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ScienceDirect
Journal of Hazardous Materials 146 (2007) 447–452
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Detoxification and/or increase of the biodegradability of aqueous solutions of dimethoate by means of solar photocatalysis

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Available online 20 April 2007

Abstract

Different methods have been used to measure changes in biodegradability/toxicity of aqueous solutions of the pesticide Laition (a commercial formula of methidathion) when it is treated by means of TiO_2 photocatalysis: short time biological oxygen demand (BOD_{st}) was used to determine the instantaneous biodegradability of the sample; BOD_5 was also chosen to determine biodegradability, employing in this case the manometric method; the BOD_5/COD ratio was also calculated. Finally, the Zahn–Wellens test was employed to evaluate the long-term biodegradation of the effluents. The inhibition of the respiration of activated sludge in the presence of toxic pollutants was used to test the toxicity of the treated sample. An alternative method based on the decrease of BOD_5 of a very biodegradable mixture (glucose + glutamic acid) upon addition of the toxic solution was also employed. Similar trends were obtained with all methods and allowed us to distinguish between two periods: At the beginning of the reaction, there is a decrease in the concentration of dimethoate to reach complete abatement of this pesticide; this produces a nearly complete detoxification of the solution and a very significant increase of biodegradability (BOD_5/COD ratio reached values close to 0.5 and important increase of BOD_5 and BOD_{st} were observed). Beyond this point, slow mineralization is detected, but further improvement of the biodegradability cannot be achieved.

Keywords: Biodegradability; Toxicity; Respirometry; Dimethoate; Solar photocatalysis

1. Introduction

Water polluted with pesticides constitutes an increasing environmental concern, mainly in areas where intensive agriculture is an important activity. Although concentration of organic matter is seldom high, pesticides show significant toxicity, which does not allow the use of biological treatments to deal with this problem [1].

Advanced oxidation processes (AOP) have been shown to be very convenient methods to deal with effluents that are toxic or refractory towards biological treatments [2]. In particular, solar photocatalysis involving titanium dioxide seems a promising alternative to be used in rural areas, due to its simple and robust equipment and the important economical and ecological advantages that the use of sunlight involves [3]. As a matter of fact, this method has been successfully employed in the treatment of wastewaters containing pesticides in laboratory experiments [4,5], but it has also been scaled-up using pre-industrial and even industrial plants [6]. Although total elimination of the active species can be achieved in most cases, complete mineralization of organic matter usually requires longer periods of treatment. For this reason, solar photocatalysis could become unattractive from the economical or technical point of view.

One possible way to overcome this inconvenience is to stop the oxidative process once detoxification of the solution has been accomplished and the organic matter is more biodegradable [7–9]. Then, a classical biological method can be employed to deal with the pre-treated effluent. However, it is difficult to find reliable criteria to determine when detoxification of the effluent has been achieved and it is biodegradable enough to be treated by biological means, as in all cases living systems are involved in the analytical process.

Different methods can be employed to measure the biodegradability/toxicity of the organic matter present in aqueous effluents. Some of these measurements involve activated sludge, which is a consortium of micro-organisms present in biological reactors of municipal wastewater treatment plants; thus,

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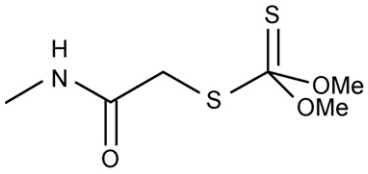
doi:10.1016/j.jhazmat.2007.04.046



Scheme 1. Chemical structure of dimethoate, active species of the commercial pesticide Laition.

they are expected to predict more reliably the real biodegradation of the effluents [10].

The aim of this work is to study the detoxification and increase of biodegradability of an aqueous solution of the commercial pesticide Laition when it is submitted to solar photocatalysis with TiO_2. This pesticide has been chosen because it is a commercial formula of dimethoate (Scheme 1), an organophosphorous pesticide whose photodegradation by titanium dioxide has been previously studied by other researchers [11–13].

2. Methods

2.1. Reagents and reactions

Commercial Laition (containing 400 g/l of active ingredient, dimethoate) was purchased from Lainco and used as received; pure dimethoate was supplied by Bayer. In all the experiments, the initial concentration of dimethoate was 50 mg/l. Under these conditions, the initial total organic carbon was 57 mg/l; only 25% of this amount is due to dimethoate, while the rest is attributable to organic additives present in Laition. Titanium dioxide (Degussa P-25) was employed as heterogeneous photocatalyst; its concentration was 0.2 g/l in all experiments. Tap water was used as solvent, whose conductivity was around 500 μS/cm; water hardness was 250 mg/l (expressed as $CaCO_3$).

Biological assays were performed using activated sludge taken from the exit of the biological reactor of the wastewater treatment plant from Alcoy (Spain). The activated sludge contained 1400 mg/l of suspended solids and it was employed without previous adaptation to the pollutants, in order to reproduce more closely the behaviour of the plant.

Solar photodegradation of the pesticide catalysed by TiO_2 was performed in a pilot plant for wastewater detoxification (Solardetox Acadus 2001, Ecosystem), based on compound parabolic collectors, CPCs [14], able to treat up to 25 l of wastewater (2.0 m^2 irradiated surface, 15.1 l irradiated volume). Accumulated and instantaneous UV radiation could be measured by a global UV radiometer (Acadus 85).

2.2. Chemical analyses

The concentration of dimethoate was determined by means of liquid chromatography (Perkin Elmer XL Autosystem, equipped with a diode-array detector and an autosampler). A reverse phase column (LiChrosphere 100 RP-18) was used, with an isocratic mixture of methanol (50%) and H_2SO_4 0.01 M (50%) as eluent (1 ml/min flow). Detection was based on the absorption at 220 nm. Samples were diluted with methanol (1:1) in order to prevent adsorption onto TiO_2 surface, and filtered through glass fibre before injection.

Total organic carbon (TOC) was determined with a Shimadzu model TOC-V CSH apparatus, based on combustion/non dispersive infrared gas analysis method, provided with an autosampler. Samples were filtered through glass microfibre before injection. The same device was also employed to measure the total nitrogen, using a chemiluminescence detector. Chemical oxygen demand (COD) determination was carried out spectrometrically, according to the dichromate method [15]; all reagents employed in this analysis were supplied by Merck. The surface tension of the sample was determined by a Krüss K-9 tensiometer.

2.3. Biological assays

Continuous respirometric assays were carried out using an activated sludge respirometer BM3-LAB (Neurtek) equipped with an oxygen sensor (WTW-Cell Ox). Oxygen uptake rate (OUR) can be obtained from the difference in the concentration of oxygen in the activated sludge when it is pumped to the oxygen sensor through two pathways of different length [15]. For BOD_{st} determination, an adaptation of the OECD-301 test was used; briefly, the biological reactor was loaded with 1 l of activated sludge and 10 ml of effluent. The BOD_{st} value was calculated by integration of the obtained respirometric curve (OUR versus time) after addition of the sample.

In the OUR inhibition experiments (OECD 209 test), activated sludge (500 ml) was brought to its maximum oxygen uptake rate (OUR_{max}) by addition of solid sodium acetate (1 g). Then, 250 ml of the aqueous solution of the pesticide was added and the final oxygen consumption (OUR_f) was measured. The inhibition was calculated by Eq. (1a). Dilution of the sludge by addition of the liquid sample was responsible of some decrease in the OUR as determined by blank experiments (inh_B); thus, a corrected inhibition has to be calculated by means of Eq. (1b):

$$\text{inh}(\%) = \frac{\text{OUR}_{\text{max}} - \text{OUR}_{\text{f}}}{\text{OUR}_{\text{max}}} \times 100 \quad (1a)$$

$$\text{corr.inh}(\%) = \frac{\text{inh} - \text{inh}_{\text{B}}}{100 - \text{inh}_{\text{B}}} \times 100 \quad (1b)$$

BOD_5 determinations were carried out according to the manometric method (OECD-301 series), using an OxiTop© (WTW) to seal the bottle and determine continuously the pressure inside.

For the inhibition of BOD_5 experiments, the manometric method was also employed. The same procedure described above for BOD_5 determination was followed, but in this case readily biodegradable glucose (150 mg) and glutamate (also 150 mg) were added to the pesticide solution (BOD_{5inh}). In a blank experiment, glucose and glutamate were added to a distilled water solution and the BOD_5 was also calculated (BOD_{5B}). The inhibition was calculated by Eq. (2).

$$\text{inhibition}(\%) = \frac{\text{BOD}_{5\text{B}} - \text{BOD}_{5\text{inh}}}{\text{BOD}_{5\text{B}}} \times 100 \quad (2)$$

For the Zahn–Wellens test (OECD-302), 2 l of the pollutant solution were added to a glass open reactor, magnetically stirred and kept in the dark at room temperature. Activated sludge (1 g/l) and mineral substances were added to the mixture (KH_2PO_4, K_2HPO_4, Na_2HPO_4, NH_4Cl, $CaCl_2$, $MgSO_4$ and $FeCl_3$). A control was run with a highly biodegradable compound, diethyleneglycol (180 mg/l). Finally, a blank experiment consisting in a mixture of 2 l of distilled water, activated sludge and mineral species was also run. In all the experiments, the pH of the solution was kept in the range 7–8. The biodegradation (D_t) was estimated by means of Eq. (3), where C_0 is the initial TOC value (determined three hours after the beginning of the experiment), C_t the TOC at the sampling time, C_{Bt} the TOC of the blank experiment at the sampling time and C_{Bo} the initial TOC of the blank (measured after three hours).

$$D_t = \left[1 - \frac{(C_t - C_{Bt})}{C_0 - C_{Bo}}\right] \times 100 \quad (3)$$

3. Results and discussion

3.1. Photodegradation of Laition

Solar photodegradation of commercial Laition catalysed by TiO_2 was studied in pilot plant. Decrease in the concentration of the active ingredient, dimethoate, COD and TOC, were determined during the photodegradative experiment (Fig. 1). Relative values were plotted versus t_{30W}, which is a convenient way to normalise solar irradiation [16].

A very fast primary degradation of the active species, dimethoate, was observed (total abatement in only 210 min). However, mineralization of the solution was a more difficult goal to be achieved, as after 670 min irradiation, 25% of the organic matter remained in the solution. This could be due either to intermediates formed in the degradative process, or to the presence of other organic compounds in the formulation of Laition that cannot be easily oxidised. The COD followed similar trends to TOC.

Average oxidation state (AOS) can be calculated by means of Eq. (4a), where TOC and COD are respectively the total organic carbon and the chemical oxygen demand of the solution (expressed as mg/l) at the sampling time. This is a good indicator of changes relative composition of dissolved organic matter [15]. Fig. 1 indicates that AOS increased all along the process until $t_{30W} = 500$ min; this means that more oxidised intermediates were formed during the process; this variation in the composition of the organic matter might also involve changes in toxicity/biodegradability although biological assays are needed to determine this point.

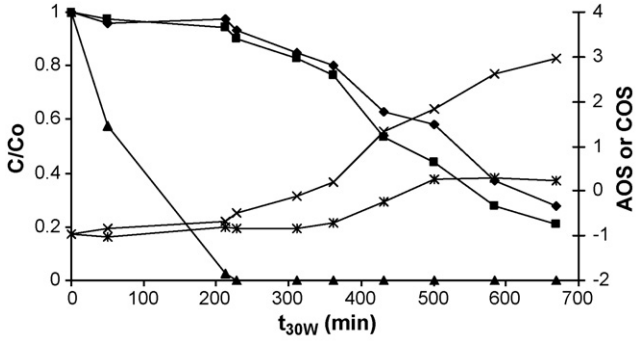


Fig. 1. Photodegradation of Laition catalysed by TiO_2 under solar irradiation. Left *Y*-axis, given as the ratios between these parameters and their initial values: (▲) concentration of dimethoate, (■) COD and (♦) TOC. Right *Y*-axis, (*) average oxidation state (AOS), and (×) carbon oxidation state (COS).

The existence of a strong oxidation of organic matter is confirmed by the carbon oxidation state (COS). This parameter was calculated by means of Eq. (4b); in this case, TOC is determined at the beginning of the experiment (generated CO_2 is also considered, with an oxidation state +4 for the carbon atom). As shown in Fig. 1, at the beginning of the reaction a value of −1 was calculated for COS, indicating the presence of rather reduced organic compounds; at the end the experiment the COS was +3; related with strong mineralisation and generation of highly oxidised intermediates.

$$\mathrm{AOS} = 4 - 1.5\frac{\mathrm{COD}}{\mathrm{TOC}} \quad (4a)$$

$$\mathrm{COS} = 4 - 1.5\frac{\mathrm{COD}}{\mathrm{TOC}_0} \quad (4b)$$

Other monitored parameters were pH, conductivity, total nitrogen and surface tension. No noticeable changes were detected for conductivity (around 540 μS/cm), due to the important amount of salts present in tap water, which are responsible of most of the measured conductivity. On the other hand, pH decreased from an initial value of 7.5 to 2.6; this is a well-known behaviour that can be attributed to the generation of carboxylic acids during the oxidative process. Also total nitrogen remained stable during the whole experiment, indicating that no volatile nitrogen containing species was formed in the photocatalytic treatment. This is in agreement with previous observations, where ammonium and nitrate were identified as the final nitrogenated products in the process [12,13]. On the other hand, surface tension increased from 66 mN/m to reach a final value of 73 mN/m, coincident with that of distilled water. This behaviour was previously observed in other commercial pesticides, and it is attributable to the destruction of the surface-active species [16].

3.2. Biological assays

Results shown in previous section indicated that solar photocatalysis was able to efficiently remove dimethoate, although mineralization required too long irradiation periods; in case the photochemical process was able to achieve an important detoxification of the mixture, solutions of Laition could be an example of those wastewaters in which the coupling of a photocatalytic pre-treatment and a biological process could be an interesting approach. To clarify this point, samples taken during the photocatalytic treatment were submitted to different biological assays. First, inhibition of the OUR of the activated sludge [16,17] was employed with this purpose. According to this method, nearly complete detoxification of the solution was reached when total

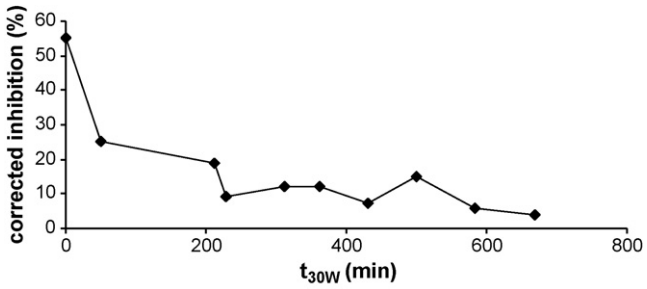


Fig. 2. Corrected inhibition values obtained for a solution of Laition after different periods of solar irradiation in the presence of TiO_2.

abatement of dimethoate was achieved (Fig. 2), as the corrected inhibition was negligible after $t_{30W} = 246$ min. This fact indicates that inhibition of OUR should be attributed to dimethoate and neither other species found in the commercial formulation of Laition, nor intermediates formed in the photodegradative process have a significant effect on the activated sludge respiration.

An alternative way to estimate the toxicity is based on BOD_5. As described in the experimental section, BOD_5 for a glutamate/glucose mixture was calculated, using as solvent aqueous solutions of Laition submitted to different periods of solar photocatalysis. Results given in Fig. 3 are qualitatively coincident with those obtained by means of activated sludge respirometry: the photocatalytic treatment produced an important detoxification of the pesticide solution. Only slight quantitative differences could be appreciated between those parameters, as in the BOD_5-based measurement, the inhibition values were somewhat higher than those obtained respirometrically. This could be attributed to an accumulative effect of some species during the five days of exposure involved in the BOD experiment.

Evgenidou et al. [12] also studied the removal of dimethoate by titanium dioxide photocatalysis. Inhibition of bioluminescence of *Vibrio fischerii* (MicroTox) was employed and similar trends were obtained in some cases, showing a clear relationship between removal of dimethoate and detoxification. However, these bacteria seem to be more sensitive towards the effect of the pollutant, and consequently, higher toxicities were obtained [17].

The previous series of experiments demonstrated that solar photocatalysis was able to detoxify efficiently aqueous solutions of Laition. However, it was also important to determine if this pre-treatment could be used to increase the biodegradability of the remaining organic matter. Also in this case, different experiments were used for this purpose.

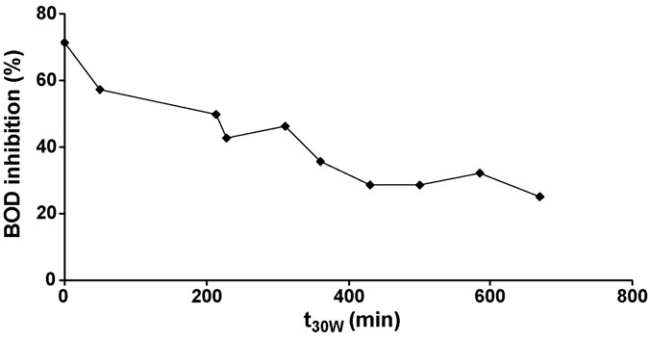


Fig. 3. Plot of the inhibition of the BOD_5 of a mixture of glutamate/glucose by aqueous solutions of Laition submitted to different periods of photocatalytic treatment.

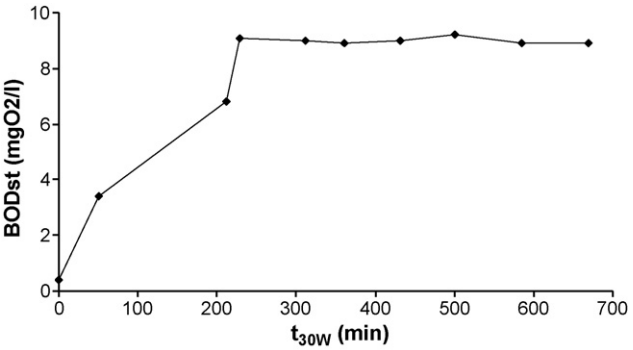


Fig. 4. BOD_{st} values obtained for a solution of Laition after different periods of solar irradiation in the presence of TiO_2.

Short time biological oxygen demand (BOD_{st}) was calculated by means of activated sludge respirometry. This is a good parameter in order to estimate the readily biodegradable organic matter [18]. Fig. 4 shows that in the early stages of the reaction, there was a noticeable increase in the BOD_{st}, from an initial value close to 0, to reach 9 mg O_2/l at $t_{30W} = 246$ min. This is again consistent with the detoxification experiments and HPLC analysis: non biodegradable dimethoate was oxidised but not mineralised; more biodegradable intermediates were formed during the process and thus, an increase in BOD_{st} was observed; it is interesting to point that the maximum value of BOD_{st} was coincident with complete removal of dimethoate and consequent detoxification according to respirometric assays; the decrease in the inhibition of the activated sludge respiration could also be responsible of this trend. Further increase in BOD_{st} could not be achieved beyond this point, probably due to the decrease in COD and TOC, as shown in Fig. 1.

BOD_5 was also used to check the amount of biodegradable organic matter in the solution [19]. Fig. 5 shows that this parameter increased during the disappearance of dimethoate, to reach its maximum value when complete abatement of the active species was accomplished ($t_{30W} = 246$ min). Then, slight decrease in the BOD_5 was observed, associated with stronger oxidation

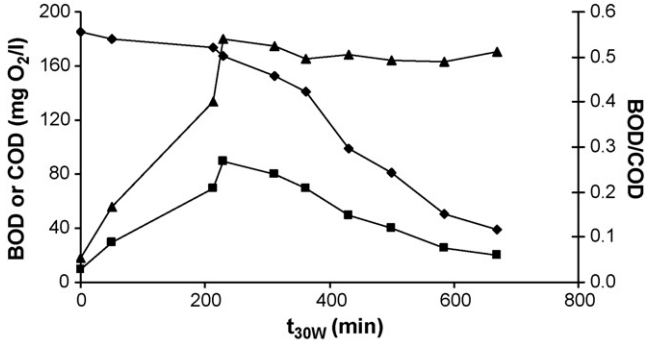


Fig. 5. Plot of the BOD_5 (■), COD (♦) and BOD_5/COD ratio (▲) of an aqueous solution of Laition after different periods of treatment.

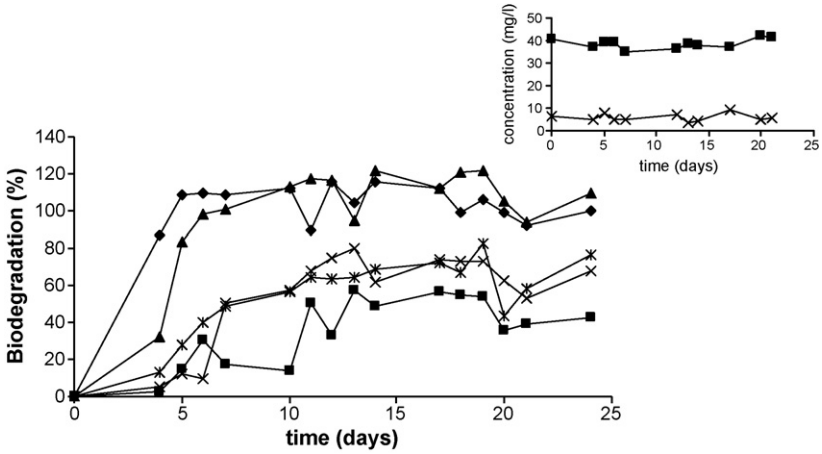


Fig. 6. Results obtained in the Zahn–Wellens test performed with Laition solution submitted to different periods of solar photocatalysis in the presence of titanium dioxide: t_{30W} = 0 min (■), t_{30W} = 160 min (×), t_{30W} = 246 min (*), t_{30W} = 403 min (▲). Results obtained for a diethyleneglycol solution, used as control, are also given (♦). The remaining concentration of dimethoate is given as an inset.

of organic matter. Similar trends were obtained for BOD_{st} and BOD_5. However, in the second case higher values are obtained, as experiments were carried out during five days and thus, not only readily biodegradable species are metabolised, as happened in the short-time measurements, which lasted typically minutes.

However, the BOD_5 to COD ratio is a more reliable parameter to evaluate the biodegradability of organic matter, as BOD_5 is highly influenced by the amount of organic matter and its oxidation state [20]. This ratio was calculated at every sampling time and results are shown in Fig. 5. Again in this case, trends were consistent with the other analytical methods: the low BOD_5/COD value of the initial sample (0.05) indicates that the Laition solution was not biodegradable; then, this parameter increased as the toxic dimethoate was removed by the solar photocatalytic treatment to reach values around 0.5; then it remained stable, indicating that irradiation periods longer than 250 min were not able to improve the biodegradability of the solution.

Finally, the Zahn–Wellens test [21,22] was performed to check the long-term biodegradability of the Laition solution after selected periods of solar photocatalysis (Fig. 6). Although the importance of the quantitative data should no be overemphasised, a clear trend could be observed: there was a significant increase in the biodegradability of the sample during the photocatalytic pre-treatment. The initial solution showed a poor long-term biodegradability (in the range 40–50%); although some biodegradation was detected, it was not due to metabolisation of dimethoate, as HPLC measurements indicated that its concentration did not decrease during the biological assay, but to the consumption of organic additives present in Laition, which are responsible of 75% of the TOC. The biodegradation of the samples taken after t_{30W} = 160 min and t_{30W} = 246 was around 70%, due to the decrease in the inhibition of the sludge respiration by the removal of dimethoate and to the formation of more biodegradable intermediates. However, it was not until the end of the treatment (400 min), when complete biodegradation of the sample was accomplished, according to this assay.

4. Conclusion

Solar photocatalysis employing titanium dioxide has proven to be an efficient pre-treatment to deal with aqueous solutions of the commercial pesticide Laition. Complete removal of the active ingredient, dimethoate, can be accomplished using moderate irradiation periods; however, mineralization of the solution is a more difficult goal to be achieved.

Two different methods, based on activated sludge respiration and BOD_5 inhibition indicated that complete removal of dimethoate was necessary to detoxify the solution. A parallel increase of the biodegradability of the effluent was detected by BOD_{st} and BOD_5 measurements, as well as by the Zahn–Wellens test. Further irradiation was able to produce stronger oxidation of organic matter and a significant degree of mineralization, but no significant enhancement of biodegradability was obtained. Thus, using solar photocatalysis as a pre-treatment to remove dimethoate and then coupling a biological reactor seems an advisable strategy to deal with aqueous solutions polluted by this commercial contaminant.

Finally, the use of redundant methods to determine the biocompatibility of the effluent allows a comparison among them. Respirometric methods are very useful to give a quick estimation of acute toxicity or short-time biodegradability, as they give a quick response; however, they are not able to determine the long-time effect of the toxic species or the intrinsical biodegradability. For this reason, the use of time consuming assays, such as Zahn–Wellens test, is still necessary for selected samples.

Acknowledgements

We want to acknowledge the financial support of *Generalitat Valenciana* (*Investigadores Emergentes*, GV06/118) Spanish *Ministerio de Educación y Ciencia* (Project PPQ2003-07596-C03-03) and European Union (Feder Founds). Ana García also wants to acknowledge the economic support of *Ministerio de Educación y Ciencia*.

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