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Photocatalysis as a potential pre-treatment process to reduce organic pesticide entries

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Introduction

Many plant protection products (PPPs) may accidentally enter aquatic environments after being washed off from viticultural machinery (VM). There, they may have negative effects on aquatic life, e.g. lowering important ecosystem services they provide. This contradicts the EU Water Framework Directive, which aims to increase the overall surface water quality. Therefore, techniques to counteract this issue are urgently needed. A promising process to reduce such PPP loads directly in wash waters from VM can be seen in photocatalysis [1]. The present study evaluated the efficiency of a commercially available TiO_2 photocatalyst by separately treating five different PPPs – which are frequently applied in viticulture - in aqueous solution when applying artificial UV-light as irradiant. To finally evaluate the TiO_2 dependent efficiencies, treated and untreated PPPs were i) analyzed for their environmental toxicity before and after a combined TiO_2 × UV treatment, and ii) for remaining PPP concentrations and major metabolites.

Fig.1: Cleaning of a viticultural machinery. *(Picture: DLR)*

Material and Methods

Photocatalyst

- TiO_2 P25 (Evonik)
  - ~100 nm
  - 1.0 g/L

Irradiant

- Batch reactor
  - 60 Wm^{-2} UVA-light
  - 365 nm

PPPs and treatment time

- Analytical standards of
  - Myclobutanil (-30 to 240 min)
  - Pyrimethanil (-30 to 720 min)
  - Glyphosate (-30 to 480 min)
  - Metiram (-30 to 720 min)
  - Dimethoate (-30 to 420 min)
  - Mixture Glyphosate x Myclobutanil (-30 to 900 min)

Toxicity tests

- 48-h acute toxicity test with *Daphnia magna* [2]
  - Juveniles <24 h
  - Test medium: ASTM medium
  - Endpoint: immobility
  - Evaluation: 48-h EC_{50} values

Chemical analysis

- Quantification of PPPs: HPLC-QToF (Agilent Technologies, accurate mass time of flight 6530B)
- Quantification of Total Organic Carbon: TOC analyzer (Shimadzu, model TOC-L)

Results and Discussion

Toxicity tests with *D. magna*

The acute assays revealed for the TiO_2 × UV treatment of Myclobutanil and Pyrimethanil a total toxicity reduction already after 60 min of treatment (Fig. 2A and 3A). This is in line with their chemical analysis, which showed substance dependent concentration reductions of ~84 and ~58% after the same treatment time (Fig. 2B & 3B).

Also for Metiram, Dimethoate, Glyphosate and the mixture of Myclobutanil × Glyphosate a reduction in toxicity was observed after distinct times of TiO_2 × UV treatment (Fig. 4A-D). However, these effects differed in size (cf. 4A and 4C) depending on the PPP itself and the time of treatment. Moreover, for Glyphosate an temporary increase of toxicity was observed (Fig. 4D). This can most likely be attributed to toxic metabolites, which were produced during the degradation of the original PPP (data not shown).

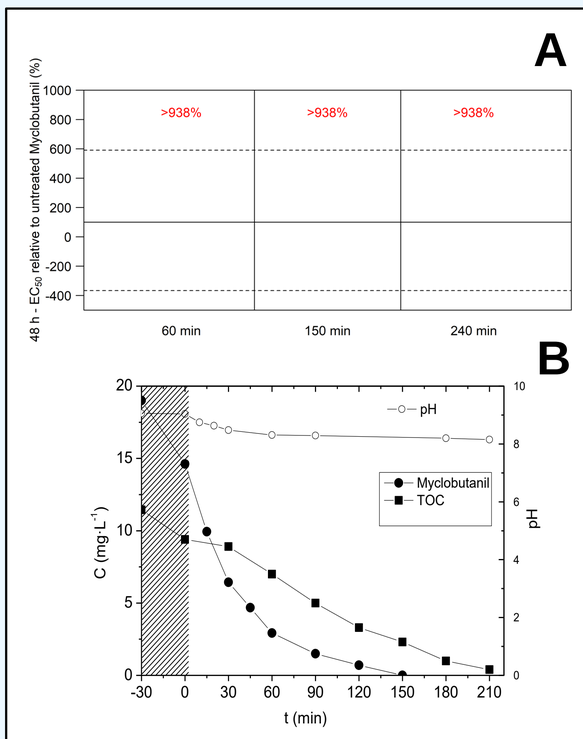

Fig.2: (A) Percentage 48-h EC_{50} values (with 95% CIs) for *D. magna* whereas gained 48-h EC_{50} values of TiO_2 × UV treated Myclobutanil were related to the respective 48-h EC_{50}-value of untreated Myclobutanil for different times of treatment. Continuous and dashed lines indicate the reference 48-h EC_{50}-value and respective 95% CI, while the percentage indicates the minimum distance to the relativized 48-h EC_{50}-values of Myclobutanil. (B) Myclobutanil concentration, total organic carbon and pH along time upon photocatalytic process.

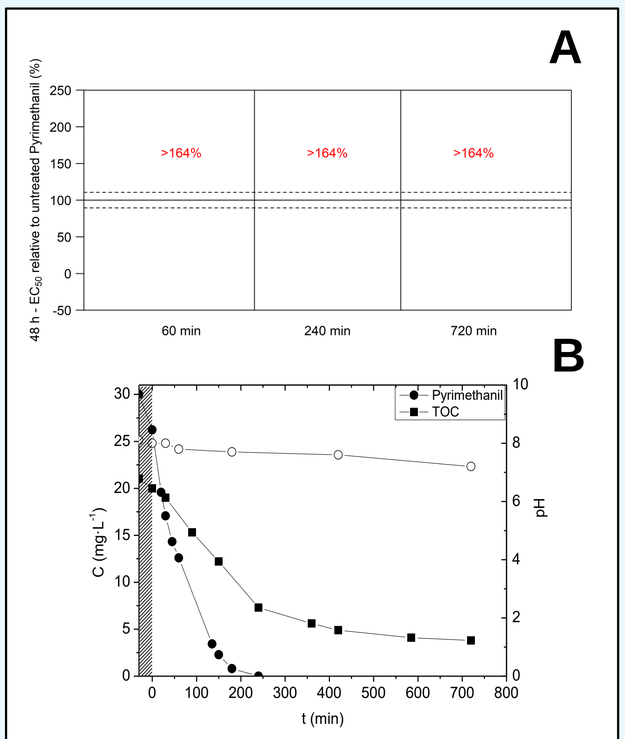

Fig.3: (A) Percentage 48-h EC_{50} values (with 95% CIs) for *D. magna* whereas gained 48-h EC_{50} values of TiO_2 × UV treated Pyrimethanil were related to the respective 48-h EC_{50}-value of untreated Myclobutanil for different times of treatment. Continuous and dashed lines indicate the reference 48-h EC_{50}-value and respective 95% CI, while the percentage indicates the minimum distance to the relativized 48-h EC_{50}-values of Pyrimethanil. (B) Pyrimethanil concentration, total organic carbon and pH along time upon photocatalytic process.

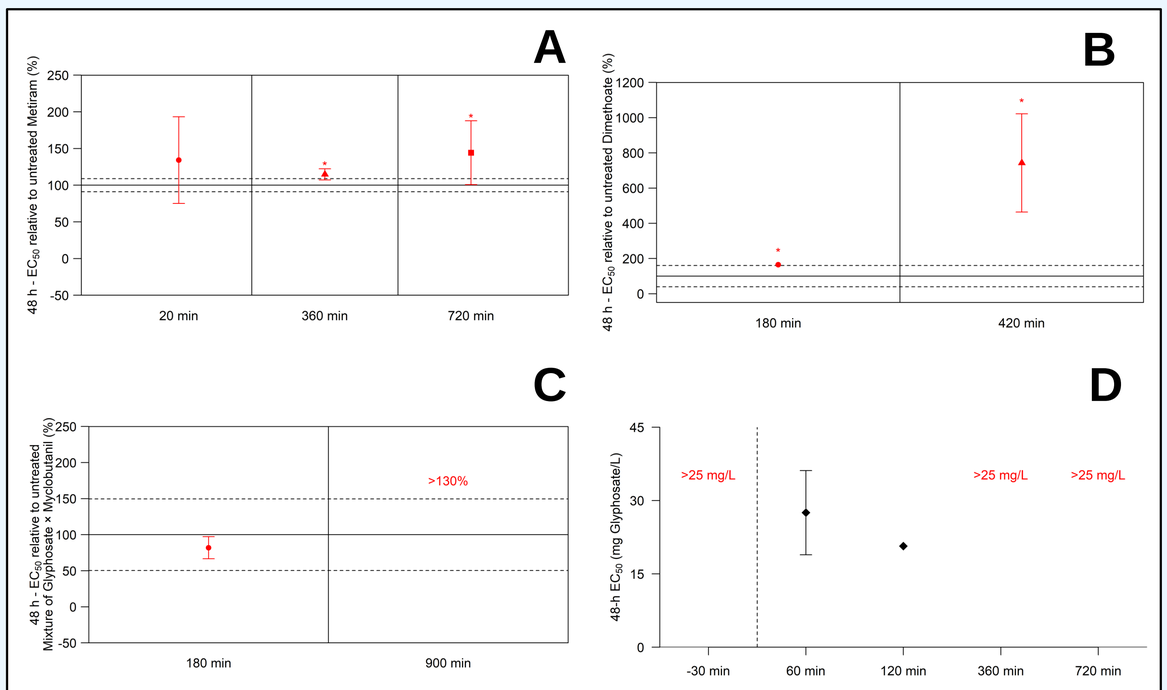

Fig.4: Percentage 48-h EC_{50} values (with 95% CIs) for *D. magna* whereas gained 48-h EC_{50} values of TiO_2 × UV treated (A) Metiram (B) Dimethoate (C) Glyphosate × Myclobutanil were related to the respective 48-h EC_{50}-value of the untreated PPP/mixture for different times of treatment. Continuous and dashed lines indicate the reference 48-h EC_{50}-value and respective 95% CI. Filled symbols indicate the relativized 48-h EC_{50}-values of the PPP/mixture, while the percentage indicates the minimum distance to the relativized 48-h EC_{50}-values of the tested PPP. Asterisks represent a stat. significant difference of respective 48-h EC_{50} values (D) 48-h EC_{50} values (with 95% CIs) of (un-) treated Glyphosate for *D. magna.* The concentration provided in red indicates that the 48-h EC_{50}-value exceeds the highest concentration tested.

Conclusions

- Photocatalysis using TiO_2 × UV seems a suitable technique to degrade PPPs that are frequently used in viticulture. However, its magnitude of success strongly depends on the applied reaction time and chemical characteristics of the treated PPP.
- **BUT:** In case the degradation process of the PPP is not fully completed, toxic intermediates may be released, which can be even more hazardous than the original PPP (see Fig. 4D).

References

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