

## Abstract

In this work we report the formation of inclusion complexes of the pesticides 1-naphthylacetic acid, 1-naphthylacetamide, napropamide and carbaryl with cucurbit[n]uril (n=7 and 8) and  $\beta$ -cyclodextrin hosts. We also report results of the photochemistry of these compounds when free in aqueous solution and included within these nano-containers. The formation of inclusion complexes was studied by electrospray ionization mass spectrometry (ESI-MS) which gave us information about stoichiometry of the complexes and about their reactivity in the gas phase. The photodecomposition and formation of products was followed by high performance liquid chromatography coupled to both mass spectrometry (HPLC-MS) and UV/VIS detector, and spectrophotometry.

The studied CBs and their host-guest complexes were readily detected in the gas phase by ESI-MS, mainly as single and double charged ions containing either  $H^+$ ,  $Na^+$  or  $K^+$ . The assignments were made based on the m/z values of the observed signals and further confirmed by fragmentation (tandem mass spectrometry – MS<sup>n</sup>). All pesticides formed 1:1 (host:guest) complexes. Carbaryl, napropamide and 1-naphthylacetamide also formed 1:2 (host:guest) complexes. Under some solution chemistry conditions, namely for concentrations of cucurbiturils above 50  $\mu$ M and at low acid and salt concentrations ( $< 10^{-5}$  M) aggregates could also be observed.

Most of the studied pesticides undergo photodegradation when free in solution. Several unknown photoproducts were observed, namely with m/z = 232 for 1-naphthylacetamide@CB[8] and m/z = 218, 240, 329 for 1-naphthylacetamide@CB[7]. Further studies using other techniques, namely GC-MS, or HPLC-MS/MS are needed to assign a structure to the photoproducts.

Spectrophotometry as well as HPLC clarifies the photodegradation process of studied pesticides. Rate of decomposition constants explain the photodecomposition of each pesticide when free and included within a host. It seems that cyclodextrin includes the pesticides more efficiently than cucurbiturils. This result in faster photodegradation of non-included compounds, followed by analytes included into complex of cucurbituril, and then those forming inclusion complexes with cyclodextrin.