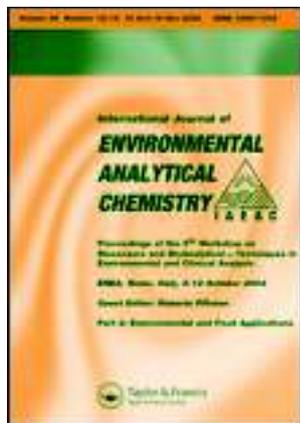


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Angelica Liguori ^a, Maurizio D'auria ^a, Lucia Emanuele ^a, Laura Scrano ^b, Filomena Lelario ^b & Sabino Aurelio Bufo ^b

^a Department of Chemistry, University of Basilicata, Via N. Sauro 85, IT-85100, Potenza, Italy

^b Department of Crop Systems, Forestry & Environment, University of Basilicata, Viale dell'Ateneo Lucano 10, IT-85100, Potenza, Italy

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Reactivity of rimsulfuron in newly formed inclusion combinations by using cyclodextrin and zeolite

ANGELICA LIGUORI[†], MAURIZIO D'AURIA[†],
LUCIA EMANUELE[†], LAURA SCRANO[‡],
FILOMENA LELARIO[‡] and SABINO AURELIO BUFO^{*‡}

[†]Department of Chemistry, University of Basilicata,
Via N. Sauro 85, IT-85100 Potenza, Italy

[‡]Department of Crop Systems, Forestry & Environment,
University of Basilicata, Viale dell'Ateneo Lucano 10, IT-85100 Potenza, Italy

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Extending our investigations on environment protection by agrochemicals diffusion and accumulation, newly formed inclusion combinations of rimsulfuron into zeolite-NaY (Z-NaY) and β -cyclodextrin (β -CD) were studied and compared. The reactivity of the included herbicide under UV-irradiation and in the dark was assessed. Many guest/host ratios were tested: the best results were found using 3 g (6.953 mmol) of rimsulfuron per kilogram of zeolite, with 80% inclusion success (5.562 mmol kg⁻¹), and a 1:2 molar ratio, 190 g of rimsulfuron per kilogram of β -CD with 58% inclusion success. The herbicide Z-NaY-combined underwent rapid and effective (half-life 2–7 h) degradation either catalytically or photochemically, giving rise to different identified by-products. On the contrary, β -CD was able to protect rimsulfuron totally both in the dark and under 24-h direct UV irradiation. On the basis of the obtained results, a different utilization of the two inclusion materials has been suggested.

Keywords: Rimsulfuron; Zeolite-NaY; β -Cyclodextrin; Inclusion compound; Chemical degradation; Photodegradation

1. Introduction

Inclusion compounds are formed by very different molecules of at least two types: the host (H) and the guest (G). Every inclusion compound may be described by the formulations H.G, H1.H2.G1, H.G1.G2, etc. [1]. With the formation of inclusion complex, the functions of the host and guest can be changed: in this manner, one may combine the advantageous properties of the individual host or guest component in the newly formed inclusion compound combinations. The combinations may be utilized in practice in many processes, where an enlarged space inside the host component has to be formed or where the guest component may be stabilized. This is very convenient

*Corresponding author. Fax: +39-0971-206226. Email: sabino.bufo@unibas.it

Table 1. Properties of inclusion hosts used.

β -Cyclodextrin		Zeolite-NaY	
Glucose number	7	Si/Al	2.86
Molecular weight	1135	Unit cell size (Å)	24.65
Cavum diameter (Å)	6.0–6.5	Primary supercages diameter (Å)	12.8
Cavum height (Å)	7.9 ± 1	Secondary supercages diameter (Å)	7.4
Cavum volume (mL mol ⁻¹)	262		
Purity (%)	98%	Purity (%)	98.6
Ash (%)	60.1	Surface area (km ² kg ⁻¹)	900
Water (w%)	13.2 ± 14.5	Water (w%)	9.5 ± 100
Solubility 25°C (g L ⁻¹)	18.5	Na ₂ O (w%)	13.0

in the case of the encapsulation and stabilization of different compounds, inorganic or organic, and also in separation or recovery/remediation processes.

Zeolites are microporous crystalline aluminosilicates with structural features that make them attractive hosts for photochemical applications [2, 3]. Intracrystalline zeolite space is also considered a novel ‘solvent’ [4]. The topological structure of Y-type zeolite consists of an interconnected three-dimensional network of relatively large spherical cavities, termed primary supercages (diameter of about 13 Å); each supercage is connected tetrahedrally to four other secondary supercages through 7.4–7.6 Å windows (table 1). Extra framework cations are necessary for the neutralization of charges due to the presence of tetrahedral aluminium. These cations can easily interact with guest molecules. The charge-compensating cations are known to occupy three different positions in the internal structure of Y-zeolites; the first type (site I), with 16 cations per unit cell, is located on the hexagonal prism faces between the sodalite units. The second type (site II), with 32 cations per unit cell, is located in the open hexagonal faces. The third type (site III), with eight cations per unit cell, is located on the walls of the largest cavity. Only cations at sites II and III are expected to be readily accessible to the organic molecule adsorbed within a supercage [2].

However, the insolubility of zeolites in water or other solvents causes inconvenience in their application, and guest substances may desorb from zeolite at elevated temperatures [5]. Thus, novel materials are sought, and cyclodextrins (CDs) have been chosen not only for their fairly dissolution in aqueous solution, but also for the inclusion complex-forming ability [6–8]. Cyclodextrin is one of the most potential hosts in the supramolecular chemical field. CDs are cyclic oligosaccharides consisting of several glucose units linked by α -1,4 glycoside bonds [1, 9] and have a hollow truncated cone shape with a non-polar, hydrophobic interior and two hydrophilic rims formed by the primary and secondary hydroxyl groups. CDs can reversibly include a variety of guest molecules to form inclusion complexes by non-covalent interaction, and usually the host-guest ratio is 1:1 in solution [10]. In the field of environmental chemistry, the abilities of CDs have been noticed for the availability of enhancing photodegradation of organic pollutants in the presence of sensitizers or catalysts [10, 11].

The contamination of soils, groundwater, and surface water by agrochemicals is currently a significant concern throughout the world. Many of these compounds are a threat to both human health and the environment. In this respect, it is useful to test different technologies with the aim of enhancing the degradation and/or sequestration methods of potentially polluting organics.

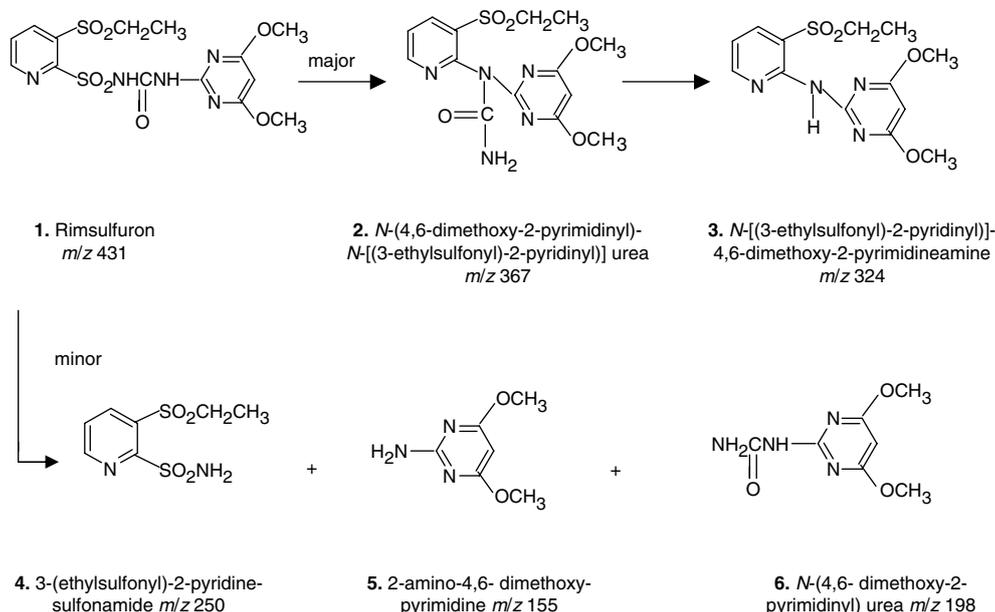


Figure 1. Chemical structure and degradation pathways of rimsulfuron [12].

With respect to pesticide application on crops and soil, a modern class of agrochemicals, named sulfonylureas, has been developed with the aim of increasing the acceptance of the market based on low application rate ($10\text{--}80\text{ g ha}^{-1}$) and selectivity of active ingredients. Rimsulfuron is a selective sulfonylurea herbicide (compound **1** in figure 1) for postemergence control of many crops. Using ^{14}C -labelled rimsulfuron, Schneiders *et al.* [12] showed that its degradation in aqueous solutions and in the soil environment does not depend on irradiation under natural sunlight, though it undergoes hydrolysis reactions. Different results were achieved in a previous study, in which Scrano *et al.* [13] stated that the half-life of the photolysis reaction under simulated sunlight in water ranges from 1 to 9 days at pH 5 and 9, respectively, and the hydrolysis rate is as high as the photolysis rate, and decreases with increasing solution pH. The main metabolite identified in neutral and alkaline conditions as well as in the acetonitrile was compound **3**, *N*-[(3-ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyridineamine; while compound **2**, *N*-(4,6-dimethoxy-2-pyrimidinyl)-*N*-[(3-ethylsulfonyl)-2-pyridinyl] urea (resulting from the intramolecular contraction of the sulfonylurea bridge), and minor metabolites prevailed in acidic conditions (figure 1) [12, 13].

The antagonistic behaviour of adsorption process and chemical degradation with respect to photodegradation on silica, clay minerals and soil was also assessed by Scrano *et al.* [14] and Bufo *et al.* [15], showing that the photochemical degradation of rimsulfuron is strongly affected by retention phenomena.

The aim of this investigation was to study and compare newly formed inclusion combinations of rimsulfuron into zeolite-NaY (Z-NaY) and β -cyclodextrin (β -CD), and assess the reactivity of the included herbicide under UV irradiation and in the dark.

2. Experimental

2.1 Chemicals

Rimsulfuron, *N*-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridine sulfonamide, was purchased as a certified standard substance (purity 97%; MW 431.45) from Dr Ehrenstorfer GmbH (Augsburg, Germany). The solubility of the pure active ingredient is $<10 \text{ mg L}^{-1}$ in distilled water and 7300 mg L^{-1} in buffer solution at pH 7 (25°C); pK_a , 4.1; K_{OW} , 0.034 at pH 7; vapour pressure, 1.1×10^{-8} Torr at 25°C [12].

β -Cyclodextrin, cycloheptaamylose, and Z-NaY were commercially available products purchased from Acros-Organics (Morris Plains, NJ) and Zeolyst International (Valley Forge, PA), respectively; their properties are listed in table 1. All of the other reagents and solvents were of analytical reagent grade or HPLC or pesticide grade, purchased from Sigma-Aldrich (Milan), and used without further purification.

2.2 Sorption procedure

Several attempts were preliminarily performed to find the best inclusion ratios avoiding any rimsulfuron alteration during the preparation of samples.

2.2.1 Z-NaY inclusion. Each experimental sample contained 4 g of Z-NaY, activated at 500°C for 7 h and spiked with 75 mL of 160 mg L^{-1} (0.3708 mM) rimsulfuron solution in 4:1 anhydrous *n*-hexane/dichloromethane. The suspension obtained was stirred 18 h (in the dark) and filtered; the solid residue was washed with 25 mL of *n*-hexane, kept in the dark, and air dried at room temperature. The inclusion powder was immediately assayed as described in section 2.3. The filtrates were collected together and analysed immediately for rimsulfuron residues as described in section 2.4.

2.2.2 β -CD inclusion. A saturated solution was prepared, dissolving 0.1198 mmol (136 mg) of β -CD in 3 mL of methanol, to which 0.0603 mmol (26 mg) of rimsulfuron dissolved in 1.5 mL of diethyl ether was added. The obtained solution was stirred 48 h, and the solvent mixture was removed by means of a rotary evaporator at 40°C under a light vacuum; the solid residue was washed and filtered with 1.5 mL of diethyl ether, dried, and kept in the dark at 4°C until the use. The filtrate was analysed for rimsulfuron residue.

2.3 Irradiation of inclusion complexes

Several samples of powdered inclusion product Z-NaY/rimsulfuron were prepared as detailed in section 2.2.1. Each sample was dispersed in 30 mL of benzene and irradiated for 24 h, with gentle stirring, using a mercury high-pressure arc lamp 125 W (Philips, Eindhoven, The Netherlands) in a thermostatic chamber at 25°C. After predetermined illumination times, samples were removed consecutively and filtered; the solid residue was extracted by vigorous stirring for 30 min and sonication in 25 mL of diethyl ether to recover rimsulfuron and its metabolites included in the host material, then filtered

and extracted again. The different liquid extracts recovered after filtration were mixed together, and the solvent mixture was removed by means of a rotary evaporator at 40°C under a light vacuum. The dried residue was dissolved in 2 mL of mixture 1:1 acetonitrile:methanol and analysed as in section 2.4.

Degradation experiments under UV irradiation were also directly performed on the inclusion powder without its dispersion in benzene. In both cases, control samples were kept in the dark at the same temperature, and the organics were extracted at the same times of irradiated samples. Three replicates were carried out for each experiment.

A considerable number of samples of inclusion product β -CD/rimsulfuron were prepared as in section 2.2.2. Each sample was irradiated in 20 mL of benzenic solvent and extracted following the same procedure used for the zeolite inclusion product.

2.4 Analyses

UV spectra of rimsulfuron in the different environments were recorded on a Cary 2300 spectrophotometer (Varian, Harbor City, CA). The disappearance of the herbicide and appearance of its degradation intermediates were monitored by HPLC-UV and LC/ESI-MS analysis of extracted solutions. HPLC-UV analysis was carried out using a chromatographic system (Thermo, San Jose, CA) equipped with a Spectra System P4000 binary pump, a UV6000 diode array detector, and a solvent degasser. The chromatographic separations were performed with a Discovery C18 column 50 \times 4.6 mm, 5 μ m (Supelco, Bellefonte, PA), using methanol:acetonitrile 0.3 mL min⁻¹ flow with an acetonitrile gradient starting from 40% and increased by 10% at 10 min intervals, with a 30-min total run. The UV detector was set at 254 nm, and the retention time of rimsulfuron was 2.9 min.

Mass analyses were performed by a LCQ classic ion trap mass spectrometer (Thermo) equipped with an atmospheric pressure interface and an electro-spray ionization source (ESI). Positive-ion ESI-MS was chosen for the identification and determination of the active ingredient and its metabolites. The voltage on the ESI needle was set at 5 kV, producing a spray current of approximately 80 mA. The capillary voltage was set at 14 V, and the temperature of the heated capillary was 200°C. The sheath gas (N₂) flow rate used was 60 (arbitrary units), and the auxiliary gas was set to zero (arbitrary units). Total ion current (TIC) and selected ion monitoring (SIM) modes were used to record the abundances of positive moieties. In the full-scan mode, masses were scanned as centroid data from 50 to 800 m/z at a rate of 2 scans per second. The instrumental control, data acquisition, and data processing were performed using the Xcalibur software package (version 1.1, Thermo).

3. Results and discussion

3.1 UV spectra

The UV spectrum of rimsulfuron in benzene presented three absorption maxima at $\lambda_{\max 1} = 210$ nm ($\epsilon_1 = 1.24 \times 10^4$ mmol cm⁻²), $\lambda_{\max 2} = 232$ nm ($\epsilon_2 = 1.02 \times 10^4$ mmol cm⁻²), and $\lambda_{\max 3} = 284$ nm ($\epsilon_3 = 0.90 \times 10^4$ mmol cm⁻²). The first absorption was not revisable in the spectrum of the pure solid compound recorded in reflectance

mode, and the other two signals were shifted to 268 nm and 348 nm, respectively. The relative reflectance spectra of the herbicide into powdered inclusion complexes showed signals weaker than the pure compound with a marked shifting of absorption maxima towards shorter wavelengths: 260 nm and 330 nm for Z-NaY/rimsulfuron combination; 258 nm and 320 nm in the case of β -CD/rimsulfuron inclusion compound. The detected displacement of UV signals can be evidence of the strong interaction of the sheltered herbicide with the host substances.

3.2 Z-NaY/rimsulfuron combination and chemical degradation

Many guest/host ratios were tested: the best result was found using 3 g (6.953 mmol) of rimsulfuron per kilogram of zeolite. In our experiment, Z-NaY was able to retain 80% of rimsulfuron ($2.4 \text{ g kg}^{-1} \equiv 5.562 \text{ mmol kg}^{-1}$) from the mixture of organic solvents used as a reaction medium in the sorption procedure (section 2.2.1). In spite of the noteworthy differences with the retention of rimsulfuron achieved in previous works on silica materials and clay minerals ($0.15\text{--}0.23 \text{ mmol kg}^{-1}$) [14] and soil ($0.11\text{--}0.21 \text{ mmol kg}^{-1}$) [15], we still consider the molar quantity of sorbate to be limited with respect to the widely large surface area of sorbent ($900 \text{ km}^2 \text{ kg}^{-1}$). On the other hand, minimized structural dimensions of rimsulfuron ($12\text{--}14 \text{ \AA}$), calculated using HyperChem[®] software (method PM3), resulted hardly sufficiently compatible with the cubbyholes offered by primary supercages of Z-NaY. This probably means that only site III, with eight cations per unit cell located on the walls of the largest zeolite cavities, was involved in the retention of the herbicide molecules, mainly by means of an electrostatic interaction between cations and sulfonamide (sulfo-ureic) moiety in consideration of the negative charge (-0.83) of oxygen atoms (calculated with the same software as above), and in analogy with the ionization process depicted in Bufo *et al.* [15]. With regard to the involvement of the sulfo-ureic portion into the sorption process, the finding of metabolite **3** (figure 1) extracted from the inclusion powder kept in the dark as control sample is remarkable. In fact, compound **3** is deprived of the sulfo-ureic fragment, and it is the unique metabolite extracted and identified at different experimental times from samples kept in the dark. Moreover, the appearance of this metabolite followed the same evolution of disappearance of the mother molecule. From the achieved result, we postulate a catalytic chemical effect of this kind of zeolite on the degradation of rimsulfuron: perhaps a sort of catalysed hydrolysis, whose occurrence is not confirmed for other pesticides in the current literature in spite of the largely established activity of different kinds of acidic zeolite commonly used in petrolchemistry [16] or water remediation from other organic pollutants [17, 18], and notwithstanding several papers are reporting results on pesticides' removal from polluted waters by absorption on zeolite [19] or their photoassisted degradation in TiO₂ coated zeolite [20, 21].

3.3 Z-NaY/rimsulfuron photochemical degradation

For each experiment, kinetic parameters were calculated by means of integrated equations describing zero-, first-, and second-order reactions using mean values of triplicate data. According to Snedecor and Cochran [22], the best fit was checked by the least-square method of estimation (data not shown). Apparently, all measured

degradation rates of the retained herbicide into the inclusion combinations, either in the darkness or under irradiation conditions, were best fitted by a Langmuir–Hinshelwood-type equation (table 2), which describes a second-order reaction [23, 24]:

$$D_t = \frac{D_{\max}t}{(t + t_{0.5})}, \quad (1)$$

where: D_t = rimsulfuron degraded at time t ; D_{\max} = maximum amount of degradable rimsulfuron (asymptote); and $t_{0.5}$ = half-life.

The included herbicide was easily degraded either in the dark or under UV radiations with (figure 2a) or without (figure 2b) the use of benzene as dispersing solvent. Several differences can be noticed. In the benzenic dispersion, degradation was remarkably accelerated by light irradiation ($t_{0.5}$, 2.0 h) with respect to the dark reaction ($t_{0.5}$, 5.3 h). The photochemical response was more effective when the dispersion solvent was used (95% of rimsulfuron degraded up to 10 h; 98% in 24 h), as compared with the direct irradiation of the inclusion powder (68% of rimsulfuron degraded up to 10 h; 89% in 24 h). The rationale of the accelerated degradation achieved in the benzenic suspension may be given two different criticisms: (1) an indirect photoreaction induced by the energy transfer from the aromatic solvent to the herbicide molecules; (2) the enormous difference between the photoactive surface of the dispersed system, whose cylindrical geometry allowed a 360° irradiation, and that of the dried inclusion powder, which was reached only by UV radiation perpendicularly diffused on particles' surfaces.

Table 2. Kinetic parameters of rimsulfuron degradation in the darkness and under irradiation (Z-NaY inclusion): (r^2), determination coefficient; ($t_{0.5}$), half-life; (D_{\max}), maximum degradable quantity or asymptote^a (values were obtained on the basis of three replicate experiments).

		r^2	D_{\max} (mmol kg ⁻¹)	$t_{0.5}$ (h)
Z-NaY inclusion dispersed in benzene	Under irradiation	0.9964	6.03	1.98
	In the dark	0.9966	4.84	5.30
Z-NaY inclusion dried powder	Under irradiation	0.9990	6.57	7.23
	In the dark	0.9958	5.14	3.34

^a r^2 , $t_{0.5}$, and D_{\max} were calculated using the linear form of equation (1): $t/D_t = t_{0.5}/D_{\max} + t/D_{\max}$.

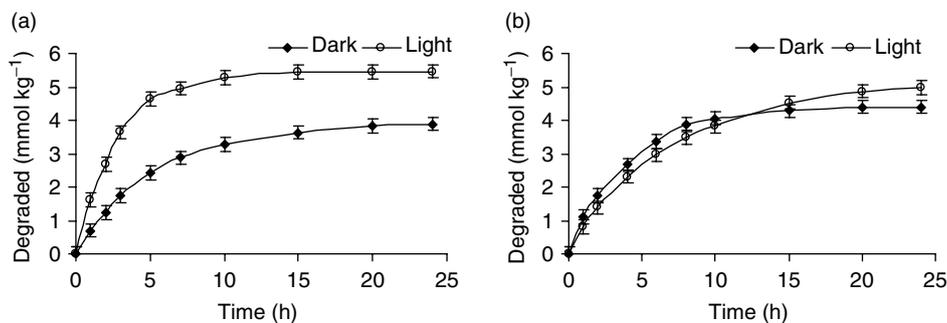
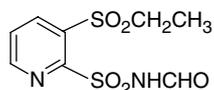


Figure 2. Curves depicting the rimsulfuron degradation in Z-NaY inclusion during the experimental time: (a) benzenic dispersion, (b) dried powder; (○) under UV irradiation; (◆) in the dark.



7. 3-(ethylsulfonyl)-2-pyridine-
(*N*-carbonyl)-sulfonamide

Figure 3. Structure of compound **7** identified by mass spectroscopy at m/z 278 in irradiated inclusion zeolite/rimsulfuron.

Curves depicting the evolution of degradation in the darkness and in the light, relative to the samples not dispersed in a liquid phase (figure 2b), show a crossing point at 10.6 h. This means that in the first part of the reaction, the chemical degradation was prevailing on the photodegradation until the concentration of remaining rimsulfuron was reduced to $1.653 \text{ mmol kg}^{-1}$; after the crossing point, the dark reaction was not as effective, whereas the UV effect was powerfully continuing.

Degradation byproducts arising in the inclusion product zeolite/rimsulfuron were identified in all the diethyl ether extracts at different times. Qualitative results were similar either when the dispersion solvent was used or not. In the first extract (to), as well as from all samples kept in the dark, only metabolite **3** (figure 1) was identified. In irradiated samples extracted for up to 10 h, compounds **3** and **5** were found, together with a new metabolite **7** at m/z 278, whose structure we propose as illustrated in figure 3. In the last extracts, it was possible also to identify compound **6**. The metabolites indicated in figure 1 as compounds **2** and **4** were not found in any sample. On account of its low stability, the impossibility of recognizing compound **2**, which was previously found only in acidic environments [12, 13], was not surprising. In the case of compound **4**, we suppose that it might have been the final product of the photolysis of the newly identified compound **7**, which in our experimental conditions was not transformed any further.

The ability of Z-NaY to favour degradation of rimsulfuron, and probably other sulfonylureas, either in the dark or under UV irradiation could be utilized for cleaning procedures of limited amounts of waste waters, such as those derived from handling this kind of herbicides (and other pesticides) at the farm level, especially leakages and spillages during the filling of dispensers and sprayers, rinsing of spraying equipments, disposal and storage of washing water, preparation of pesticide/water mixtures, and so on [25].

3.4 β -CD/rimsulfuron combination

Also, in the case of the β -CD/rimsulfuron complex, different trials were attempted: the best guest/host ratio was met using a 1:2 molar ratio (190 g of rimsulfuron per kilogram of β -CD). Only 58% of the herbicide was retained in the inclusion host with a final molar ratio of 0.29 (about $110 \text{ g rimsulfuron kg}^{-1} \beta$ -CD). We postulate that a steady inclusion complex grew up in solution between β -CD and the herbicide by means of the numerous primary hydroxyl groups, which can easily form hydrogen bonds with $-\text{SO}_2$ and $-\text{C}=\text{O}$ groups of rimsulfuron.

After the 24-h trial, the sorbed rimsulfuron was totally recovered without any apparent chemical alterations from samples being irradiated or from being kept

in the dark. In other words, the host substance was able to retain and fully protect rimsulfuron from UV irradiation. This result allowed us to consider that, since the guest molecule included into β -CD remains relatively isolated from the external environment, inclusion combinations could be used to obtain slow-release formulations, extending in time the effectiveness of the active ingredient and reducing its dispersion in the environment [26]. Another possible use of CDs is based on the amphiphilic properties of these compounds and their high capacity to easily capture both hydrophobic and hydrophilic organic contaminants from sediments and soils enhancing the microbiological degradation of these substances [27].

4. Conclusion

Z-NaY and β -CD were able to form new inclusion combinations with the herbicide, but the inclusion potential towards rimsulfuron, and probably other sulfonylurea herbicides, appeared remarkably different. The β -CD inclusion efficiency was about 50-fold higher than Z-NaY (255.4 and 5.562 mmol kg⁻¹, respectively). Also, the action of the host towards the herbicide was notably diverse. The inorganic material favoured rapid degradation of rimsulfuron either in the dark or under UV irradiation, whereas the organic basket was able to protect the agrochemical in both conditions. This behaviour indicates a different possible use of the tested materials. Z-NaY inclusion could be employed as a cleaning technology with the aim of enhancing the degradation of this kind of herbicide in restricted environments; meanwhile, β -CD could be used for the recovery of the herbicide residues from sediments or soil in environmental remediation procedures. Moreover, β -CD could be utilized to obtain commercial formulations planned to prolong the activity of this chemical in soil. The combination of sulfonylureas with the bio-degradable β -CD could avoid the introduction in the formulations of usual additives that often cannot be rapidly destroyed by soil microorganisms.

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