Effect of different cyclodextrins on herbicide photodegradation in soil solution.

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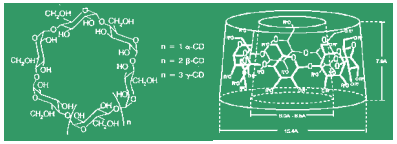
INTRODUCTION

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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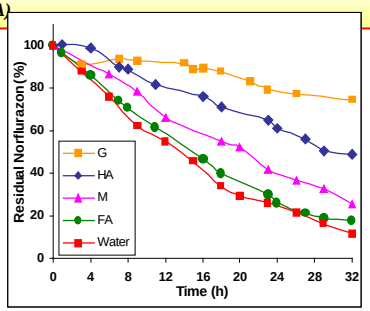
- **Cyclodextrins: 0.01 M.**
- β-Cyclodextrin **(BCD)**
- 2-Hydroxypropyl-β-Cyclodextrin **(HP)**
- Randomly-methylated-β-cyclodextrin **(RM)**

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.

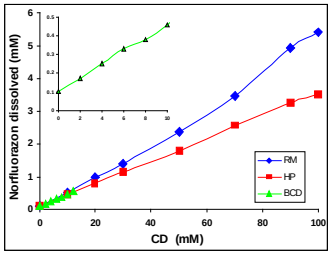
RESULTS AND DISCUSSION

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).

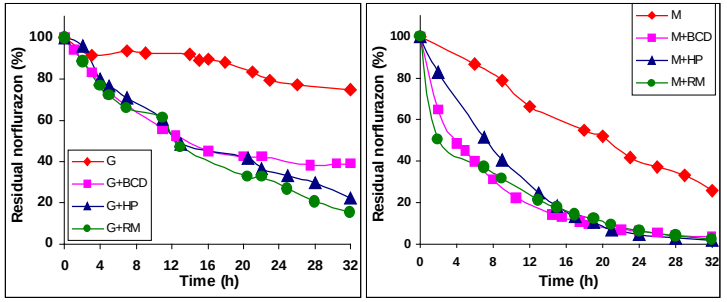


The increase in NFL solubility in the presence of the three cyclodextrins employed indicates the formation of inclusion complexes between the herbicide and the CDs. For the concentration used in photodegradation experiments (0.01M), linear increases up to 1.72, 4.46 and 4.95 fold in NFL solubility in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