

Document downloaded from:

<http://hdl.handle.net/10251/58305>

This paper must be cited as:

Vicente Candela, R.; Soler Escoda, JM.; Arqués Sanz, A.; Amat Payá, AM.; Frontistis, Z.; Xekoukoulotakis, N.; Mantzavinos, D. (2014). Comparison of different TiO₂ samples as photocatalyst for the degradation of a mixture of four commercial pesticides. *Journal of Chemical Technology and Biotechnology*. 89:1259-1264.



The final publication is available at

<http://dx.doi.org/10.1002/jctb.4382>

Copyright Wiley

Additional Information

This is the accepted version of the following article: Vicente Candela, R.; Soler Escoda, JM.; Arqués Sanz, A.; Amat Payá, AM.; Frontistis, Z.; Xekoukoulotakis, N.; Mantzavinos, D. (2014). Comparison of different TiO₂ samples as photocatalyst for the degradation of a mixture of four commercial pesticides. *Journal of Chemical Technology and Biotechnology*. 89:1259-1264., which has been published in final form at <http://dx.doi.org/10.1002/jctb.4382>.

1
2
3 **Comparison of different TiO₂ samples as photocatalyst for the degradation of a**
4
5 **mixture of four commercial pesticides**
6
7
8

9 R. Vicente^{1*}, J. Soler¹, A. Arques¹, A.M. Amat¹, Z. Frontistis², N.P. Xekoukoulotakis²,
10
11 D. Mantzavinos³
12

13
14 (1) Universitat Politècnica de València, Departamento de Ingeniería Textil y Papelera,
15 Plaza Ferrándiz y Carbonell, 1, 03801-Alcoy, Spain
16

17
18 (2) Department of Environmental Engineering, Technical University of Crete,
19 Polytechnioupolis, GR-73100 Chania, Greece
20

21
22 (3) Department of Chemical Engineering, University of Patras, Caratheodory 1,
23 University Campus, GR-26504 Patras, Greece
24
25
26
27

28
29 * Corresponding author
30

31 Email: rvicente@txp.upv.es; Tel.: ++34 966528471; Fax: ++34 966528438
32
33
34
35

36 **Abstract**
37

38 BACKGROUND: The presence of pesticides in surface and ground waters can trigger
39 serious environmental problems, particularly in those areas where agriculture is the
40 major economic activity. In this respect, photochemical advanced oxidation processes
41 may be employed to decontaminate such matrices.
42
43
44
45

46
47 RESULTS: Semiconductor photocatalysis was employed to treat a mixture of four
48 commercial pesticides (oxydemethon-methyl, methidathion, carbaryl and dimethoate at
49 25 mg/L each). Laboratory scale experiments under UV-A irradiation were performed
50 to evaluate the relative activity of six commercially available titania samples at 0.5 g/L
51 concentration with Evonik P25 (a 75:25 mixture of anatase:rutile) being the most
52
53
54
55
56
57
58
59
60

1
2
3 effective one in terms of pesticides degradation. Experiments were then performed in a
4
5 pilot plant reactor under natural sunlight leading to quantitative removal of pesticides in
6
7 less than 300 min; this was accompanied by a substantial reduction of acute toxicity to
8
9 *Vibrio fischeri* (i.e. from an initial value of 50% to 15%), as well as moderate
10
11 mineralization, i.e. 40% COD and 25% DOC removal.

12
13
14 CONCLUSIONS: The use of sunlight, a renewable energy source, alongside a
15
16 commercially available, inexpensive and active titania photocatalyst may offer a
17
18 sustainable treatment option to detoxify this type of wastewaters.
19

20
21 **Keywords:** titanium dioxide, pesticides, photocatalysis, detoxification, sunlight
22
23

24 25 1. Introduction

26
27 Solar-based photochemical processes for wastewater treatment have been demonstrated
28
29 as a promising alternative to deal with aqueous effluents which cannot be treated by
30
31 conventional means, in particular those containing highly toxic chemicals, such as
32
33 pesticides.¹ These methods are based on the photochemical generation of highly reactive
34
35 species, such as hydroxyl radicals, singlet oxygen, or excited states of some molecules.
36
37 Among the systems which can be used under sunlight irradiation are photocatalysis with
38
39 semiconductors (mainly TiO₂),² the photo-Fenton process³ or organic sensitizers.⁴
40
41
42
43
44

45
46 Titanium dioxide is a photochemically active solid semiconductor which can be
47
48 employed for different purposes, among them, in wastewater treatment.⁵⁻⁷ It has been
49
50 demonstrated to promote the oxidation of a wide number of pollutants; in particular, its
51
52 application to detoxify solutions containing pesticides has deserved attention from
53
54 researchers,⁸ because of the important environmental concern associated with the high
55
56 toxicity of these chemicals. Regarding the use of sunlight in photochemical processes to
57
58
59
60

1
2
3 remove pesticides, TiO₂, as well as photo-Fenton have deserved attention from different
4
5 research groups. The use of solar photo-Fenton process is gaining momentum in recent
6
7 years,⁹⁻¹³ and even experiments at industrial plant scale have been performed.¹⁴
8
9 However, TiO₂ has also been studied and it has been demonstrated to remove efficiently
10
11 pesticides under solar irradiation;¹⁵ complete detoxification of the solution has also been
12
13 reported in some cases.^{16,17}
14
15

16 The structure of TiO₂ has a remarkable influence on its photocatalytic properties and
17
18 several titania catalysts are commercially available. Hence, comparing the performance
19
20 of different commercial types of titanium dioxide in the detoxification of solutions
21
22 containing pesticides seems meaningful. For this purpose the photodegradation of a
23
24 mixture of four commercial pesticides, namely oxydemeton- methyl, methidathion,
25
26 carbaryl and dimethoate (structures are shown in Figure 1) has been studied in the
27
28 presence of different TiO₂ samples; this mixture of pesticides has been chosen since the
29
30 photodegradation of the individual components using titania under sunlight has already
31
32 been reported.¹⁶⁻¹⁸ Preliminary experiments employing several titania samples were
33
34 performed at laboratory scale under artificial UV-A irradiation, while selected reactions
35
36 were then scaled-up to pilot plant under natural sunlight. Furthermore, bioassays were
37
38 employed in order to follow the changes in the biocompatibility of the mixture. Finally,
39
40 results were compared with those obtained with solar photo-Fenton with the same
41
42 mixture of pollutants.
43
44
45
46
47
48

49 **2. Materials and methods**

50 2.1 Reagents

51
52 Four commercial pesticides, based on oxydemeton-methyl, methidathion, carbaryl
53
54 dimethoate were used for the photodegradation experiments: commercial name, purity
55
56
57
58
59
60

1
2
3 and main excipients are shown in Table 1. Pure ingredients were also employed as
4
5 standards.

6
7 The employed TiO₂ were Evonik P25, Hombikat, Millennium PC50, Millennium
8
9 PC100, Millennium PC105 and Kronos 7101; their main characteristics are summarized
10
11 in Table 2.

12 13 2.2. Reactions

14
15 Preliminary experiments were conducted at laboratory scale with the mixture of
16
17 pesticides (25 mg/L of each active ingredient) and 0.5 g/L of titanium dioxide.
18
19 Irradiation took place in an immersion well, laboratory scale photoreactor, purchased
20
21 from Ace Glass (Vineland, NJ, USA). It consists of an inner, double-walled,
22
23 borosilicate glass housing the lamp (390 mm length, 53 mm outer diameter) and an
24
25 external cylindrical reaction vessel (310 mm length, 73 mm internal diameter, 350 mL
26
27 capacity) joined together with an internally threaded connection with the aid of a nylon
28
29 bushing connector and an O-ring. UV-A irradiation was provided by a 400 W, high-
30
31 pressure mercury lamp (Osram, HQL, MBF-U), which was placed inside the inner
32
33 borosilicate glass and was cooled by a water jacket to maintain during photocatalytic
34
35 experiments a constant temperature of 32 ± 2 °C. The reaction vessel was covered with
36
37 aluminum foil. The photon flux emitted from the lamp was determined actinometrically
38
39 using the potassium ferrioxalate method and was found to be 1.12×10^{-5} Einstein/s.¹⁹

40
41 The solution was slurried with the appropriate amount of catalyst and magnetically
42
43 stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption
44
45 of organic compounds on the TiO₂ surface. After that period, the UV-A lamp was
46
47 turned on, while air was continuously sparged in the liquid and the reaction mixture was
48
49 continuously stirred.

50
51 Selected reactions were scaled-up using a pilot plant (Solardetox Acadus-2001,
52
53
54
55

Ecosystem) based on compound parabolic collector (CPC) technology, which has been described elsewhere.²⁰ 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 m² 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 TiO₂). 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/m²), V_i the irradiated volume (L), V_t the total volume (L) and I the average UV irradiance, considered as 30 W/m².

$$t_{30W} = \frac{UV_{ac} \cdot V_i}{I \cdot V_T} \quad (1)$$

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

1
2
3 phase. The eluent consisted of an isocratic mixture of 50% acetonitrile and 50% water,
4
5 with a flow rate of 1 mL/min. A diode array detector was employed monitoring
6
7 absorbance at 210 nm. Before injection, samples were diluted with methanol (1:1) to
8
9 dissolve any organics adsorbed onto TiO₂ and filtered through polypropylene (0.45 µm,
10
11 VWR). Identification and quantitation were based on comparison of retention times and
12
13 areas with standards.
14

15
16 A GCMS-QP2010S (Shimadzu) gas chromatograph was employed to identify the main
17
18 organic additives present in the commercial formula of the pesticides, and major
19
20 intermediates formed along the process. Temperature was increased from 60°C to 250°C
21
22 with a 5°C/min rate. A Meta X5 Teknokroma column was used. Samples were
23
24 previously concentrated by solid phase extraction: 50 mL of the aqueous solution (pH
25
26 ca. 7) were flowed through a LiChrolut EN 200 mg (Merck) cartridge; then organics
27
28 were recovered with 3 mL of methanol.
29
30

31
32 Dissolved organic carbon (DOC) was determined with a Shimadzu TOC-V CSH
33
34 apparatus. Chemical oxygen demand (COD) was determined spectrometrically
35
36 according to the standard dichromate method; digestion was performed at 148°C in a
37
38 Thermoreaktor TR300 (Merck) and the photometric determination was performed in a
39
40 Spectroquant NOVA 60 (Merck). Samples submitted to these assays were filtered but
41
42 not diluted with methanol.
43
44

45
46 Toxicity was evaluated according to the method of inhibition of bioluminescence of
47
48 *Vibrio fischeri* bacterium (ISO 11348-3 norm, using lyophilized bacteria). The standard
49
50 procedure was employed for reconstitution of the bacteria, using a salty solution
51
52 obtained from Macherey-Nagel. The luminescence was measured by means of a
53
54 Luminometer Lumifix-Bio-10, also purchased from Macherey-Nagel. Toxicity was
55
56 determined after 15 min of incubation. Distilled water and zinc sulphate were used in
57
58
59
60

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 TiO₂). This concentration of pesticides is in line with those employed in other experiments and with data reported on a pilot plant 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:

$$\ln \frac{C_o}{C} = kt \quad (2)$$

1
2
3 As seen in Figure 3, the four pesticides exhibited similar reactivities at the conditions
4 under consideration; this said, oxydemethon-methyl and methidathion, that contain
5 phosphothioester groups appear to be more readily degradable than the other two
6 pesticides as this moiety has been found to be susceptible to oxidative degradation.¹⁶
7
8 Conversely, the lowest k values were obtained for carbaryl, as the carbamate group
9 seems to be more resistant to photocatalytic oxidation. Regarding the different types of
10 titanium dioxide, their performance decreased in the order: P25 > Kronos > Millennium
11 family > Hombikat. According to Hurum and coworkers,²¹ mixed-phase titania
12 catalysts like Evonik P25 show greater effectiveness than others due to three factors: (i)
13 the smaller band gap of rutile extends the useful range of photoactivity into the visible
14 region; (ii) the stabilization of charge separation by electron transfer from rutile to
15 anatase slows down recombination; (iii) the small size of the rutile crystallites facilitates
16 this transfer, creating catalytic hot spots at the rutile/anatase interface. Conversely, the
17 inconsiderable effectiveness of Hombikat UV100 may be attributed to its large surface
18 area which is usually associated with large amounts of crystalline defects or weak
19 crystallization, both favouring the recombination of photogenerated electrons and
20 holes.²² A complementary explanation is that organics adsorbed on TiO₂ surface may
21 serve as an external charge recombination centre, whereas the degradation is initiated
22 off the surface. In such case, the net degradation can be less efficient when more
23 substrates are adsorbed on high-surface area titania samples.²³
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48

49 3.2. Pilot plant experiments

50 Having assessed the relative activity of different photocatalysts at laboratory scale under
51 UV-A irradiation, it was decided to investigate the solar detoxification of wastewaters
52 containing 25 mg/L of each active ingredient in a pilot plant employing the two most
53
54
55
56
57
58
59
60

1
2
3 promising titania samples, namely Evonik P25 and Kronos 7101 at 0.5 g/L. Figure 4
4 clearly shows that P25 was substantially more active than Kronos leading to nearly
5 complete degradation of all four pesticides in less than 300 min; on the other hand,
6 conversion did not exceed 80% for either pesticide after 300 min with Kronos. If the
7 data of Figure 4 are plotted in the form of equation (2), the apparent rate constants
8 ranged from 0.0085 to 0.0141 min⁻¹ for P25 and 0.0042 to 0.0051 min⁻¹ for Kronos.
9

10
11
12
13
14
15
16 It is interesting to compare these results with those of the photo-Fenton degradation of
17 the same mixture of commercial pesticides in a pilot plant, reported in a previous
18 paper.¹³ Under the studied conditions, photo-Fenton appears to be more efficient as the
19 rate constants obtained with TiO₂ are 1-2 orders of magnitude below those reported for
20 photo-Fenton (between 0.29 and 0.52 min⁻¹). The normalized irradiation time
21 (expressed as t_{30W}) required for the elimination of the active ingredients ranges from
22 225 to 325 min with P25, whereas in the case of Kronos at t_{30W} = 350 min, degradation
23 varies between 75 and 90%. In sharp contrast, solar photo-Fenton is able to achieve
24 complete elimination of the active ingredients in t_{30W} = 30-40 min.
25
26
27
28
29
30
31
32
33
34
35

36 Unlike the relative fast degradation of the individual components, matrix mineralization
37 was slow, as can be seen in Figure 5. For example, the extent of COD and TOC removal
38 was 40% about and 25%, respectively at the end of the experiment with Evonik P25,
39 which implies that certain organic species, other than the active ingredients, initially
40 present in the commercial formulation and/or photocatalytic degradation by-products
41 are more resistant to oxidation than the pesticides themselves (see Table 1 for the
42 excipients found in the employed commercial formulae). It is also notable that COD and
43 TOC mainly decreased during the early stages of the reaction and remained fairly
44 constant thereafter; this implies that COD and TOC reduction may partly be due to
45 adsorption onto the catalyst surface and/or evaporation of some volatile components of
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 the mixture of the commercial products rather than to oxidative degradation. The
4
5 presence of organics might also have some influence on the degradation rate as shown
6
7 in a previous paper, where results obtained in the individual photodegradation in the
8
9 presence of P25 of pure and commercial products were compared; in all cases, reduction
10
11 up to 50% on the k values were observed.²⁴

12
13
14 Figure 6 shows the temporal evolution of inhibition to marine bacteria *V. fischeri* for the
15
16 two catalysts under investigation. Toxicity decreased from an initial value of 50% for
17
18 the untreated mixture to 15% at the end of the experiment with P25; this is consistent
19
20 with the complete removal of the active ingredients as confirmed by HPLC analysis.
21
22 Interestingly, toxicity appeared to increase during the early (i.e. up to about 100 min)
23
24 stages of the reaction most probably due to the formation of some toxic intermediates;
25
26 this is a well-documented behavior that has been observed in photocatalysis, as well as
27
28 other advanced oxidation studies,²⁵ where the toxicity of the original effluent was found
29
30 to increase steeply and reach a maximum during the early stages of the treatment
31
32 presumably due to the formation of toxic intermediates. At longer treatment times,
33
34 toxicity decreased to acceptable levels as toxic intermediates were degraded further.²⁶
35
36 On the other hand, there was no toxicity decrease when Kronos 7101 was employed;
37
38 this is compatible with the presence of residuals pesticides and the formation of toxic
39
40 by-products associated with the poorer performance of this material.
41
42
43
44

45 Although the mixture studied in this work is too complex to determine reliable
46
47 mechanistic data, the individual behaviour of each compound was studied in previous
48
49 publications.^{16-18, 27} In all cases, pesticide removal was observed to involve a very
50
51 significant detoxification of the solution, using respirometric measurements and the
52
53 luminescence of *V. fischeri* assay.
54
55
56
57
58
59
60

1
2
3 In the case of the photo-Fenton treatment of the same mixture of pesticides, the gross
4
5 composition of the phototreated solution was analyzed by GC-MS.¹³ Despite the high
6
7 number of compounds that were present, the dominant ones were determined. At the
8
9 early stages of the process, these were pesticides and solvents, including some
10
11 chlorinated compounds; then fragments corresponding to the pesticides were released
12
13 together with the remaining amounts of the parent pollutants; at the end of the process
14
15 low molecular weight ketones and aldehydes became dominant; carboxylic acids might
16
17 have also been formed but their polarity is too high to be detected by this analysis. GC-
18
19 MS analysis was also performed for samples taken at t_{30W} ca. 80 min and 250 min, with
20
21 Evonik P25 titania and a similar trend was observed; for the sample at $t_{30W} = 80$ min,
22
23 pesticides and some photodegradation by-products (naphtol, organophosphorated
24
25 compounds) still remained in the solution, together with solvents such as chlorophenol,
26
27 xylene or cyclohexanone. For the sample taken at $t_{30W} = 250$ min only residual amounts
28
29 of some of these compounds could be determined (e.g. cyclohexanone, acetophenone)
30
31 and hence most of the remaining organics might consist of low molecular weight highly
32
33 oxidized compounds (e.g. carboxylic acids) that could not be detected by GC-MS. This
34
35 could also explain changes in the changes in toxicity, as at the end of the process most
36
37 of the potentially toxic species (e.g pesticides and chlorinated compounds) were
38
39 removed.
40
41
42
43
44
45
46

47 Conclusions

48
49 The conclusions drawn from this work regarding the photocatalytic treatment of
50
51 pesticides can be summed up as follows:
52
53
54
55
56
57
58
59
60

1
2
3 (1) Various commercially available titania samples were screened and a 75:25
4 anatase:rutile mixture (Evonik P25) was more active than others containing only
5 anatase.
6
7
8

9
10 (2) Complete removal of commercial pesticide formulations was feasible and this
11 coincided with wastewater detoxification. Nonetheless, mineralization was not possible
12 at the conditions employed in this work.
13
14
15

16 (3) P25 titania was able to detoxify the solution at pilot plant scale under solar
17 irradiation. Pesticides removal was also reached by the less efficient Kronos 7101,
18 although in this case an important remnant toxicity was detected at the end of the
19 process.
20
21
22
23
24
25
26

27 **Acknowledgements**

28
29 R. Vicente, A. Arques and A.M. Amat want to thank the financial support of Spanish
30 Ministerio de Educación y Ciencia (CTQ2012-38754-C03-02).
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

References

1. Malato S, Fernández-Ibáñez P, Maldonado MI, Blanco J and Gernjiak W, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. *Catal. Today* **147**: 1-59 (2009)
2. Bahnemann D, Photocatalytic water treatment: solar energy applications. *Sol. Energy* **77**:445-459 (2004)
3. Pignatello JJ, Oliveros E and MacKay A, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit. Rev. Environ. Sci. Technol.* **36**:1-84 (2006)
4. Marín ML, Arques A, Santos-Juanes L, Amat AM and Miranda MA, Organic photocatalysis for the oxidation of pollutants and model compounds, *Chem. Rev.* **112**: 1710-1750 (2012)
5. Hoffmann MR, Martin ST, Choi W and Bahnemann DF, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* **95**:69-96 (1995)
6. Zhao J, Chen C and Ma W, Photocatalytic degradation of organic pollutants under visible light irradiation, *Topics Catal.* **35**:269-278 (2005)
7. Gaya UI and Abdullah AH, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *J. Photochem. Photobiol. C: Photochem. Rev.* **9**:1-12 (2008)
8. Konstantinou IK and Albanis TA, Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways. *Appl. Catal B: Environ.* **42**:319-335 (2003)

- 1
2
3 9. Vilar VJP, Moreira FC, Ferreira ACC, Sousa MA, Gonçalves C, Alpendurada MF
4 and Boaventura RAR, Biodegradability enhancement of a pesticide-containing bio-
5 treated wastewater using a solar photo-Fenton treatment step followed by a biological
6 oxidation process, *Water Res* **46**: 4599-4613 (2012)
7
8
9
10
11 10. Moreira FC, Vilar VJP, Ferreira ACC, dos Santos FRA, Dezotti M, Sousa MA,
12 Gonçalves C, Boaventura RAR and Alpendurada M., Treatment of a pesticide-
13 containing wastewater using combined biological and solar-driven AOPs at pilot scale
14
15
16
17
18
19
20
21 11. Ballesteros Martín MM, Sánchez Pérez JA, Acién Fernández FG, Casas López JL,
22 García-Ripoll A, Arques A, Oller I and Malato Rodríguez S, Combined photo-Fenton
23 and biological oxidation for pesticide degradation: effect of photo-treated intermediates
24 on biodegradation kinetics, *Chemosphere*, **70**: 1476-1483 (2008)
25
26
27
28
29
30
31 12. Ballesteros Martín MM, Sánchez Pérez JA, Casas López JL, Oller I and Malato
32 Rodríguez S, Degradation of a four pesticide mixture by combined photo-Fenton and
33 biological. *Water Res*, **43**:653-660 (2009)
34
35
36
37 13. Amat AM, Arques A, García-Ripoll A, Santos-Juanes L, Vicente R, Oller I,
38 Maldonado M.I and Malato S. A reliable monitoring of the biocompatibility of an
39 effluent along an oxidative pre-treatment by sequential bioassays and chemical
40 analyses. *Water Res*. **43**: 784-792 (2009)
41
42
43
44
45 14. Zapata A, Oller I, Sirtori C, Rodríguez A, Sánchez-Pérez JA, López A., Mezcuca M
46 and Malato S, Decontamination of industrial wastewater containing pesticides by
47 combining large scale homogeneous solar photocatalysis and biological treatment.
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 15. Oller I, Gernjak W, Maldonado MI, Pérez-Ibáñez P, Blanco J, Sánchez-Pérez JA
4
5 and Malato S, Degradation of the insecticide dimethoate by solar photocatalysis at pilot
6
7 plant scale, *Environ. Chem. Lett.* **3**:118-121 (2005).

8
9
10 16. García-Ripoll A, Amat AM, Arques A, Vicente R, López MF, Oller I, Maldonado
11
12 MI and Gernjak W, Increased biodegradability of Ultracid™ in aqueous solutions with
13
14 solar TiO₂ photocatalysis, *Chemosphere* **68**:293-300 (2007)

15
16 17. Arques A, Amat AM, García-Ripoll A and Vicente R, Detoxification and/or increase
17
18 of the biodegradability of aqueous solutions of dimethoate by means of solar
19
20 photocatalysis, *J. Hazard. Mater.* **146**:447-452 (2007)

21
22
23 18. García A, Amat AM, Arques A, Sanchís R, Gernjak W, Maldonado MI, Oller I and
24
25 Malato S, Detoxification of aqueous solutions of the pesticide “SevnoI” by solar
26
27 photocatalysis, *Environ. Chem. Lett.* **4**:169-172 (2006)

28
29
30 19. Chatzisyneon E, Stypas E, Bousios S, Xekoukoulotakis N and Mantzavinos D,
31
32 Photocatalytic treatment of black table olive processing wastewater. *J. Hazard. Mater.*
33
34 **154**:1090-1097 (2008)

35
36
37 20. Bernabeu A, Vicente R, Peribañez MA, Arques A and Amat AM, Exploring the
38
39 applicability of solar driven photocatalytic processes to control infestation by zebra
40
41 mussel, *Chem Eng. J.* **171**:400-404 (2011)

42
43
44 21. Hurum D, Agrios A, Gray K, Rajh T and Thurnauer C, Explaining the enhanced
45
46 photocatalytic activity of Degussa P25 mixed-phase TiO₂ using EPR. *J. Phys. Chem. B*
47
48 **107**: 4545-4549 (2003)

49
50
51 22. Wang G, Xu L, Zhang J, Yin T and Han D, Enhanced photocatalytic activity of
52
53 TiO₂ powders (P25) via calcination treatment. *Int J Photoenergy*, **Article ID 265760**, 9
54
55 pages (2012)

1
2
3 23. Ryu J and Choi W, Substrate-specific photocatalytic activities of TiO₂ and
4
5 multiactivity test for water treatment application. *Environ. Sci. Technol.* **42**: 294–300
6
7 (2008)
8
9

10 24. García-Ripoll A, Arques A, Vicente R, Doménech A and Amat AM. Treatment of
11
12 aqueous solutions containing four commercial pesticides by means of TiO₂ solar
13
14 photocatalysis. *J. Solar Energy Eng.* **130**: 410111-410115 (2008).
15
16

17
18 25. Mantzavinos D. and Psillakis E, Enhancement of biodegradability of industrial
19
20 wastewaters by chemical oxidation pre-treatment. *J. Chem. Technol. Biotechnol.* **79**:
21
22 431-454 (2004)
23
24

25 26. Herrmann JM, Guillard C, Arguello M, Agüera A, Tejedor A, Piedra L and
26
27 Fernández-Alba A, Photocatalytic degradation of pesticide pirimiphos-methyl:
28
29 Determination of the reaction pathway and identification of intermediate products by
30
31 various analytical methods, *Catal. Today* **54**:353–367 (1999)
32
33

34
35 27. Arques A, García-Ripoll A, Sanchís R, Santos-Juanes L, Amat AM, López MF and
36
37 Miranda MA, Detoxification of aqueous solutions containing the commercial pesticide
38
39 Metasystox by TiO₂-mediated solar photocatalysis, *J. Sol. Energy Eng.* **129**:74-79
40
41 (2007)
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

List of Tables and Figures

Table 1: Main characteristics of the commercial pesticides used in this work.

Table 2: Main characteristics of the various TiO₂ catalysts used in this work. A stands for anatase and R for rutile.

Figure 1: Chemical structures of the pesticides employed in this work: oxydemeton-methyl (A); methidathion (B); carbaryl (C); dimethoate (D).

Figure 2: Change of concentration of (a) dimethoate; (b) carbaryl; (c) methidathion; (d) oxydemeton-methyl as a function of UV-A irradiation time and various titanium samples. Millennium PC50 (◇); Millennium PC100 (□); Millennium PC105 (▲); Evonik P25 (×); Kronos 7101 (*); Hombikat UV100 (●).

Figure 3: Pseudo-first order rate constants for the photocatalytic degradation of dimethoate (black bars), carbaryl (dark grey bars), methidathion (light grey bars) and oxydemeton-methyl (white bars).

Figure 4: Change of concentration of dimethoate (◆, ◇); (b) carbaryl (■, □); (c) methidathion (▲, △); (d) oxydemeton-methyl (●, ○) as a function of solar irradiation time with Evonik P25 (closed symbols) or Kronos 7101 (open symbols).

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

Figure 6: Evolution of toxicity to *V. fischeri* as a function of solar irradiation time with Evonik P25 (◆) or Kronos 7101 (■).

Table 1: Main characteristics of the commercial pesticides used in this work.

Pesticide	Commercial name	Purity (%)	Excipients	Supplier
Methyl-oxymeton	Metasystox R	25 (w/v)	Xylene Chlorobenzene	Bayer
Methodathion	Ultracid	40 (w/v)	Acetophenone	Syngenta
Carbaryl	Sevnol	85 (w/w)	-	MAFA
Dimethoate	Laition	40 (w/v)	Xylene Cyclohexanone	Lainco

For Peer Review

Table 2: Main characteristics of the various TiO₂ catalysts used in this work. A stands for anatase and R for rutile.

Catalyst	Crystal form	BET area (m ² /g)	Particle size (nm)	Supplier
Evonik P25	75%A:25%R	50	21	Degussa AG
Hombikat UV100	A > 99%	<250	5	Sachtleben Chemie GmbH
Millennium PC50	A > 97%	45-55	20-30	Millennium Inorganic Chemicals
Millennium PC100	A > 95%	80-100	15-25	Millennium Inorganic Chemicals
Millennium PC105	A > 95%	75-95	15-25	Millennium Inorganic Chemicals
Kronos 7101	A>92.5%	>125	15	ECKART

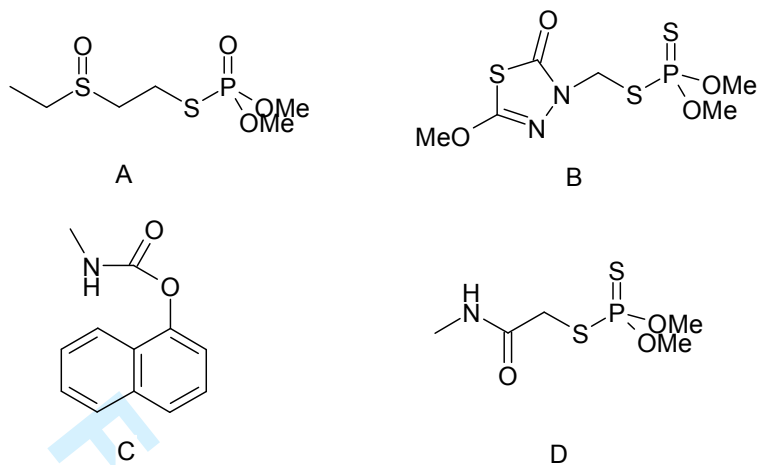
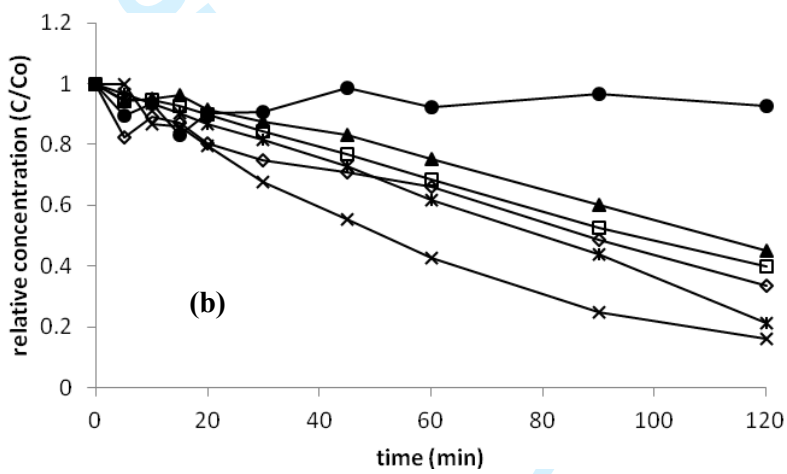
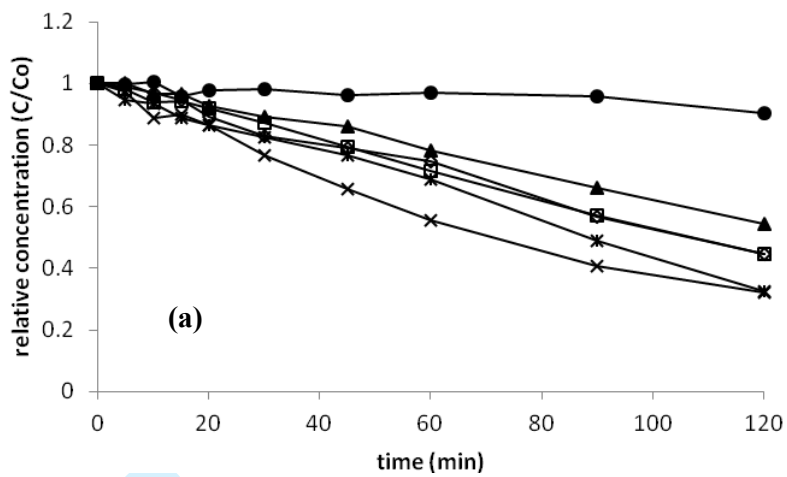


Figure 1: Chemical structures of the pesticides employed in this work: oxydemeton-methyl (A); methidathion (B); carbaryl (C); dimethoate (D).



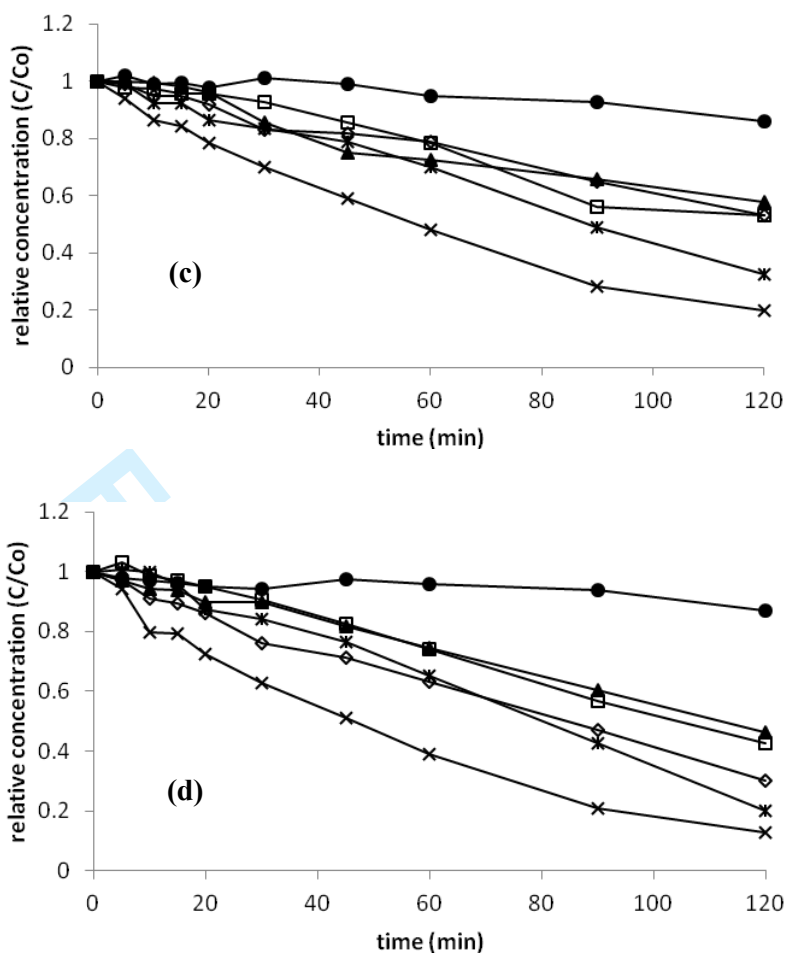


Figure 2: Change of concentration of (a) dimethoate; (b) carbaryl; (c) methidathion; (d) oxydemethon-methyl as a function of UV-A irradiation time and various titanium samples. Millennium PC50 (◇); Millennium PC100 (□); Millennium PC105 (▲); Evonik P25 (×); Kronos 7101 (*); Hombikat UV100 (●).

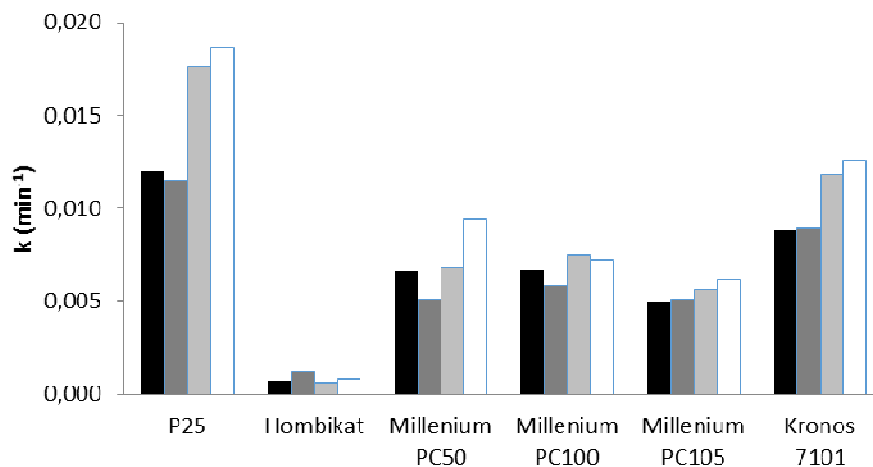


Figure 3: Pseudo-first order rate constants for the photocatalytic degradation of dimethoate (black bars), carbaryl (dark grey bars), methidathion (light grey bars) and oxydemeton-methyl (white bars).

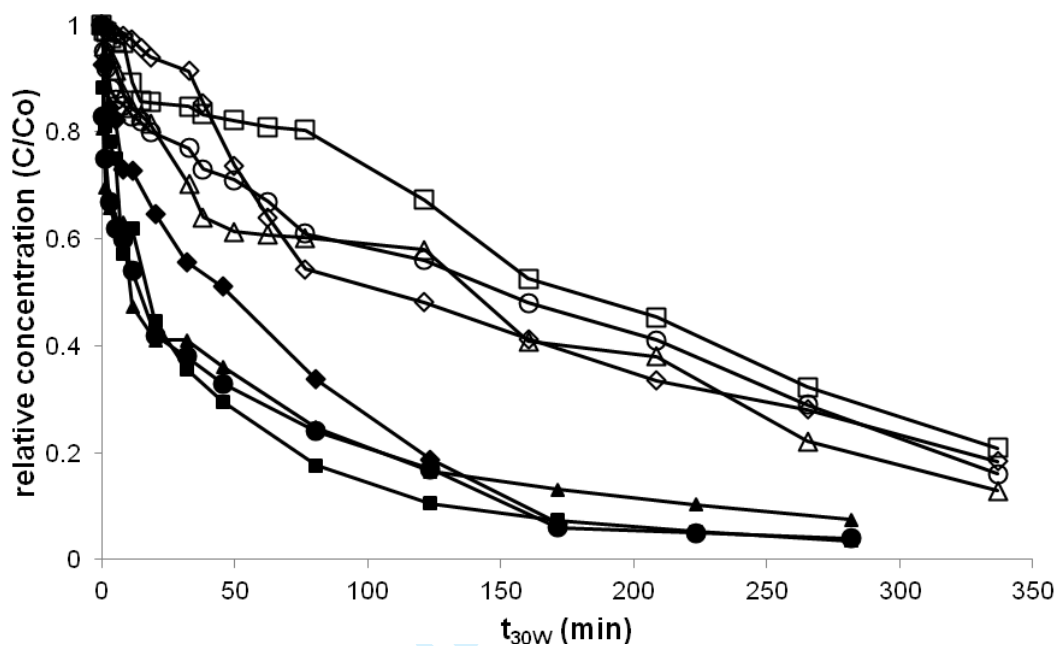


Figure 4: Change of concentration of dimethoate (♦, ◇); (b) carbaryl (■, □); (c) methidathion (▲, △); (d) oxydemeton-methyl (●, ○) as a function of solar irradiation time with Evonik P25 (closed symbols) or Kronos 7101 (open symbols).

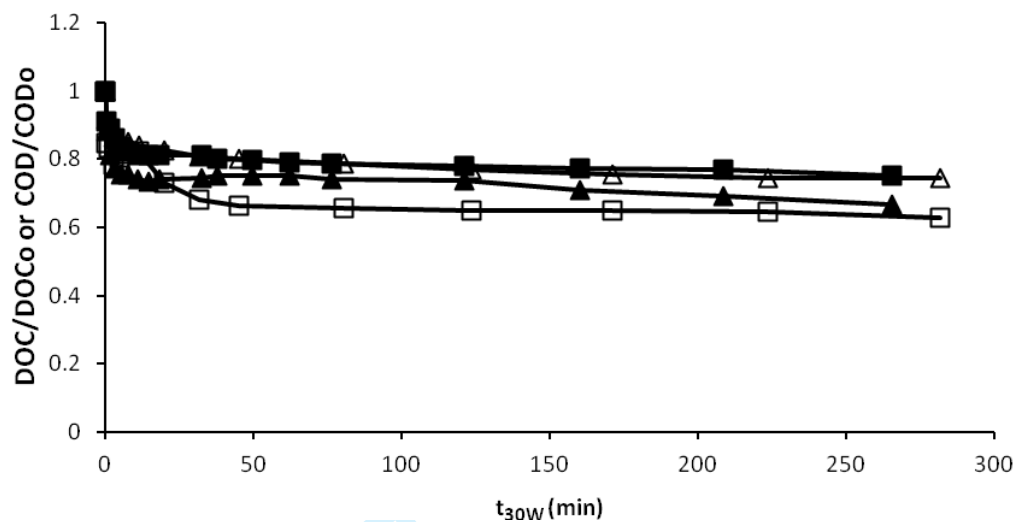


Figure 5: Evolution of COD (■,□) and DOC (◆,◇) as a function of solar irradiation time with Evonik P25 (open symbols) or Kronos 7101 (closed symbols).

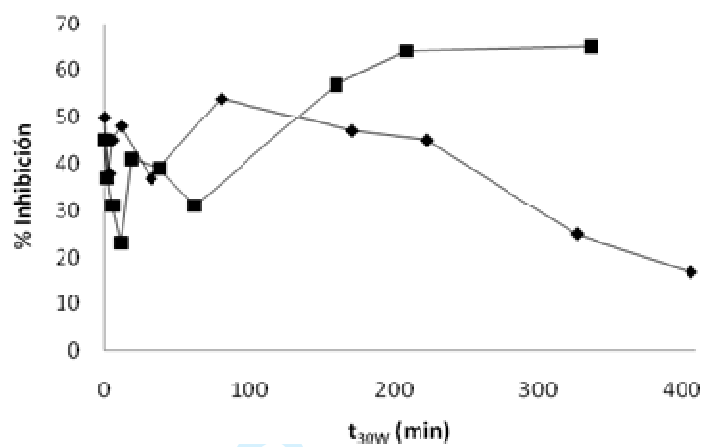


Figure 6: Evolution of toxicity to *V. fischeri* as a function of solar irradiation time with Evonik P25 (♦) or Kronos 7101 (■).