Combination of photo-induced fluorescence and GC-MS for elucidating the photodegradation mechanisms of diflubenzuron and fenuron pesticides

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Introduction

Diflubenzuron (DFB) and fenuron (FEN) are non-fluorescent benzoyl- and phenylurea pesticides. Recently, we have applied classical photo-induced fluorescence (PIF) and direct laser PIF (DL-PIF) methods, based respectively on UV and laser irradiation, to transform DFB and FEN into strongly fluorescent photoproducts [1,2]. Combining these methods with gas chromatography-mass spectrometry (GC-MS), we have elucidated the photodegradation mechanisms of both pesticides.

Material and methods

In the case of PIF, a Kontron SFM-25 spectrofluorimeter and an Osram 200-W high-pressure mercury lamp were used, and in the case of DL-PIF, a Varian Cary Eclipse spectrofluorimeter with a Powerlite Precision 9010 pulsed ND:YAG pump laser beam was utilized. FEN aqueous solutions and DFB methanol-water mixtures at pH 4 were prepared. A Thermo Fisher Scientific model ISQ-Trace-1300 GC-MS was used for the separation and identification of DFB and FEN photoproducts.

Results and discussion

Applying the PIF and DL-PIF methods, one fluorescent DFB photoproduct was obtained at $\lambda_{ex}/\lambda_{em} = 230/342$ nm, and two fluorescent FEN photoproducts were found at $\lambda_{ex}/\lambda_{em} = 225/308$ nm and 280/342 nm. GC-MS confirmed that phenol and hydroxylamine were the main DFB and FEN fluorescent photoproducts. Indeed, fluorescence spectral characteristics similar with standards indicated that hydroxyl-aniline was the common, main photoproduct of both pesticides, and that phenol was the second main photoproduct of FEN. GC-MS indicated also the presence of a number of photoproducts formed during the photodegradation of both pesticides. Finally, we showed that the photodegradation mechanisms of DFB and FEN were complex and involved several reaction steps, such as dehalogenation, decarboxylation, demethylation, deamination and hydroxylation, in agreement with literature data [3,4].

Conclusion

Using GC-MS, we were able to separate and to identify several DFB and FEN photoproducts formed during the photodegradation of both pesticides. Combination of the PIF methods and GC-MS allowed us to propose schemes of reaction mechanisms for the DFB and FEN photodegradation.

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