

# Optimization of pre-industrial solar photocatalytic mineralization of commercial pesticides

## Application to pesticide container recycling

Sixto Malato\*, Julián Blanco, Christoph Richter, Manuel I. Maldonado

Plataforma Solar de Almería (PSA), Crta. Senés km. 4, Tabernas, Almería 04200, Spain

Received 27 June 1999; received in revised form 24 September 1999; accepted 26 September 1999

### Abstract

One of the most important sources of polluted water with high pesticide content is the rinsing of empty pesticide containers. In this paper, a pre-industrial  $\text{TiO}_2$ -solar photocatalytic treatment is used to prevent such pollution of continental waters and 10 commercial pesticides are used at various initial concentrations to demonstrate the treatment. Total organic carbon (TOC) analysis is employed to confirm the total mineralization of the contaminants. The results are compared with phenol degradation under the same experimental conditions. Relative photonic efficiency related to TOC ( $\zeta_{r, \text{TOC}}$ ) is calculated to facilitate comparison with other experimental devices. Furthermore, a kinetic model is proposed for fitting experimental data by an approximate kinetic solution which has the analytical form of a Langmuir–Hinshelwood equation but without its original significance. Finally, an example of calculation of solar plant size from experimental and solar radiation data is shown. ©2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Solar photocatalysis; Pesticide degradation; Pesticides mineralization; Titanium dioxide

### 1. Introduction

Various ongoing water-monitoring surveys in the EC and the USA have shown the presence of herbicides [1] and some of their metabolites [2] in surface and ground water at concentrations ranging from  $\text{sub-}\mu\text{g l}^{-1}$  to  $\mu\text{g l}^{-1}$  levels [3]. Their persistence in natural waters [4] has led to a search for a highly effective method to mineralize them into environmentally compatible compounds. Unlike the low level contamination involved in drinking water, waste water from

agricultural or industrial activities may be highly contaminated. The major sources of pollution by pesticides are waste water from agricultural industries, pesticides formulating and manufacturing plants. Wastewater from those sources may contain pesticides at levels as high as several hundred  $\text{mg l}^{-1}$ . The main characteristics of this wastewater are its extreme toxicity, low volume and well-defined location. Suitable treatment is therefore required to prevent it, which is easier than cleaning up the environment afterwards. Such point sources of pollution may be ideally treated in small-scale treatment units.

The alternative of using air stripping and adsorption on granulated activated carbon, merely transfer-

\* Corresponding author. Tel.: 34-50-387940; fax: 34-50-365015.  
E-mail address: Sixto.Malato@psa.es (S. Malato).

ring toxic materials from one medium to another, is not a long-term solution to the problem of loading hazardous waste on the environment. Incineration is capable of converting toxic compounds to carbon dioxide, water and inorganic acids, but negative public perception has slowed and very often prevented its implementation. Concerns over emissions of undestroyed components and organic products of incomplete combustion have caused incineration to be a source of continuing controversy. Biological treatment techniques are well established and relatively cheap. However, the biological methods are susceptible to toxic compounds that inactivate the waste-degrading micro-organisms. This paper focuses on the application of solar advanced oxidation processes (SAOPs) to the treatment of commercial pesticides. Although, specifically, this work concentrates on the recycling of used pesticide containers, the results obtained may be applied to any of the previously mentioned major causes of water pollution by pesticides.

In the area of El Ejido, a town in the province of Almería in southern Spain, intensive agriculture in 400 km<sup>2</sup> of greenhouses consumes approximately 1.5 million plastic bottles of pesticide per year. So far, these empty plastic bottles have simply been discarded. Although, the amount of product remaining in each bottle after use is minimal, the numbers are so important that they become a danger to the environment (poisoning of fauna and flora, not only on land, but at sea as well, by bottles carried to sea by flooding, contamination of water supply by ground filtration, etc.). A solution to this problem has arisen with the possibility of recycling the plastic bottles for other uses. After selective collection and transport to the recycling plant, the plastic must be washed before processing for its reuse. The water used for this becomes contaminated with a mixture of different pesticides that must then be treated to eliminate them. It is in the detoxification of this water that solar photocatalysis intervenes, as a very promising process made even more by the availability of strong sunlight throughout the year as a cheap energy source in this region. By employing sunlight, the common drawback of the relatively high cost of UV-lamps and electricity can be overcome. Thus, the availability of sunlight and the lack of other alternatives justify the application of a new technology that has not yet been evaluated on an industrial scale.

## 2. Experimental

### 2.1. Photoreactor

The current configuration of the PSA CPC field has six modules (collector surface 8.9 m<sup>2</sup>, photoreactor volume 108 l, total plant volume 247 l) mounted on a fixed platform tilted 37° (local latitude). This plant has been operating since 1994 as previously described in detail elsewhere [5–7]. The 6 modules are connected in series and the water flows directly from one to the other and finally to a tank. A centrifugal pump then returns the water to the collectors. At the beginning of the experiments, with collectors covered, all the chemicals are added to the tank and mixed until constant concentration is achieved throughout the system. Then the cover is removed and samples are collected at predetermined times (*t*).

### 2.2. Evaluation of solar UV radiation

Solar ultraviolet (UV) radiation is an essential parameter for the correct evaluation of data obtained during photocatalytic experiments in a solar water decontamination pilot plant. The following equipment was used. A global UV-radiation measurement sensor (KIPP&ZONEN, model CUV3), with a typical sensitivity of 264 μV W<sup>-1</sup> m<sup>2</sup> mounted on a platform at a 37° angle (the same angle as the CPCs), sends a signal to a computer in which the data (UV<sub>G</sub>) are stored. This radiometer provides data in terms of incident W<sub>UV</sub> m<sup>-2</sup>, which gives an idea of the energy reaching any surface in the same position with regard to the sun.

Use of the experimental time as the calculation unit could give rise to misinterpretation of results, because the reactor consists of illuminated and non-illuminated elements. Large experimental reactors such as this one require much instrumentation and the reactor must also be as versatile as possible, substantially increasing the non-illuminated volume. This is because when time is the independent variable, the differences in the incident radiation in the reactor during an experiment are not taken into account. Goslich et al. [8] have proposed a very useful mathematical approach for the treatment of such data obtained in real solar experiments using a relationship between experimental time (*t*), plant volume (*V<sub>t</sub>*), collector surface (*A<sub>r</sub>*) and the radiant power

density ( $UV_G = W m^{-2}$ ) measured by the radiometer. In this case, Eq. (1) has the same meaning as that proposed by Goslich et al. with only slight modifications.

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{V_t}$$

$$\Delta t_n = t_n - t_{n-1} \quad (1)$$

where  $t_n$  is the experimental time of each sample,  $\overline{UV}_{G,n}$  the average  $UV_G$  during  $\Delta t_n$  and  $Q$  the accumulated energy (per unit of volume,  $kJ l^{-1}$ ) incident on the reactor for each sample taken during the experiment. Although, the accumulated energy is expressed in terms of  $kJ l^{-1}$ , it corresponds to energy reaching the collector surface and therefore, the collector efficiency (ratio  $A_r/V_t$ , collector reflectivity and photoreactor transmissivity) is included in it. Consequently, when  $Q_{UV}$  is used, the reaction rate is expressed in terms of  $mg kJ^{-1}$  of UV incident on the collector surface. Sometimes it is necessary to explain the results in terms of illumination time instead of  $Q_{UV}$ . For this purpose, it may be assumed that the average solar UV on a perfectly sunny day for 2 h around noon is about  $30 W_{UV} m^2$ . Under these conditions and in the reactor used in this work,  $1 kJ l^{-1}$  is equivalent to 6.5 min illumination time.

As remarked by Wolfrum and Turchi [9], this procedure for determining kinetics in a partially illuminated photoreactor is accurate only if the concentration of reactants is constant along the entire reactor (i.e., if the system is at steady state). In the present case, steady state can be assumed because conversion of reactant each time through the reactor is slight, and the concentration throughout the system is almost constant. Flow rate is very high ( $6000 l h^{-1}$ ) compared with the total volume of the photoreactor (108 l) i.e., one loop per minute, and therefore, very little conversion each time round.

### 2.3. Materials

The simulated rinsates were prepared by combining only 10 different formulations (see Fig. 1): Rhône-Poulenc Rufast<sup>®</sup> (Acrinathrin,  $C_{26}H_{21}F_6O_5$ , pyrethroid, 15% w/v), Merck Vertimec<sup>®</sup> (Avermectine B<sub>1</sub>  $C_{48}H_{72}O_{14}$ , no family, 1.8% w/v), AgrEvo Thiodan<sup>®</sup> (Endosulphan- $\alpha$ - $\beta$ ,  $C_9H_6Cl_6O_3S$ , organochlorine, 35% w/v), AgrEvo Dicarzol<sup>®</sup>

(Formetanate  $C_{11}H_{16}ClN_3O_9$ , carbamate, 50% w/w), Bayer Confidor<sup>®</sup> (Imidacloprid,  $C_9H_{10}ClN_5O_2$ , no family, 20% w/v), Ciba-Geigy Match<sup>®</sup> (Lufenuron,  $C_{17}H_8Cl_2F_8N_2O_3$ , benzoylurea, 5% w/v), Bayer Tamaron SO<sup>®</sup> (Methamidophos,  $C_2H_8NO_2PS$ , organophosphorus, 50% w/v), Dupont Vydate<sup>®</sup> (Oxamyl,  $C_7H_{13}N_3O_3S$ , oxime carbamate, 24% w/v), AgrEvo Scala<sup>®</sup> (Pyrimethanil,  $C_{12}H_{13}N_3$ , anilinopyrimidine, 40% w/v) and AgrEvo Previcur<sup>®</sup> (Propamocarb,  $C_9H_{20}N_2O_2$ , carbamate, 72.2% w/v). They were used without purification, i.e. all impurities and additives contributed to the total organic carbon (TOC) content. For each pesticide the TOC content was determined by pre-experiments. Mineralization of the simulated rinsates was followed by total organic carbon analysis using direct injection of the slurries into a Heraeus-Foss Electric TOC-2001 (UV-Peroxydisulfate method).

The P-25 titanium dioxide catalyst (Degussa) was selected as the most widely used in photocatalytic decontamination. The  $TiO_2$ /water mixtures were prepared by adding the powder directly, rapidly obtaining a homogeneous milky suspension ( $200 mg l^{-1}$ ). The water used in the pilot plant experiments has an equivalent laboratory quality (Type III and IV ASTM), with a TOC content of a little over ( $<0.5 mg l^{-1}$ ).

### 3. Results and discussion

Since hydroxyl radicals react non-selectively, numerous intermediates are formed en-route to complete mineralization at different concentrations. Furthermore, formulation adjutants may affect the degradation process and, unfortunately, very little information on the effects of adjutants in photocatalysis degradation is available [10–15]. Due to this, all tests have been carried out using commercial products, because the treatment plant must destroy not only active matter, but any other organic compound contained in the formulation as well. More than 300 different formulations are currently used in the greenhouses of Almería and it is impossible to carry out experiments with all of them. The 10 commercial products selected were chosen because either they are extensively used in this area, they belong to the most usual pesticide families and/or they have very different chemical structures.

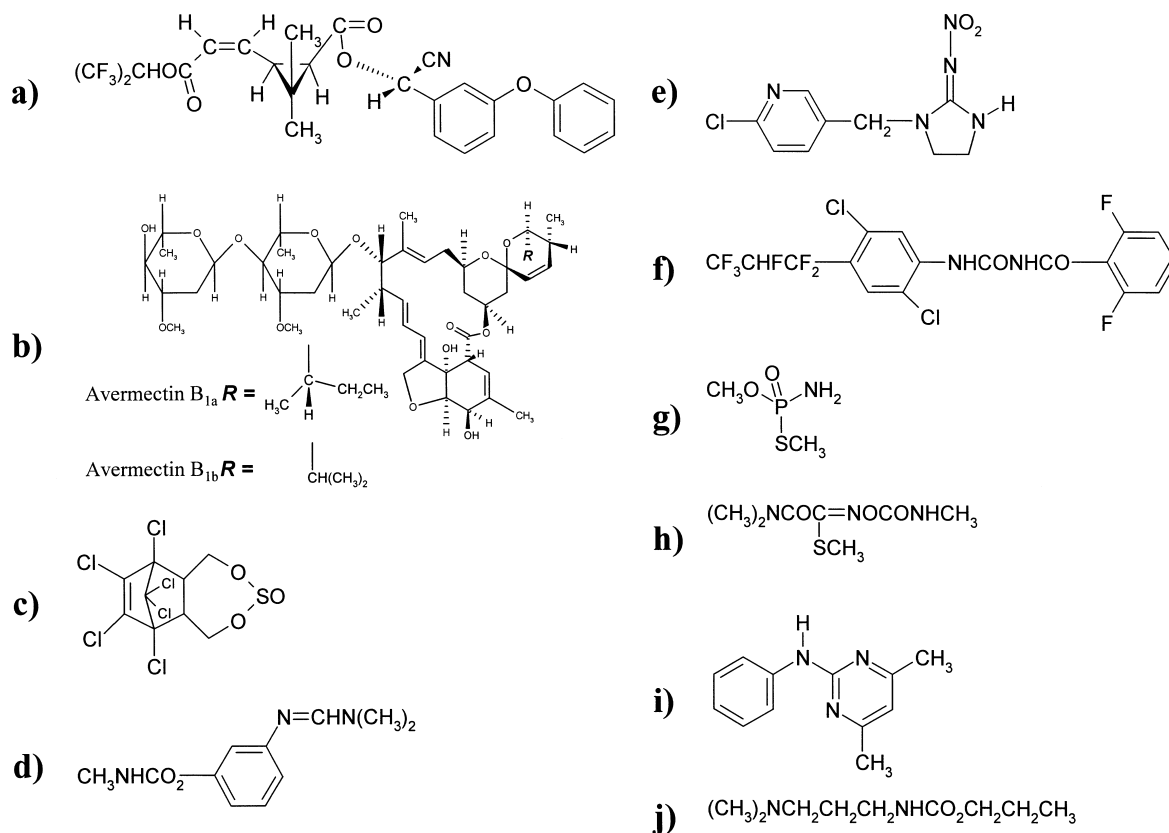


Fig. 1. Structures of the active ingredients in the 10 pesticides selected: (a) Acrinathrin, (b) Avermectine B<sub>1</sub>, (c) Endosulphan, (d) Formetanate, (e) Imidacloprid, (f) Lufenuron, (g) Methamidophos, (h) Oxamyl, (i) Pyrimethanil, (j) Propamocarb.

In all the experiments, the same TOC (e.g. 10 mg l<sup>-1</sup>) of each pesticide was added to achieve the initial TOC concentration (e.g. 100 mg l<sup>-1</sup>). Unfortunately, this could not be done with precision, as some of the pesticide usually adheres to the reactor walls due to hydrophobic ingredients. As a consequence, initial TOC measured was usually too low at the beginning of treatment, but reached a maximum as the intermediates grew and the emulsion became clear. This was not the cause of any appreciable error because the period of solubility is approximately the same as the typical photocatalysis induction period [16] before abatement of TOC due to partial oxidation of the organics. In Fig. 2, it is possible to see that mineralization, once begun, maintains the same slope until at least 60–70% of the initial TOC has been degraded. This means that all the TOC is in solution when

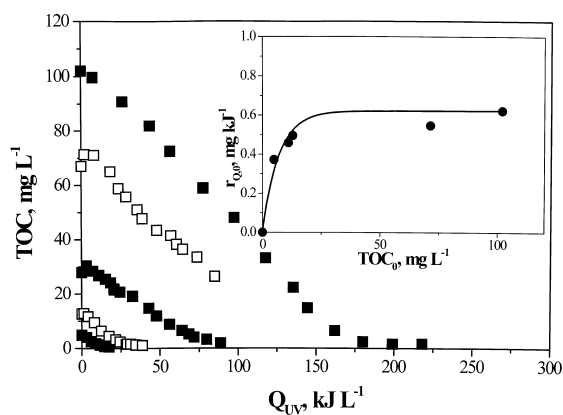


Fig. 2. Pesticides decomposition at different initial concentrations. 'Maximum rate' as function of maximum TOC is shown in the inserted graphic.

mineralization has begun. Therefore, in this work, the maximum TOC ( $\text{TOC}_{\text{max}}$ ) in each experiment was used for calculations instead of the initial amount.

It is well-known that in photocatalysis the degradation rate observed for an organic substrate follows saturation behavior. After a certain concentration is achieved, the rate increments very little and in some cases a decrease is observed. As the water used for plastic washing is intended to be decontaminated by photocatalysis, the optimum pesticide concentration in this water before the photocatalytic treatment must permit the maximum reaction rate. Moreover, the more pesticides, the more foam is produced by formulation surfactants, and this would produce operating problems in the plastic-washing process. Just as the more pesticides, the more intermediates and by-products are formed, increasing the difficulty of the photocatalytic process. So, the final concentration of pesticides in the wastewater from the plastic recycling plant must be optimized before applying SAOP.

The results shown in Fig. 2 are examples of the experiments carried out, each of which was repeated at least once. As the reaction is not expected to 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 the TOC is a sum parameter often including several hundred products that undergo manifold reactions. One parameter has been chosen in order to obtain a practical point of comparison for various experiments: the maximum gradient of the degradation curve, which is the gradient of the tangent at the inflection point ( $r_{Q,0}$ ). It has the unit of a zero-order rate constant ( $\text{mg kJ}^{-1}$  instead of  $\text{mg min}^{-1}$ ) and therefore appears to be easy to handle. Furthermore, this gradient can be roughly considered as the initial rate of the mineralization reaction, because it is preceded by a period of nearly constant TOC level. This parameter  $r_{Q,0}$  is referred to as ‘maximum rate’. In the graphic insert in Fig. 2, it may be observed that the initial rate is steady from 20–30 mg of TOC per litre. At this concentration, saturation occurs and the reaction rate becomes constant. A similar procedure for analyzing the TOC degradation rate with very complicated mixtures of organics has been used before by Pérez et al [17] with paper pulp effluents. Similar tests at higher catalyst concentrations have not been performed because

Table 1  
Relative photonic efficiencies for the mixture of pesticides at different initial concentrations with phenol ( $C_0 = 20 \text{ mg l}^{-1}$ ;  $\text{TOC} = 15.3 \text{ mg l}^{-1}$ ) as the standard reference

$\text{TOC}_{\text{max}}$ ( $\text{mg l}^{-1}$ )	$r_{Q,0}$ ( $\text{mg kJ}^{-1}$ )	$\zeta_{r,\text{TOC}}$
102.0	0.623	0.721
71.4	0.548	0.634
12.8	0.496	0.574
11.0	0.459	0.531
4.9	0.373	0.432

solution opacity increases and no improvement in the mineralization will be obtained [18].

The concept of relative photonic efficiencies  $\zeta_r$ , introduced by Serpone et al. [19], has been used because it seems to be a very useful tool that renders comparison of process efficiencies with different experimental devices but, instead of  $\zeta_r$ ,  $\zeta_{r,\text{TOC}}$  is used (Eq. (2)). This is also a relative photonic efficiency, but relating mineralization rates instead of initial substrate degradation rates. In the present case, the parameter used for calculating the rate of photocatalysis with the mixture of 10 pesticides was TOC degradation, and therefore was preferred because relative efficiencies based on the disappearance of organic carbon are more informative. Phenol ( $20 \text{ mg l}^{-1}$ ) has been used to calculate  $\zeta_{r,\text{TOC}}$  in order to follow the method proposed by the above mentioned authors.

$$\zeta_{r,\text{TOC}} = \frac{\text{rate of mineralization of pesticides mixture}}{\text{rate of phenol mineralization}} \quad (2)$$

Phenol and pesticide experiments were performed under exactly the same conditions. Since under sunlight, it is not possible to work under conditions of constant illumination, Eq. (1) is used to avoid this uncertainty and reaction rates used to determine  $\zeta_{r,\text{TOC}}$  are calculated using  $Q_{\text{UV}}$  instead of time. The initial rates obtained with phenol have been  $2.63 \text{ mg kJ}^{-1}$  for the initial substrate and  $0.864 \text{ mg kJ}^{-1}$  for the TOC. Relative photonic efficiencies of the pesticides mixtures are reported in Table 1.

All the efficiencies are lower than one, indicating that the maximum photocatalytic oxidative degradation of the test substances, at the selected initial concentration, is less efficient than for  $20 \text{ mg l}^{-1}$  of phenol. But considering the composition of the

mixture (see Fig. 1), this is reasonable. It should be emphasized that photodecomposition gives rise to intermediates, which could also be adsorbed competitively on the surface of the catalyst. The concentration of these intermediates varies throughout the reaction up to their mineralization and thus, the general Langmuir–Hinshelwood (L–H) equation may take the following form:

$$r = \frac{kKC}{1 + KC + \sum_{i=1}^n K_i C_i} \quad (3)$$

where  $r$  is the photocatalytic reaction rate,  $k$  the reaction rate constant,  $K$  the reactant adsorption constant,  $C$  the substrate concentration at any time and  $i$  the number of intermediates formed during degradation. As the number of intermediates formed during the degradation of the pesticide mixture is expected to be much more (qualitatively and quantitatively) than during phenol degradation, the overall reaction rate should be lower than for phenol.  $\zeta_{r, \text{TOC}}$  is around 0.50 when  $\text{TOC}_{\text{max}}$  (pesticides experiments) is very similar to  $\text{TOC}_0$  (phenol experiments).

Once the optimum initial concentration of pesticide for degradation is known, a model for predicting plant behavior is necessary. This model must allow calculation of the area of solar collectors required for treating water contaminated with different amounts of pesticides. Although, different authors admit that the Langmuir–Hinshelwood (L–H) model is not a perfect explanation of the mechanism of the photocatalytic process [20–22], they do agree on its usefulness, since the behavior of the reaction rate versus reactant concentration can very often be adjusted to a mathematical expression with it. In the present case, instead of using the L–H model ( $r = kKC/(1 + KC)$ ) directly, the use of a previously developed model [18] has been preferred for fitting experimental data in large solar photocatalytic plants, by an approximate kinetic solution of the general photocatalytic kinetic system, which has the analytical form of an L–H equation. That model was developed for pentachlorophenol degradation and mineralization, but its behavior with complex mixtures had not been checked. With these considerations, the rate of TOC disappearance is given by Eq. (4) (analogous to L–H model but without its original significance).

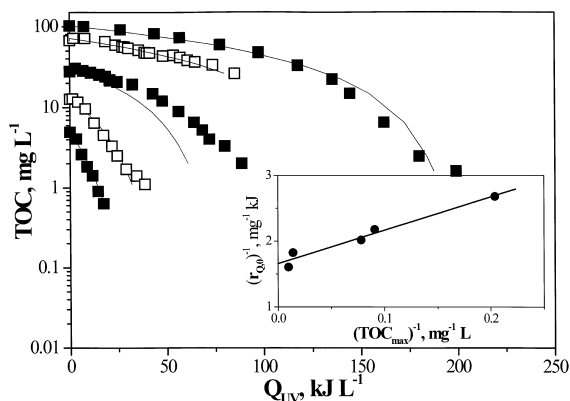


Fig. 3. Application of the proposed kinetic model for mineralization of a pesticide mixture. The inset shows the fit of Eq. (5).

$$r_{Q,0} = \frac{\beta_1 [\text{TOC}]_{\text{max}}}{\beta_2 + \beta_3 [\text{TOC}]_{\text{max}}} \quad (4)$$

The experimental results shown in Fig. 2 have been used to calculate the constants ( $\beta_i$ ). By inversion of Eq. (4) these constants can be calculated from the intercept and the slope of the line of fit (Eq. (5)), which is shown in the inset in Fig. 3.

$$\frac{1}{r_{Q,0}} = \frac{\beta_3}{\beta_1} + \frac{\beta_2}{\beta_1} \frac{1}{[\text{TOC}]_{\text{max}}} \quad \frac{\beta_3}{\beta_1} = 1.67 \text{ mg}^{-1} \text{ kJ}$$

$$\frac{\beta_2}{\beta_1} = 5.07 \text{ kJ l}^{-1} \quad (5)$$

Using these values, experimental results and the corresponding lines of fit are shown in Fig. 3. The lines of fit were drawn with Eq. (6) using the constants reported previously.

$$\frac{1}{\beta_1} \left\{ \beta_2 \ln \left( \frac{[\text{TOC}]_{\text{max}}}{[\text{TOC}]} \right) + \beta_3 ([\text{TOC}]_{\text{max}} - [\text{TOC}]) \right\} = Q_{\text{UV}} \quad (6)$$

The experimental results agree reasonably well with the model proposed and the constants calculated. This equation allows TOC degradation to be predicted as a function of initial TOC and available radiation, and the reverse, incident energy on the reactor necessary to reach a specific degree of mineralization. Nevertheless, UV radiation data for the final plant location must be available. As seen in Fig. 3, fits are not perfect, but taking into account the experimental and

accumulative errors, the adjustment may be considered acceptable. These errors could have been produced in the following measurements: (i) reactor volume and experiment time; (ii) analytical determinations; (iii) UV radiation measurement and (iv) calculation of  $r_{Q,0}$  from the maximum slope of each of the experiments shown in Fig. 2.

As has been commented in Section 1, the El Ejido (Almería) area consumes approximately 1.5 million plastic bottles of pesticides per year. As the photocatalytic treatment proposed in this paper is focused on the treatment of the amount of product remaining in each bottle, several tests have been performed to assess this quantity. Two different situations have been considered: the bottles are disposed of without washing and after one rinse. The latter is the most logical because these products are very expensive and, therefore, growers usually rinse them out and add the rinse water to their pesticide dosing tanks. In the first case, 0.673 g of TOC remain in the bottle and in the second, 0.083 g. These amounts are the averages of 100 empty bottles of different formulations. So, considering 1.5 million bottles, 1000 or 125 kg of pesticides (calculated as TOC) must be treated in each of the two situations mentioned above.

The graphic inserted in Fig. 2 shows 20–30 mg of TOC per litre as the initial rate steady state. At this concentration, saturation occurs and the reaction rate becomes constant. So, 25 mg of TOC per litre has been chosen as the initial concentration for photocatalytic treatment plant design. This means the water in the plastic-washing process will be recirculated until this concentration is achieved. Applying Eq. (6),  $56.4 \text{ kJ l}^{-1}$  will be necessary to reduce the TOC from 25 to  $1 \text{ mg l}^{-1}$ . Considering the total amount of pesticide expected from the 1.5 million containers per year,  $5000 \text{ m}^3$  or  $40\,000 \text{ m}^3$  per year of wastewater, respectively, will be produced, depending on whether growers wash the bottles out once or not. So,  $2.8 \times 10^9$  or  $2.25 \times 10^9 \text{ kJ}$  per year of solar UV will be necessary. Although, UV-radiation data for the plant location must be available for plant design, using UV radiation at the Plataforma Solar de Almería (Latitude  $37^\circ 5'$ , Longitude  $2^\circ 21'$ , 500 m up sea level) the plant size may be estimated. The average yearly UV radiation at the PSA is  $18.6 \text{ W}_{\text{UV}} \text{ m}^{-2}$  (4380 sunny hours per year). Therefore,  $2.93 \times 10^5 \text{ kJ m}^{-2}$  per year are available.

So, the treatment plant would have a collector surface of between 1000 and  $8000 \text{ m}^2$ , if we managed to collect all the bottles generated in the province of Almería. It has been proven that by rinsing the bottles the waste-water effluent can be reduced up to eight times, and therefore is essential to the process costs. If the treatment plant were located in an area with sunny conditions similar to the PSA, the average yearly UV radiation would be almost the same.

#### 4. Conclusions

A method for treating waste water is proposed, which although specifically calculated for water from washing pesticide bottles, could be used for a wide range of applications: rinse water polluted by pesticide formulations from containers used in greenhouses or aircraft sprayers, from the pesticide manufacturing industry, from washing fruits and vegetable prior to marketing, etc. The detoxification of water contaminated by pesticides (usually at low–medium concentrations, but highly toxic) is a field where solar photocatalysis could be applied in the future. Effluents are never contaminated by pure pesticides, however, because they are not marketed that way. An appropriate method of analysis is therefore required for the decontamination procedure. TOC analysis is highly recommended for this because of its versatility and, at the same time, its suitability for ‘on-line’ treatment plant installations.

Useful design equations may be obtained with a Langmuir–Hinshelwood type model, in spite of not fitting the heterogeneous photocatalytic reaction mechanism. For now these equations must be obtained at pilot plant size, however, they will be useful for larger plants if the same type of collector is used.

#### Acknowledgements

We wish to acknowledge the whole Plataforma Solar de Almería team for their help in the construction and operation of the photocatalytic reactor. The authors also thank Mrs. Deborah Fuldauer for the correction of English.

## References

- [1] D.W. Kopling, F.M. Thurman, D.A. Goosby, *Environ. Sci. Technol.* 30 (1996) 335.
- [2] A. Agüera, A.R. Fernández-Alba, *Analisis* 26 (1998) 123.
- [3] M. Castillo, D. Barceló, A.S. Pereira, F.R. Aquino, *Trends Anal. Chem.* 18 (1999) 26.
- [4] M.G. Hayo, *Agric. Ecosyst. Environ.* 60 (1996) 81.
- [5] S. Malato, J. Blanco, C. Richter, M. Vincent, *Sol. En.* 56 (1996) 401.
- [6] S. Malato, J. Blanco, C. Richter, D. Curcó, J. Giménez, *Water Sci. Technol.* 35 (1997) 157.
- [7] J.M. Herrmann, J. Disdier, P. Pichat, S. Malato, J. Blanco, *Appl. Catal. B: Environmental* 17 (1998) 15.
- [8] R. Goslich, D. Bahnemann, H.W. Schumacher, V. Benz, M. Mfiller, in: M. Becker M. Böhmer (Eds.), *Solar Thermal Concentrating Technologies*, in: Proc. 8th Int. Symp., Köln, Germany, October 1996, C.F. Müller Verlag, Heidelberg, 1997, p. 1337.
- [9] E.J. Wolfrum, C.S. Turchi, *J. Catal.* 136 (1992) 626.
- [10] A. Agüera, F. Alamansa, S. Malato, M.I. Maldonado, A. Fernández-Alba, *Analisis* 26 (1998) 245.
- [11] I.R. Chiarenzelly, R.J. Scrudato, D.E. Rafferty, M.L. Wunderlich, R.N. Roberts, J.J. Pagano, M. Yates, *Chemosphere* 30 (1995) 173.
- [12] M.R.S. Mak, T. Hung, *Toxicol. Environ. Chem.* 36 (1992) 155.
- [13] L. Muszkat, L. Bir, L. Feigelson, *J. Photochem. Photobiol. A: Chemistry* 87 (1995) 85.
- [14] J.M. Sullivan, J.H. Grinstead, D.J. Kiserow, K.C. Pugh, J. Gautney, in: D.E. Keff, R.E. Hogan T. (Eds.), *Solar Engineering 1994*, ASME, New York, 1994, p. 131.
- [15] K. Tanaka, K. Abe, S.Y. Sheng, T. Hisanaga, *Environ. Sci. Technol.* 26 (1992) 2534.
- [16] H. Tahiri, N. Serpone, R. Le van Mao, *J. Photochem. Photobiol. A: Chemistry* 93 (1996) 199.
- [17] M. Pérez, F. Torrades, J.A. Garcia-Hortal, X. Doménech, J. Peral, *J. Photochem. Photobiol. A: Chemistry* 109 (1997) 281.
- [18] C. Minero, E. Pelizzetti, S. Malato, J. Blanco, *Sol. En.* 56 (1996) 421.
- [19] N. Serpone, G. Sauvé, R. Koch, H. Tahiri, P. Pichat, P. Piccini, E. Pelizzetti, H. Hidaka, *J. Photochem. Photobiol. A: Chemistry* 94 (1996) 191.
- [20] A.P. Davis, *Chemosphere* 56 (1993) 1119.
- [21] C. Minero, *Sol. En. Mat. Sol. Cells* 38 (1995) 421.
- [22] N. Serpone, F. Pelizzetti, H. Hidaka, in: D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, The Netherlands, 1993, p. 225.