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Effect of different cyclodextrins on herbicide photodegradation in soil solution

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Investigation of the photolysis of labile pesticides is important in environmental chemistry because it presents basic data on their fate and persistence in natural environments exposed to sunlight action. Many agricultural chemicals, particularly pesticides, are broadly present in nature as soil contaminants that can be incorporated into water courses. Compounds absorbing UV light at $\lambda \geq 290$ nm when exposed to sunlight can undergo direct photolysis. In comparison, indirect photolysis occurs by sensitizers transmitting absorbed UV energy to molecules with absorption bands below 290 nm. The absorption spectrum of norflurazon is scantily extended up to 380 nm. This predicts some limited extent for the natural photodegradation of the herbicide under direct sunlight irradiation.

Cyclodextrins (CDs) are cyclic oligosaccharides having high inclusion abilities, specially for hydrophobic molecules. In the field of environmental chemistry, the abilities of CDs have been noticed for the availability of promoting degradation of organic pollutants. Likewise, recent investigations are managed to soil decontamination using CDs as photosensitiser for organic pollutants. On this basis, this work aims to obtain laboratory-scale information on the effects of different CDs on photodegradation of norflurazon monitored in different colloid components of soils in water suspensions on the basis of their correlations with the photodegradabilities of the herbicide in the CD-less systems, as well as their dependence on the radical generation abilities of different colloid components and also on type of cavities of CDs, with the possibility to obtain an effective tool to *in situ* decontamination of soils using CD as photosensitisers.

The selected colloid components were: a natural metal-fulvic acid complex, two synthetic humic acids, three different standard clay minerals (illite, kaolinite and montmorillonite), the clay fraction from two different soils (a silt loam soil and a clay soil) and a synthetic acicular goethite. The CDs employed were: beta-cyclodextrin (BCD), hydroxi-propyl-beta-cyclodextrin (HPBCD) and methyl-beta-cyclodextrin (RAMEB). The interaction of norflurazon with BCD, HPBCD and RAMEB yielded the formation of inclusion complexes at a 1:1 stoichiometric ratio in solution. Apparent stability constants of 360.16, 359.47, and 558.51 M^{-1} and an increase in herbicide solubility by up to 5-, 35- and 54-fold for BCD, HPBCD and RAMEB, respectively, were determined from the phase solubility diagrams at 25°C in water. In general, the presence of the different soil components in suspension provoked a reduction in the norflurazon photodegradation rate. In all cases the rate of photodecomposition followed first-order kinetics. On the other hand, the presence of the different CDs under study showed an inductive photodegradation effect on the herbicide and the promotion effects could be mainly assigned to the inclusion effects of CDs to catalyze interactions of the norflurazon with reactive radicals generated by the different colloid components.

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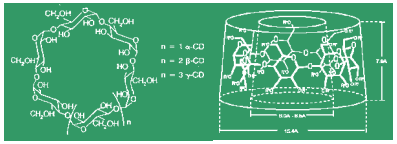
INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides which have received considerable attention due to their ability to include a wide variety of organic and inorganic guest molecules in their hydrophobic cavities.



In the field of environmental chemistry, CDs promote the degradations of certain organic pollutants through the enhancement of their solubility and, therefore, their desorption from soils.

On this basis, this work aims to obtain a laboratory-scale information on the effect of different CDs (β-CD, RAMEB, and HPBCD) on the photodegradation of the herbicide norflurazon (NFL) monitored in the presence of different soil components in water suspensions, in comparison with its photodegradation in the CD-less systems.

MATERIALS AND METHODS

- Herbicide Norflurazon **(NFL)**: 20 mg/L.
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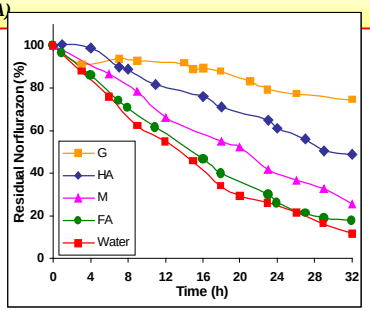
- **Cyclodextrins: 0.01 M.**
- β-Cyclodextrin **(BCD)**
- 2-Hydroxypropyl-β-Cyclodextrin **(HP)**
- Randomly-methylated-β-cyclodextrin **(RM)**

Soil colloidal components: 80 mg/L.
Montmorillonite Swy-1 **(M)**
Synthetic humic acids (Fluka) **(HA)**
Natural metal-fulvic acid complex **(FA)**
Synthetic goethite **(G)**

SUNTEST photoreactor, wavelengths >290 nm.
Norflurazon was analysed by HPLC/DA.

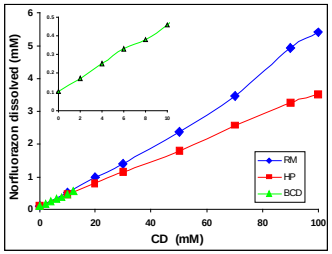
RESULTS AND DISCUSSION

NFL photodegradation profiles in aqueous solution and in suspensions of different soil colloidal components: montmorillonite (M), goethite (G), natural fulvic acids (FA) and synthetic humic acids (HA).



In general, the presence of the different soil components in suspension provoked a reduction in NFL photodegradation rate, due to the screen effect of soil particles and probably to the adsorption of NFL on these colloidal components. In all cases the rate of photodecomposition followed a first-order kinetic.

Phase solubility diagrams of NFL in the presence of different CDs (BCD, HP and RM).

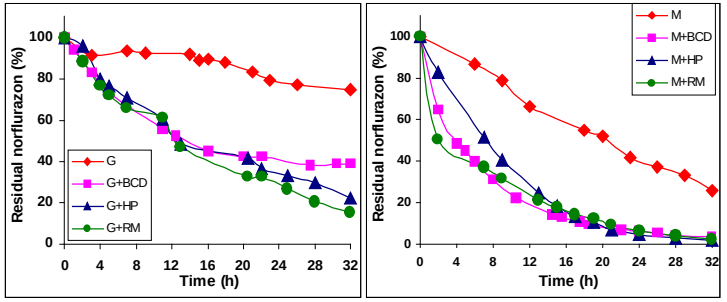


The increase in NFL solubility in the presence of the three cyclodextrins employed indicates the formation of inclusion complexes between the herbicide and the CDs. For the concentration used in photodegradation experiments (0.01M), linear increases up to 1.72, 4.46 and 4.95 fold in NFL solubility in aqueous solution were obtained using BCD, HP and RM, respectively.

First order kinetic constant (K_d) and half live ($t_{1/2}$) for NFL photodegradation in aqueous solution in the absence and in the presence of different soil colloidal components and different CDs. *($t_{1/2}$ in hours; K_d 10^3 h^{-1}).*

	NFL		NFL-BCD		NFL-HP		NFL-RM	
	K_d	$t_{1/2}$	K_d	$t_{1/2}$	K_d	$t_{1/2}$	K_d	$t_{1/2}$
Water	65.3	10.61	80.2	8.6	89.1	7.8	91.1	7.6
G	9.3	74.5	30.0	23.1	54.9	12.6	44.9	15.4
HA	23.7	29.2	27.9	24.8	32.8	17.2	40.2	21.1
FA	57.9	12.0	48.9	14.2	70.8	9.8	91.5	7.6
M	42.0	16.4	108.8	6.4	131.2	5.3	151	6.4

The presence of cyclodextrins (CDs) in aqueous suspensions of soil colloidal components showed an increase of NFL photodegradation, due to the competition generated in these system between the sorption on their surfaces and the formation of inclusion complexes with the CDs. Less NFL molecules are adsorbed on the soil components, increasing their light exposure. Besides, the hydroxyl groups surrounding the CDs cavity can act as photosensitizers, facilitating the photodegradation of the herbicide when it is forming an inclusion complex.



NFL photodegradation profiles in aqueous suspensions of montmorillonite (M) and goethite (G) in the presence of different CDs (BCD, HP and RM).

CONCLUSIONS

The selected cyclodextrins showed an inductive photodegradation effect on the herbicide norflurazon, which could be mainly assigned to the inclusion effects of CDs to catalyze interactions between norflurazon and certain reactive radicals generated by the different colloidal components. This work reveals that the effect of the CDs on the herbicide enhanced solubilization, coupled to an increased photodegradation using CDs as photosensitisers, could be a promising method for pesticide-contaminated soil and water remediation.