

## Effect of pH and dissolved organic matter on the photochemical fate of acetamiprid

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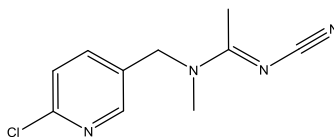
### Summary

In this study the effect of pH and dissolved organic matter (DOM) on the photodegradation rate of acetamiprid (ACT) was studied. Observed photodegradation rate constants in the range of 0.0010 – 0.0026 h<sup>-1</sup> and 24 – 36 h<sup>-1</sup> were obtained using a solar simulator (290-800 nm) and a medium pressure mercury (MP Hg) lamp, respectively. In both experiments an increase in pH from 5 to 9 did not significantly change the photodegradation rate constant of ACT. A different behaviour was found for ACT degradation in the presence of DOM. When samples were irradiated with MP Hg lamp the observed photodegradation rate constant of ACT decreased with an increase of DOM concentration.

*Keywords:* Neonicotinoid insecticides; DOM; Photolysis; Solar simulator; MP Hg lamp

### Introduction

Acetamiprid (ACT) is a neonicotinoid pesticide (Fig. 1) used for the control of sucking insects in a variety of crops with a wide commercial expansion [1,2]. The compound has a relatively low acute and chronic toxicity in mammals; however, the compound is highly toxic to birds and moderately toxic to bees and aquatic invertebrates [1]. ACT is highly water soluble, and concentrations between 20 and 380 ng L<sup>-1</sup> have been found in surface and wastewaters [1,2]. Dissolved organic matter (DOM) present in such type of matrices can play a significant role on the photochemical fate of organic contaminants like pesticides [3,4]. In this way, the aim of this study was to investigate the effect of pH and DOM on the photodegradation rate of ACT using a xenon and MP Hg lamp to simulate the solar radiation that reaches Earth's surface and the UV lamps used in wastewater treatments, respectively.



**Figure 1** – Chemical structure of acetamiprid ((E)-N1-[(6-chloro-3-pyridyl)methyl]-N2-cyano-N1-methylacetamidine).

### Materials and Methods

#### Photolysis – Solar simulator

ACT solutions 5.0 mg L<sup>-1</sup> prepared in 10 mmol L<sup>-1</sup> phosphate buffer at pH 5, 7, and 9 were exposed to simulated sunlight in a Luzchem SolSim (model LZC-PMV) solar simulator as described elsewhere [5]. The output of the Xe lamp was adjusted with a 1/8" Esco optical glass filter and dimmer to best match the AM 1.5 solar spectrum with irradiation from 290-800 nm

[5]. Data for the determination of the photochemical rates were obtained by withdrawing aliquots of samples (100  $\mu\text{L}$ ) at intervals ranging from 3 – 72 h and analysed by HPLC-DAD. Experiments were also carried out with ACT 5.0  $\text{mg L}^{-1}$  prepared in 10  $\text{mmol L}^{-1}$  phosphate buffer at pH 7 in the presence of Aldrich Humic Acid (AHA) 20  $\text{mg L}^{-1}$ .

### Photolysis – MP Hg Lamp

ACT solutions 5.0  $\text{mg L}^{-1}$  prepared in 10  $\text{mmol L}^{-1}$  phosphate buffer at pH 5, 7, and 9 were exposed to a MP Hg lamp as described elsewhere [3]. Experiments were also carried out with ACT 5.0  $\text{mg L}^{-1}$  prepared with AHA at 10 and 20  $\text{mg L}^{-1}$ . 2 mL of sample were taken at intervals ranging from 0 – 15 min and analysed by HPLC-DAD. In both experiments (solar simulator and MP Hg lamp) control samples were kept in the dark and analysed by HPLC-DAD.

### Results and Discussion

Table 1 shows the results obtained for the photolysis of ACT 5  $\text{mg L}^{-1}$  at different conditions of pH and AHA concentrations using a solar simulator (290-800 nm) and a MP Hg lamp.

**Table 1** – Observed photodegradation rate constants ( $k_{\text{obs}}$ ) and half-life times ( $t_{1/2}$ ) of acetamiprid (ACT) 5  $\text{mg L}^{-1}$  obtained at different conditions of pH and AHA concentrations.

Conditions	Solar simulator*		MP Hg lamp*	
	$k_{\text{obs}}$ ( $\text{h}^{-1}$ )	$t_{1/2}$ (h)	$k_{\text{obs}}$ ( $\text{h}^{-1}$ )	$t_{1/2}$ (h)
pH 5.0	$0.0010 \pm 6 \times 10^{-5}$	693	$36 \pm 0.6$	0.019
pH 7.0	$0.0009 \pm 1 \times 10^{-5}$	770	$36 \pm 3$	0.019
pH 9.0	$0.0009 \pm 1 \times 10^{-5}$	770	$34 \pm 3$	0.020
AHA 10 $\text{mg L}^{-1}$	-	-	$31 \pm 3$	0.022
AHA 20 $\text{mg L}^{-1}$	$0.0026 \pm 5 \times 10^{-5}$	267	$24 \pm 0.6$	0.029

\* Results are presented as mean value  $\pm$  standard deviation (n = 3).

Observed photodegradation rate constants were significantly higher when samples were irradiated with a MP Hg lamp. The electronic absorption spectrum of ACT shows little overlap with the spectrum of sunlight and therefore the compound is only slightly affected by direct photolysis. An increase of the pH had no effect on the degradation of the insecticide. However, the addition of DOM showed a different behaviour. An increase of DOM concentration inhibited the overall degradation of ACT under MP Hg irradiation. DOM contains a variety of organic moieties, in particular phenolic functional groups, which may act as light attenuator or antioxidant decreasing compounds degradation [4].

### Conclusions

DOM plays a significant role on the photochemical fate of ACT in aquatic systems. In the environment DOM is likely to increase the photodegradation of ACT. In wastewater treatment plants where MP Hg lamps are used, DOM might increase its persistence.

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