Assessment of solar photocatalysis to purify on-site rinse waters from tractor cisterns used in grapevine pest control: field experimentation

P. Pichat*, S. Vannier**, J. Dussaud*** and J.-P. Rubis****

*Laboratoire 'Photocatalyse, Catalyse et Environnement', CNRS UMR 'IFoS', Ecole Centrale de Lyon, 69134 Ecully CEDEX, France (E-mail: pichat@ec-lyon.fr)
**Chambre d’Agriculture de Vaucluse, Site Agroparc, 84912 Avignon, CEDEX 9, France
***Ahlstrom Research and Services, impasse L. Champin, 38780 Pont-Evêque, France
****Lycée Viticole, 2260, route du Grès, 84100 Orange, France

Abstract The aim of this study was to assess in a vineyard the effect of purifying by solar photocatalysis the title rinse waters (currently most often rejected) in terms of efficacy and on-site practicality for the wine grower. The on-site, self-functioning, solar purifying unit included a corrugated-steel inclined plate of area \( S = 1 \text{ m}^2 \) onto which a \( \text{TiO}_2 \)-coated thin material had been slightly pressed, a tank, and an aquarium-type pump powered by a photovoltaic panel (appropriate for isolated locations). For a vineyard of area \( A = 0.15 \text{ km}^2 \) corresponding to each of four typical vine treatments in summer was analysed (major pesticides for each treatment, TOC, Microtox test and, in one case, \( \text{BOD}_5 \)) by independent laboratories, before and after purification for 8 days. The \( S/A \) ratio tested was found insufficient even if the photocatalytic treatment markedly improved the quality of the rinse waters. From the relatively low final organic content reached in one case, it is calculated that a three-time higher \( S/A \) ratio might suffice, but new trials are necessary to determine whether it is valid for other typical cases. Inferred contribution of inorganic ions to the post-photocatalytic treatment toxicity points to the need for an additional detoxification. These field experiments have also demonstrated that the purifying prototype is robust, and easy to install and use on site by the wine grower.

Keywords Agriculture; pesticides; photocatalysis; sunlight

Introduction Wastewaters generated by agricultural activities must be treated as any other wastewaters. In this regard, new regulations are progressively issued. For example, a French decree published in 1997 includes the purification of waters used to rinse the cisterns employed to spray chemicals of various kinds over plantations and fields. Because the locations where pest control products are utilized are often scattered and hence isolated, collecting the rinse waters to be purified is not practical and can be very expensive. Therefore, purification on the side of the cultivated parcels will undeniably be economically advantageous. Biological purification by use of tanks or beds is one the widely investigated means. The study presented here concerns the use of photocatalysis over titanium dioxide.

Photocatalysis over semiconductors (e.g. Fujishima et al., 1999; Pichat, 2003) is based on the excitation of the semiconductor by photons whose energy is at least equal to that of the band gap. The electrons – thus promoted to the conduction band – can be transferred to surface/adsorbed electron-acceptor groups, molecules or ions, and the associated electron vacancies/positive holes in the valence band can be filled by electron-donor surface/adsorbed species. Therefore redox reactions can be produced.

Regarding the species generated by interfacial capture of electrons it is generally admitted that in air or aerated water, dioxygen can act as an electron-acceptor yielding
superoxide or hydroperoxyl radicals. Hole transfers are believed to produce hydroxyl radicals from adsorbed water molecules or surface basic hydroxyl groups or hydroxide anions. The hydroxyl radical is an extremely powerful oxidant as its oxidation potential, 2.8 V versus NHE, is only slightly lower than that of fluorine (3.0 V). Direct electron transfer from electron-rich organic molecules to the semiconductor valence band is also thought to occur (Cermenati et al., 1997).

Several environment-related applications have been derived from this radical chemistry, like air purification (e.g. Fu et al., 1996; Fujishima et al., 1999; Pichat et al., 2000; Lewandowski and Ollis, 2003; Disdier et al., in press) and water decontamination (e.g. Fujishima et al., 1999; Pichat 2003), as well as the elaboration of self-cleaning materials (e.g. Paz et al., 1995; Fujishima et al., 1999; Roméas et al., 1999a,b).

TiO2 is a semiconductor which presents the advantage of being non-toxic, stable, well-known and relatively inexpensive. In addition, until now, no sample of other semiconductor oxides has been found more active than the most active anatase specimens.

For the treatment of air and water, photocatalysis over TiO2 is a technique that is a priori simple (no liquid chemicals are used), robust and flexible. Its operating cost, which arises mainly from the electricity and the UV lamps, can be almost suppressed if solar irradiation instead of UV lamps can be used provided the needs and location of the treatment allow it. For all these reasons and because it can operate without attendance, photocatalytic water purification appears well appropriate for isolated places. The size of the photocatalytic device can be adapted to the local needs. As it is based on adsorption of pollutants on TiO2, this method is well-suited for purifying waters containing low concentrations of pollutants as is the case for agriculture rinse waters. Furthermore, it can degrade any organic compound, with the exception of the s-triazine nucleus and trifluoroacetic acid (Pichat, 2003).

Experimental

This field experimentation was done in a vineyard of area 0.15 km², near Orange in southern France, within a wide region producing wines of great renown and benefiting from the solar irradiation of the Mediterranean climate (overall daily solar energy during the photocatalytic purification periods were comprised between 2320 and 2910 J cm⁻² day⁻¹). The vine treatments were those usually employed against mildew, oidium and grapevine worms. The sprayed quantity was about 2 m³ for each treatment using cisterns of 400 or 800 L. After the spraying was finished, about 30 L of tap water was poured into the cistern in which 1 to 2 litres of the treatment mixture remained. The resulting cistern content was sprayed at high speed over the vineyard. Then about 30 L of tap water was again poured into the cistern and then collected into a tank. The rinse water (about 90 L) thus collected from the cisterns employed was that subjected to photocatalytic purification.

The photocatalytic solar panel (2 m long; 0.5 m wide) was made of corrugated-steel onto which a TiO2-coated thin fibrous material had been adhered (Figure 1). This panel was oriented southward and inclined by an angle of about 45° with respect to the horizontal. The use of corrugated steel was thought to increase the contact time of the pollutants with TiO2 by slowing down the water flow rate on the TiO2-coated material and creating turbulences. The coating on a thin fibreglass tissue was prepared by use of a mixture containing TiO2 (Millennium PC 500; anatase; 317 m² g⁻¹; elemental crystallite size: 20–30 nm; average pore size: 6.1 nm) and an aqueous colloidal suspension of SiO2 (particle size: 20–30 nm; TiO2/SiO2 mass ratio: 1). This mixture was impregnated on the tissue by use of a ‘size press’ (Ahstrom patent, 1999). The impregnated tissue was allowed to dry at room temperature. The total mass supported was 80 g m⁻² of tissue.
whose mass was 50 to 60 g m\(^{-2}\) before coating. Silica was used to better anchor titanium dioxide. However, it substantially restricted the accessibility of pollutants to TiO\(_2\). That was shown by both SEM examination of the coating using various energies of the electron beam and a study of the photo-induced \(^{18}\)O\(_2\)-Ti\(^{16}\)O\(_2\) isotopic exchange – a reaction that requires contact between gaseous oxygen and TiO\(_2\) – over the coating compared with the same mass of powder TiO\(_2\) (Enriquez et al., 2004). The material used in this study corresponded to a compromise between the photocatalytic activity of TiO\(_2\) and the fixation of TiO\(_2\) on the fibreglass tissue.

A 100 L tank containing the water to be treated was placed below the solar panel. It was made of a plastic material approved for food so that no additional chemical could be released into the water during the photocatalytic treatment. To distribute the water at the top of the photocatalytic panel we used an aquarium-type pump driven by a photovoltaic panel (43 cm × 30 cm). That renders the system entirely solar, which allows one to place the photocatalytic device far from any electrical network in agreement with the most frequent agricultural needs. The pumped water diffused along the whole width of the photocatalytic panel from a hole at the top, the average flow rate being 50 cm\(^3\) s\(^{-1}\). The panel was covered by a Pyrex glass plate to protect the TiO\(_2\)-coated material from rain and atmospheric dust.

Analyses (major pesticides, TOC, Microtox test and, in one case, BOD\(_5\)) were performed by conventional methods in registered, public laboratories in France.
Results and discussion

Evaporation

The volume of the water treated decreased during the photocatalytic purification despite the glass cover placed over the photocatalytic panel. Over 8 days, the decrease comprised, on average, 2.5–5.6 L day$^{-1}$, depending on the weather (solar irradiation, temperature, wind) and the initial volume for each pest control treatment. In any rustic, inexpensive and easy-to-use photocatalytic solar device for the wine grower or farmer, evaporation seems unavoidable.

Assuming that only water was evaporated, given the low volatility of the pesticides, corrected concentrations, calculated as if the water volume had not changed, are listed in Table 1.

Variations in the initial concentrations in the rinse waters

In cases 1 and 2 (Table 1) the concentration of cymoxanil in the rinse water was below the detection limit, although the quantity of cymoxanil sprayed per km$^2$ was only 6.25 times lower than that of folpet. Cymoxanil being about a thousand-fold more soluble than folpet (source: www.inra.fr/agritox), we think this result indicates that cymoxanil was much more efficiently sprayed; therefore, no detectable residue of this pesticide was left in the cistern.

The folpet amount in the rinse water was about 7.25 times higher in case 2 than in case 1 (Table 1), taking into account the difference in the rinse initial water volume, though folpet was sprayed at the same dose. Combination of two pest control products in case 1 could be a cause of this divergence, as well as differences in spraying and rinsing, whether these latter differences were associated or not with the presence of another pest control substance.

In case 1, the dose of the folpet-containing product was higher than that of the product containing tebuconazole and triadimenol by a factor of 12. By contrast, much higher concentrations of tebuconazole and triadimenol than folpet were found in the rinse water (Table 1). This apparent discrepancy could arise from differences in solubility (0.8 mg L$^{-1}$ for folpet, 32 mg L$^{-1}$ for tebuconazole and 95 mg L$^{-1}$ for triadimenol; source: www.inra.fr/agritox) in the water used to rinse the cistern so that more folpet could have remained in the cistern. But, on the other hand, tebuconazole and tradimenol could have been dissolved more efficiently in the water used to treat the vine and accordingly could have been sprayed more readily. These observations clearly illustrate that the same accuracy cannot be expected in field experiments compared with laboratory experiments and thereby show the interest of field validation.

Regardless of the causes – various associations of pest control materials, irregularities in the spraying and rinsing stages, etc. – the variations in the concentrations of pesticides in rinse water reported here show that the photocatalytic purification device should be greatly over-sized to render it capable of achieving a good result in every case.

Photocatalytic removal of the pesticides

For tebucanazole and triadimenol (case 1; Table 1) at $C_0$ in the same range, $\ln(C_0/C_{4d,corr}) = k$ had the same value (≈0.95) in agreement with the very similar chemical structures of these compounds.

The existence of competition between pesticides is illustrated by the case of folpet for which $k \approx 3.4$ when it was the only pesticide in the rinse water (case 2) and $k \approx 0.7$ when it was mixed with tebuconazole and triadimenol (case 1) whose $C_0$ were much higher.

Decrease in competition between initial pollutants in the course of the photocatalytic purification is illustrated by the lower value of $\ln (C_0/C_{4d,corr}) = k'$ compared with
### Table 1 Variations in the concentrations of pesticides and TOC, and in the values of COD, BOD5, and toxicity

<table>
<thead>
<tr>
<th>Pesticides (μg litre⁻¹) or tests</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cymoxanil</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>173</td>
<td>138</td>
</tr>
<tr>
<td>Folpet</td>
<td>306</td>
<td>213</td>
<td>146</td>
<td>nd</td>
</tr>
<tr>
<td>Triadimenol</td>
<td>15600</td>
<td>8800</td>
<td>8050</td>
<td></td>
</tr>
<tr>
<td>Tebuconazole</td>
<td>38000</td>
<td>21208</td>
<td>14579</td>
<td></td>
</tr>
<tr>
<td>Quinoxyfen</td>
<td></td>
<td></td>
<td></td>
<td>12300</td>
</tr>
<tr>
<td>Chlorpyriphos</td>
<td></td>
<td>370</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Dinocap</td>
<td>9890</td>
<td>267</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>Mancozeb</td>
<td></td>
<td></td>
<td></td>
<td>486</td>
</tr>
<tr>
<td>TOC (mg litre⁻¹)</td>
<td>170</td>
<td>160</td>
<td>130</td>
<td>21</td>
</tr>
<tr>
<td>COD (mg O₂ litre⁻¹)</td>
<td></td>
<td>22</td>
<td>24</td>
<td>15.3</td>
</tr>
<tr>
<td>BOD₅ (mg O₂ litre⁻¹)</td>
<td></td>
<td>221</td>
<td>22</td>
<td>221</td>
</tr>
<tr>
<td>Microtox 5 min (equitox/m³)</td>
<td>&lt; 2.2</td>
<td>&lt; 2.2</td>
<td>&lt; 2.2</td>
<td>472</td>
</tr>
<tr>
<td>Microtox 15 min (equitox/m³)</td>
<td>76.2</td>
<td>4.4</td>
<td>3.2</td>
<td>11.2</td>
</tr>
<tr>
<td>Microtox 30 min (equitox/ m³)</td>
<td></td>
<td></td>
<td></td>
<td>472</td>
</tr>
</tbody>
</table>

N.B. C₀, C₄d, and C₈d are, respectively, the concentrations before and after photocatalytic purification for 4 and 8 days. The abbreviation corr indicates that the concentration is corrected for changes in water volume during the photocatalytic treatment. The relative standard deviation was ca. 10% for all measurements that were performed by registered standard methods in independent laboratories for each water sample. Cymoxanil: 1-(2-cyano–2-methoxyiminoacetyl)-3-ethylurea; folpet: N-(trichloromethylthio)phthalimide; triadimenol: (1RS,2RS;1RS,2SR)–1-(4-chlorophenoxy)-3,3-dimethyl–1-(1H–1,2,4-triazol–1-yl)butan–2-ο; tebuconazole: (RS)–1-p-chlorophenyl-4,4-dimethyl–3-(1H–1,2,4-triazol–1-ylmethyl)pentan-3-ο; quinoxyfen: 5,7-dichloro-4-quinolyl 4-fluorophenyl ether; chlorpyriphos: O,O-diethyl O-3,5,6-trichloro–2-pyndyl phosphorothioate; dinocap: 2,6-dinitro-4-octylphenyl crotonates and 2,4-dinitro-6-octylphenyl crotonates in which 'octyl' is a mixture of 1-methylheptyl, 1-ethylhexyl and 1-propylpentyl groups; mancozeb: manganese ethylenebis(dithiocarbamate) (polymeric) complex with zinc salt. Equitox is the reverse of LC 50–24 h, the concentration that reduces the living bacteria number by 50% within 24 h after exposure.
\[\ln(C_{4d,corr}/C_{8d,corr}) = k' \text{ for both folpet (}k' = 0.67; k'' = 1.1) \text{ and quinoxyfen (}k = 0.24; k'' = 0.93) \text{ in case 4 (Table 1).}\]

Moreover, it is doubtful that the much lower \(k'\) value for quinoxyfen than for folpet at equivalent \(C_0\) might come from distinct reactivities as numerous positions of attack exist in both compounds. The water solubility of quinoxyfen is about 0.1 mg L\(^{-1}\) (source: [www.inra.fr/agritox](http://www.inra.fr/agritox)), which is very low and markedly lower than folpet solubility. Consequently, it is plausible that it took time for the tiny particles of quinoxyfen to deagglomerate and, accordingly, to be then more easily degraded on the TiO\(_2\)-coated fibreglass tissue.

After 8 days of treatment the pesticides analysed were almost completely removed in cases 2 and 3 corresponding to the lowest initial total amount of pesticide, as well as to very low initial TOC levels (Table 1). The percentages removed were lower in case 4 and, above all, in case 1 (Table 1) in accordance with the highest initial total amounts of pesticides, especially in case 1, whereas the quantities removed were higher in accordance with the fact that photocatalytic rates are proportional to concentrations at low concentrations.

These results confirm ([Malato et al., 2000](#)) that, even in the complex mixtures contained in the rinse waters, pesticides can be eliminated. However, the surface of the photocatalytic solar panel used was clearly insufficient in some cases for the area of vineyard treated, at least for an 8 day-purification.

**Photocatalytic removal of TOC**

The total mass of organic C (pesticides + additives) removed after 8 days ranged from 0.6 to 36 g, i.e. 24–50% of the initial mass comprised between 2 and 72 g. Starting from a higher TOC led to a greater removed mass, as expected.

In case 4, measurements of the chemical oxygen demand (COD) and of the biochemical oxygen demand in five days (BOD\(_5\)) were also carried out (Table 1). BOD\(_5\) was higher than initially after 4 days and lower after 8 days of photocatalytic treatment (Table 1) even if the values were not corrected for the change in volume. These results indicate that the amount of biodegradable chemical matter first increased and then decreased in the course of the degradation process; this is corroborated by the variations in the ratio COD/BOD\(_5\). This type of variations is not unexpected as many organic intermediate products can be formed and their biodegradability cannot be predicted. In the long run, when complete mineralisation is almost completely achieved, the biodegradability of the remaining organic compounds should increase because carboxylic acids are the near-to-end intermediate products in photocatalytic oxidation ([Pichat, 2003](#)).

This result again clearly demonstrates the need for photocatalytic purification with a greater solar panel and/or a longer purifying period (**vide infra**).

**Toxicity variations resulting from the photocatalytic treatment**

The toxicity, evaluated by the Microtox test, was greatly reduced in case 1, after 8 days (Table 1). In case 2, the initial toxicity was the lowest in line with the lowest \(C_0\) of pesticide and the lowest TOC content (along with case 3); consequently, it was even difficult to measure it; only the initial value for 15 min exposure was above the lowest significant value, and it was decreased by the photocatalytic treatment. In case 3, the decrease in toxicity after 8 h was low compared with the decrease in case 1. In case 4, substantial decreases in toxicity were observed after 4 days, irrespective of the exposure time of the test bacteria; however, the toxicity was higher after 8 days than after 4 days; an increase with respect to the original toxicity was even observed for 5 and 15 min exposure of the bacteria (but not for 30 min). Evaporation cannot totally account for the increase as it
was similar to that in the other cases. In sum, very distinct results were obtained according to the case. The recalcitrant toxicity of case 4 could come, at least in part, from the Zn\(^{2+}\) ions initially bound to the organic moiety of mancozeb.

It must be kept in mind that the inorganic ions (e.g. Cu\(^{2+}\)) initially present in the agrochemicals are generally not photocatalytically transformed. Therefore, if the residual toxicity is due to inorganic ions it cannot be reduced further by photocatalysis, in general. Supplementary water decontamination might be necessary.

As the other measurements, the Microtox tests indicate that the purifying device investigated had not a sufficient size with respect to the vineyard area to meet the needs. However, it must be underlined that the tolerance of the aquatic organisms might widely differ from that of the bacterium tested. In this respect, complementary tests should be performed to estimate the remaining toxicity of the water after filtration through a column of local soil, that is, containing microorganisms. Other methods for measuring the toxicity should also be used.

### Purification efficacy: estimation of the solar panel area needed

All the indications of water overall quality that were measured have shown that the photocatalytic solar panel area used, \(S\), and a purifying period of 8 days were insufficient to properly clean the rinse waters tested. The necessary increases in \(S\) and/or purifying time \(t\) might in principle be calculated on the basis that the TOC amount removed is proportional to the photon dose, \(S \Phi t\), where \(\Phi\) is the UV radiant flux received by the panel per area and time units, provided \(\Phi\) is low enough (Al-Sayyed et al., 1991). This proportionality is likely to be true for solar irradiation, the maximum \(\Phi\) being ca. 2.7 W m\(^{-2}\) for the 280–320 nm spectral range in the location where the vineyard is situated. An improvement could thus be obtained by increasing \(t\) from 8 to 12 days, as the minimum interval between two vine treatments allows it. Another improvement regarding the TOC level after photocatalytic treatment can be achieved by increasing \(S\). In one of the cases where the TOC was relatively low, calculation of \(S\) indicated that a 2 m\(^2\) panel for 0.1 km\(^2\) (e.g., 316 m \(\times\) 316 m) of vineyard – which is quite acceptable – would lead to a final TOC lower than 2 mg L\(^{-1}\) within 12 days. However, the conclusion about the ratio between \(S\) and the treated vineyard area \(A\) cannot be based on this only case. New trials (with a greater \(S\) and a smaller volume of rinse water) are necessary to determine whether it is valid for other typical cases.

Note, however, that even if the \(S/A\) ratio allows one to attain a low organic content, the toxicity, as evaluated by the Microtox test, could remain of concern because of the inorganic ions issued from the heteroatoms of the organic part of the pest control mixtures or already present in these mixtures. Nevertheless, it must not be forgotten, that presently these rinse waters are most often discarded in the environment.

### On-site practicability

The simplicity of installation and use, as well as the robustness of the photocatalytic device, have been demonstrated. The experimentation has proved that this device can remain unattended, which meets the agricultural needs. The TiO\(_2\)-coated fibrous material has been shown to be solid and to withstand the use in open air. The rinse waters were not filtered as the amount of suspended matter was visually not important.

### Conclusion

This application of solar TiO\(_2\) photocatalysis shows promise, even though further on-site experimentation is needed to get a definitive answer about its viability. The solar
A photocatalytic panel is easy to fabricate. Both the fibrous material supporting TiO₂ and the ready-to-be-industrialized TiO₂ deposition method are cheap; the efficacy could be improved. Extension to other types of rinse water in agriculture can readily be envisaged. Favorable conditions to apply solar photocatalysis are: (i) sufficient time intervals between two successive pest control treatments; and (ii) treatment periods occurring when the average solar irradiation during the photocatalytic purification is relatively constant.

References