photon flux emitted from the lamp was determined actinometrically using the potassium ferrioxalate method and was found to be $1.12 \times 10^{-5}$ Einstein/s.$^{19}$

The solution was slurried with the appropriate amount of catalyst and magnetically stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption of organic compounds on the TiO$_2$ surface. After that period, the UV-A lamp was turned on, while air was continuously sparged in the liquid and the reaction mixture was continuously stirred.

Selected reactions were scaled-up using a pilot plant (Solardetox Acadus-2001,
Ecosystem) based on compound parabolic collector (CPC) technology, which has been described elsewhere. It consisted of four borosilicate tubes (internal diameter, 29.2 mm, external diameter 32 mm), through which the solution to be treated was flown; two aluminium parabolic mirrors concentrated the solar radiation in the axis of each tube. The plant total surface was 0.26 m\(^2\) and the irradiated volume 1.83 L. The surface had a dihedral angle of 30° with the horizon, with a southern orientation. The plant was equipped with a radiometer (Acadus 85), which measured the received UV-A radiation (which accounts for ca. 7% of the total solar energy). For every experiment, a reservoir was loaded with 4 L of solution (containing 25 mg/L of each active ingredient and 0.5 g/L of TiO\(_2\)). Then, this mixture was continuously pumped into the plant, and after exposure to sunlight, it was recirculated back to the reservoir.

Accumulated UV radiation was expressed as \( t_{30W} \); this parameter is employed to normalize the changing irradiation conditions of solar experiments. \( t_{30W} \) was calculated according to equation (1), where \( UV_{ac} \) is the accumulated solar radiation (J/m\(^2\)), \( V_i \) the irradiated volume (L), \( V_t \) the total volume (L) and \( I \) the average UV irradiance, considered as 30 W/m\(^2\).

\[
t_{30W} = \frac{UV_{ac} \cdot V_i}{I \cdot V_t} \quad (1)
\]

2.3. Analytical techniques

Analytical determination of the concentration of each pesticide was done by means of high performance liquid chromatography using a Perkin Elmer, Autosystem XL Hitachi D-7000 model, equipped with a diode array detector and an autosampler. A partition reversed-phase column LiChrospher ® 100 RP-18 (5 µm) was employed as stationary
phase. The eluent consisted of an isocratic mixture of 50% acetonitrile and 50% water, with a flow rate of 1 mL/min. A diode array detector was employed monitoring absorbance at 210 nm. Before injection, samples were diluted with methanol (1:1) to dissolve any organics adsorbed onto TiO$_2$ and filtered through polypropylene (0.45 µm, VWR). Identification and quantitation were based on comparison of retention times and areas with standards.

A GCMS-QP2010S (Shimadzu) gas chromatograph was employed to identify the main organic additives present in the commercial formula of the pesticides, and major intermediates formed along the process. Temperature was increased from 60ºC to 250ºC with a 5ºC/min rate. A Meta X5 Teknokroma column was used. Samples were previously concentrated by solid phase extraction: 50 mL of the aqueous solution (pH ca. 7) were flowed though a LiChrolut EN 200 mg (Merck) cartridge; then organics were recovered with 3 mL of methanol.

Dissolved organic carbon (DOC) was determined with a Shimadzu TOC-V CSH apparatus. Chemical oxygen demand (COD) was determined spectrometrically according to the standard dichromate method; digestion was performed at 148ºC in a Thermoreaktor TR300 (Merck) and the photometric determination was performed in a Spectroquant NOVA 60 (Merck). Samples submitted to theses assays were filtered but not diluted with methanol.

Toxicity was evaluated according to the method of inhibition of bioluminescence of *Vibrio fischeri* bacterium (ISO 11348-3 norm, using lyophilized bacteria). The standard procedure was employed for reconstitution of the bacteria, using a salty solution obtained from Macherey-Nagel. The luminescence was measured by means of a Luminometer Lumifix-Bio-10, also purchased from Macherey-Nagel. Toxicity was determined after 15 min of incubation. Distilled water and zinc sulphate were used in
control experiments. All samples were filtered and neutralized before analysis.

3. Results and discussion

3.1. Laboratory scale experiments

Preliminary experiments at laboratory scale were carried out to assess the relative activity of the six titania samples for the photocatalytic degradation of the ingredients of the pesticide mixture (25 mg/L of each pollutant and 0.5 g/L of the corresponding TiO$_2$). This concentration of pesticides is in line with those employed in other experiments and with data reported on a pilot plat devoted to the depuration of waters originated in the rinsing of bottles and greenhouse plastics in contact with pesticides.$^{14}$

Plots of the relative pollutant concentration vs. time are shown in Figure 2. As can be seen, the extent of pesticide degradation after 120 min of reaction was systemically over 50% for the P25 and Kronos catalysts, while the use of Hombikat UV100 led to insignificant removal (i.e. no more than 10%). Adsorption of pesticides onto titania surface was not very significant (systematically below 10% after 30 min). In this context, it is interesting to indicate that an apparent increase in the concentration of some pesticides (e.g. methidathion) was observed at the early stages of the reaction. This is a well-known behaviour that can be attributed to a modification of the adsorption-desorption equilibrium upon irradiation.$^{16}$

Assuming that the reaction of pesticides follows pseudo-first order kinetics, the apparent rate constant (k) can be computed from the data of Figure 2, if they are plotted in the form of:

$$\ln \frac{C_o}{C} = kt \quad (2)$$
As seen in Figure 3, the four pesticides exhibited similar reactivities at the conditions under consideration; this said, oxydemethon-methyl and methidathion, that contain phosphothioester groups appear to be more readily degradable than the other two pesticides as this moiety has been found to be susceptible to oxidative degradation. Conversely, the lowest $k$ values were obtained for carbaryl, as the carbamate group seems to be more resistant to photocatalytic oxidation. Regarding the different types of titanium dioxide, their performance decreased in the order: P25 > Kronos > Millennium family > Hombikat. According to Hurum and coworkers, mixed-phase titania catalysts like Evonik P25 show greater effectiveness than others due to three factors: (i) the smaller band gap of rutile extends the useful range of photoactivity into the visible region; (ii) the stabilization of charge separation by electron transfer from rutile to anatase slows down recombination; (iii) the small size of the rutile crystallites facilitates this transfer, creating catalytic hot spots at the rutile/anatase interface. Conversely, the inconsiderable effectiveness of Hombikat UV100 may be attributed to its large surface area which is usually associated with large amounts of crystalline defects or weak crystallization, both favouring the recombination of photogenerated electrons and holes. A complementary explanation is that organics adsorbed on TiO$_2$ surface may serve as an external charge recombination centre, whereas the degradation is initiated off the surface. In such case, the net degradation can be less efficient when more substrates are adsorbed on high-surface area titania samples.

3.2. Pilot plant experiments

Having assessed the relative activity of different photocatalysts at laboratory scale under UV-A irradiation, it was decided to investigate the solar detoxification of wastewaters containing 25 mg/L of each active ingredient in a pilot plant employing the two most
promising titania samples, namely Evonik P25 and Kronos 7101 at 0.5 g/L. Figure 4 clearly shows that P25 was substantially more active than Kronos leading to nearly complete degradation of all four pesticides in less than 300 min; on the other hand, conversion did not exceed 80% for either pesticide after 300 min with Kronos. If the data of Figure 4 are plotted in the form of equation (2), the apparent rate constants ranged from 0.0085 to 0.0141 min\(^{-1}\) for P25 and 0.0042 to 0.0051 min\(^{-1}\) for Kronos.

It is interesting to compare these results with those of the photo-Fenton degradation of the same mixture of commercial pesticides in a pilot plant, reported in a previous paper.\(^{13}\) Under the studied conditions, photo-Fenton appears to be more efficient as the rate constants obtained with TiO\(_2\) are 1-2 orders of magnitude below those reported for photo-Fenton (between 0.29 and 0.52 min\(^{-1}\)). The normalized irradiation time (expressed as \(t_{30W}\)) required for the elimination of the active ingredients ranges from 225 to 325 min with P25, whereas in the case of Kronos at \(t_{30W} = 350\) min, degradation varies between 75 and 90%. In sharp contrast, solar photo-Fenton is able to achieve complete elimination of the active ingredients in \(t_{30W} = 30-40\) min.

Unlike the relative fast degradation of the individual components, matrix mineralization was slow, as can be seen in Figure 5. For example, the extent of COD and TOC removal was 40% about and 25%, respectively at the end of the experiment with Evonik P25, which implies that certain organic species, other than the active ingredients, initially present in the commercial formulation and/or photocatalytic degradation by-products are more resistant to oxidation than the pesticides themselves (see Table 1 for the excipients found in the employed commercial formulae). It is also notable that COD and TOC mainly decreased during the early stages of the reaction and remained fairly constant thereafter; this implies that COD and TOC reduction may partly be due to adsorption onto the catalyst surface and/or evaporation of some volatile components of
the mixture of the commercial products rather than to oxidative degradation. The presence of organics might also have some influence on the degradation rate as shown in a previous paper, where results obtained in the individual photodegradation in the presence of P25 of pure and commercial products were compared; in all cases, reduction up to 50% on the k values were observed.24

Figure 6 shows the temporal evolution of inhibition to marine bacteria *V. fischeri* for the two catalysts under investigation. Toxicity decreased from an initial value of 50% for the untreated mixture to 15% at the end of the experiment with P25; this is consistent with the complete removal of the active ingredients as confirmed by HPLC analysis. Interestingly, toxicity appeared to increase during the early (i.e. up to about 100 min) stages of the reaction most probably due to the formation of some toxic intermediates; this is a well-documented behavior that has been observed in photocatalysis, as well as other advanced oxidation studies,25 where the toxicity of the original effluent was found to increase steeply and reach a maximum during the early stages of the treatment presumably due to the formation of toxic intermediates. At longer treatment times, toxicity decreased to acceptable levels as toxic intermediates were degraded further.26

On the other hand, there was no toxicity decrease when Kronos 7101 was employed; this is compatible with the presence of residuals pesticides and the formation of toxic by-products associated with the poorer performance of this material.

Although the mixture studied in this work is too complex to determine reliable mechanistic data, the individual behaviour of each compound was studied in previous publications.16-18,27 In all cases, pesticide removal was observed to involve a very significant detoxification of the solution, using respirometric measurements and the luminescence of *V. fischeri* assay.
In the case of the photo-Fenton treatment of the same mixture of pesticides, the gross composition of the phototreated solution was analyzed by GC-MS. Despite the high number of compounds that were present, the dominant ones were determined. At the early stages of the process, these were pesticides and solvents, including some chlorinated compounds; then fragments corresponding to the pesticides were released together with the remaining amounts of the parent pollutants; at the end of the process, low molecular weight ketones and aldehydes became dominant; carboxylic acids might have also been formed but their polarity is too high to be detected by this analysis. GC-MS analysis was also performed for samples taken at $t_{30W}$ ca. 80 min and 250 min, with Evonik P25 titania and a similar trend was observed; for the sample at $t_{30W} = 80$ min, pesticides and some photodegradation by-products (naphtol, organophosphorated compounds) still remained in the solution, together with solvents such as chlorophenol, xylene or cyclohexanone. For the sample taken at $t_{30W} = 250$ min only residual amounts of some of these compounds could be determined (e.g. cyclohexanone, acetophenone) and hence most of the remaining organics might consist of low molecular weight highly oxidized compounds (e.g. carboxylic acids) that could not be detected by GC-MS. This could also explain changes in the changes in toxicity, as at the end of the process most of the potentially toxic species (e.g pesticides and chlorinated compounds) were removed.

Conclusions

The conclusions drawn from this work regarding the photocatalytic treatment of pesticides can be summed up as follows:
(1) Various commercially available titania samples were screened and a 75:25 anatase:rutile mixture (Evonik P25) was more active than others containing only anatase.

(2) Complete removal of commercial pesticide formulations was feasible and this coincided with wastewater detoxification. Nonetheless, mineralization was not possible at the conditions employed in this work.

(3) P25 titania was able to detoxify the solution at pilot plant scale under solar irradiation. Pesticides removal was also reached by the less efficient Kronos 7101, although in this case an important remnant toxicity was detected at the end of the process.

Acknowledgements

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References


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Figure 5: Evolution of COD (■,□) and DOC (●,◇) as a function of solar irradiation time with Evonik P25 (open symbols) or Kronos 7101 (closed symbols).

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<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Commercial name</th>
<th>Purity (%)</th>
<th>Excipients</th>
<th>Supplier</th>
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<tbody>
<tr>
<td>Methyl-oxydemeton</td>
<td>Metasystox R</td>
<td>25 (w/v)</td>
<td>Xylene, Chlorobenzene</td>
<td>Bayer</td>
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<tr>
<td>Methidathion</td>
<td>Ultracid</td>
<td>40 (w/v)</td>
<td>Acetophenone</td>
<td>Syngenta</td>
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<tr>
<td>Carbaryl</td>
<td>Sevnol</td>
<td>85 (w/w)</td>
<td>-</td>
<td>MAFA</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>Laition</td>
<td>40 (w/v)</td>
<td>Xylene, Cyclohexanone</td>
<td>Lainco</td>
</tr>
</tbody>
</table>
Table 2: Main characteristics of the various TiO$_2$ catalysts used in this work. A stands for anatase and R for rutile.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystal form</th>
<th>BET area (m$^2$/g)</th>
<th>Particle size (nm)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evonik P25</td>
<td>75%A:25%R</td>
<td>50</td>
<td>21</td>
<td>Degussa AG</td>
</tr>
<tr>
<td>Hombikat</td>
<td>A &gt; 99%</td>
<td>&lt;250</td>
<td>5</td>
<td>Sachtleben Chemie GmbH</td>
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<td>Millennium UV100</td>
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<td>45-55</td>
<td>20-30</td>
<td>Millennium Inorganic</td>
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<tr>
<td>Millennium PC50</td>
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<td>80-100</td>
<td>15-25</td>
<td>Millennium Inorganic</td>
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<tr>
<td>Millennium PC100</td>
<td>A &gt; 95%</td>
<td>75-95</td>
<td>15-25</td>
<td>Millennium Inorganic</td>
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<tr>
<td>Millennium PC105</td>
<td>A &gt; 95%</td>
<td>75-95</td>
<td>15-25</td>
<td>Millennium Inorganic</td>
</tr>
<tr>
<td>Kronos 7101</td>
<td>A&gt;92.5%</td>
<td>&gt;125</td>
<td>15</td>
<td>ECKART</td>
</tr>
</tbody>
</table>
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