Photostabilization of the herbicide norflurazon microencapsulated with ethylcellulose in the soil–water system

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ABSTRACT

Ethylcellulose-microencapsulated formulations (ECFs) of norflurazon have been shown to reduce leaching, maintaining a threshold concentration in the topsoil than the commercial formulation (CF). Since photodegradation contributes to field dissipation of norflurazon, the objective of the present work was to study if such formulations can also protect from its photodescomposition. For this purpose, aqueous solutions of CF and ECFs, containing the most important soil components (goethite, humic and fulvic acids and montmorillonite) were tested. To get a more realistic approach, studies in soil were also performed. The results were well explained by a simple first order model. DT_{50} value was 3 h for CF under irradiation, which was considerably lower than those corresponding to the systems where ECF was used (35 h for ECF; 260 h for ECF–goethite; 53 h for ECF–humic acids; 33 h for ECF–montmorillonite; and 28 h for ECF–fulvic acids). ECF protected against photodegradation in both aqueous solution and soil due to the gradual release of the herbicide, which reduced the herbicide available to be photodegraded. These lab-scale findings proved that ECF could reduce the herbicide dosage, minimizing its photolysis, which would be especially advantageous during the first hours after foliar and soil application.

1. Introduction

Transformation of pesticides in the environment is a highly complex process affected by biological and physicochemical factors. Photodegradation is one of the most destructive pathways for pesticides after their field application. Water is the most studied environmental compartment in which the pesticides reside. This is because of the need to predict the photochemical transformations of xenobiotics in aquatic environments [1–3]. However, plants, especially, leaf surface, and soil surface are the first reaction environment for a pesticide after application. Photolysis in such situations becomes an important mechanism of pesticide dissipation. The heterogeneity of both, soil and plant, together with the capricious transmission of sunlight onto these media makes the photolysis on them difficult to understand [4]. Therefore, additional studies should be conducted to determine photolysis rates on such surfaces, since few studies have been reported so far. Recently, new methodologies with different degree of complexity have been developed to study the pesticide photochemistry on leaf and soil surfaces [5–8]. However, no standardized

predictive method for assessing the importance of photolysis on soil surfaces has been reported yet. Likewise, soils are a complex system containing several variable parameters, each of which can affect the photochemistry of a chemical adsorbed on the surface. For instance, both photoproducts and photolysis rates of several pesticides have been shown to be affected by moisture content, mineral base, texture and organic matter content [4,9,10].

Pesticide photolysis on soil surface results in a loss of its efficacy in controlling weeds and pests [11]. Thus, the application rate of the pesticide is increased to overcome its photodegradation. In this sense, several approaches have been used to reduce the environmental and economic costs of pesticides losses by photolysis, being one of them the development of photo-stable formulations of pesticides. Most of them rely on in the use of clay and modified clays with a different degree of photo-stabilization [12,13]. Information about obtaining pesticide encapsulated formulations by using other materials or a cheaper technology has been barely dealt. Effects of cyclodextrins on the photodegradation rates of organophosphorous pesticides were studied by Kamiya and Nakamura [14]. Demchak and Dybas [15] showed a decreased photodegradation of a natural pesticide by its encapsulation in protein zein. Huston and Pignatello [16] reported alachlor photodegradation from its microencapsulated commercial formulation when studied a waste water treatment. No further studies have been reported, which

implies that the information about pesticide photodegradation from microencapsulated formulations is scarce so far.

Norflurazon (NFZ) is a fluorinated pyridazinone herbicide that is registered for soil-applied usage on cotton, soybean, tree fruit and nut crops, citrus, and cranberries [17]. Unfortunately, this herbicide suffers losses when it is applied to soil [18]. Losses by leaching in sandy soil columns have been also observed by Singh et al. [19] and Morillo et al. [20]. To prevent herbicides leaching, ethylcellulose-microencapsulated formulations (ECFs) of norflurazon and alachlor have been prepared by using a simple and non-expensive technique [21,22]. These formulations not only provided a suitable release, reduced leaching, while maintaining the threshold concentration of the herbicide in the topsoil [23–25], but also remained the herbicidal activity longer than the commercial formulation [26,27]. Since photodegradation contributes significantly to field dissipation when norflurazon remains on the soil surface, with a half-life of 41 days [28], it would be interesting to study if such norflurazon formulations could also protect it from photodegradation. Therefore, the aim of the present work was to examine the effect of the microencapsulation in ethycellulose (EC) on the photodegradation of the herbicide NFZ. For this purpose, the photoprotective effect of CF *vs*. ECFs was tested by using different aqueous solutions containing the most important soil components (goethite, humic and fulvic acids and montmorillonite). Since up to 50% of the norflurazon initially applied as ECF remained in the topsoil layer in soil columns [23] it would be interesting to investigate how the microencapsulation in EC could protect NFZ at this soil level, which is also the most exposed to sunlight. Considering this, a realistic study, using an agricultural sandy soil has also been performed.

2. Materials and methods

2.1. Chemicals

Norflurazon Technical grade (97.8% purity) and its commercial formulation (Zorial 80, content of norflurazon 80%) were kindly supplied by Syngenta Agro S.A. (Barcelona, Spain). Ethylcellulose (30–50 mPa, 48–49.5% w/w as ethoxyl) was purchased from Fluka (Buchs, Switzerland). Polyvinyl alcohol (PVA) with MW 30,000–70,000 was obtained from Sigma (St. Louis, USA). HPLC-grade acetronitrile, methanol, and chloroform were purchased from Merck (Darmstadt, Germany). All reagents were of analytical grade.

2.2. Soil

Soil surface sample (0–20 cm depth) was collected, air-dried, sieved through a 2 mm sieve, and stored in plastic containers until used in the experiments. The soil used was a loamy sand (classified as Typic Xeropsament) with 84 g/kg clay, 40 g/kg silt, 876 g/kg sand, 9.2 g/kg organic matter, pH 8.0, 69 g/kg calcium carbonate, and a cationic exchange capacity of 4.8 cmol/kg.

2.3. Soil colloidal components

SWy Montmorillonite (Mo, from Source Clay Minerals Repository, USA); synthetic humic acid (HA, from FLUKA); natural metal–fulvic acid complex (FA) extracted from a Typic Haphorthod soil, Scotland [29], with an iron content three times that of aluminum (22.16% Fe and 7.54% Al); synthetic acicular goethite (Go) with a specific surface area of 43 m^2 g^{-1} and point zero of charge 8.2 [30].

2.4. Microsphere preparation and characterization

Using a previously described procedure [22], the ethylcellulose-microencapsulated formulation was obtained by the oil-in-water emulsion solvent evaporation technique, using EC as the polymer and PVA as the emulsifier. Briefly, EC (1 g) was dissolved in 15 mL of chloroform. Norflurazon (0.2 g) was dissolved in this polymer solution at room temperature. The herbicide–polymer solution was then emulsified into an aqueous phase by dropwise addition into 150 mL of aqueous solution containing 112.5 mg (0.075%) of PVA with stirring at 600 rpm. The ratio of organic to aqueous phase was 1/10. After 24 h of stirring to allow the total evaporation of the inner organic phase, the microspheres obtained were filtered and washed with 250 mL of distilled water to remove any undesired residuals. The product was dried in vacuum desiccators until a constant weight was obtained. All experiments were performed in triplicate. The herbicide loading (amount of herbicide encapsulated by the microspheres) and encapsulation efficiency (amount of herbicide encapsulated with respect to the herbicide used) of microspheres were 15.9% and 78% (w/w), respectively, as previously shown in Sopeña et al. [23].

2.5. Photochemical procedures

Photodegradation studies have been carried out with a Suntest CPS photoreactor (Heraeus, Hanau, Germany) equipped with a Xe lamp (500 W/m^2) with a permanent filter, which selects wavelengths ≥290 nm.

2.5.1. Experiments in aqueous solution

An aqueous NFZ suspension (250 mL, 20 mg L^{-1}) applied as CF and ECF was magnetically stirred and irradiated in quartz flasks during 32 h. Previous studies with the herbicide norflurazon had shown that the time of 32 h is fair enough to get a reliable evaluation of the herbicide photodegradation in aqueous solutions [31]. The same experiment was carried out in the presence of 20 mg of different soil components. Dark control experiments were conducted in a similar manner over the irradiation periods but flasks were covered with aluminum foil. All experiments were carried out in triplicate. Samples collection and subsequent filtration (0.22 μm Millipore glass fiber membrane) was carried out at different time intervals. NFZ quantification in the samples was performed by HPLC (see below). At the end of the experiments, the ECF-suspensions were centrifuged (10,000 × g for 10 min) to eliminate the majority of water and the rest was lyophilized. The solids collected were extracted with methanol (recovery was 97.5%).

Degradation curves were fitted to three kinetic models: a simple first-order equation, a first-order multicompartment (Gustafson and Holden) model and a first-order sequential (hockey-stick) model. Parameters were optimized according to recommendations by FOCUS [32] using the least-squares method with Microsoft Excel Solver. Simple first-order kinetics (Eq. (1)) was found to be the best descriptor for the experimental data [33]. The linearized form of Eq. (1) (Eq. (2)) was used to calculate the degradation constants (k):

$$Ct = C_0 e^{-kt} \tag{1}$$

$$\mathrm{Ln}\,Ct = \mathrm{Ln}\,C_0 - kt \tag{2}$$

and the time required for 50% disappearance (DT$_{50}$) of NFZ (Eq. (3)), as follows:

$$\mathrm{Ln}\,C_{50} = \mathrm{Ln}\left(\frac{C_0}{2}\right) = \mathrm{Ln}\,C_0 - kt_{50}$$
$$t_{50} = \mathrm{Ln}\frac{2}{k} = \mathrm{DT}_{50} \tag{3}$$

where Ct is the concentration of pesticide remaining in soil ($mg\,kg^{-1}$) at time t (h), C_0 is the initial concentration of pesticide ($mg\,kg^{-1}$) and k is the rate of degradation (h^{-1}).

2.5.2. Experiments in soil

Sterilized soil (10 g) was mixed in triplicate with 1 mg of norflurazon applied as CF and ECF and then shaken thoroughly for 24 h. After mixing, the samples were transferred to Petri-dishes (13 cm), which provided a surface of $132.7\,cm^2$ and a soil layer thickness less than 1 mm. Previous studies have shown that when soil thickness was of 1.5 mm or greater, sunlight penetration is very slight [34]. The soil moisture content was maintained at field capacity throughout experiment by difference of weight, adding sterilized water when needed. 1 g of treated soil (dry basis) was sampled at different times (0, 6, 14, 22, 28, 34, 60, 94 h). The NFZ remaining in each soil sample was extracted with 6 mL of methanol in centrifuge tubes, which were shaken by using a vortex for 3 min and later on allowing that soil was settled down. Quantification of NFZ was made by HPLC (see below). Dark controls were also performed in the same manner by covering the Petri-dishes with aluminum foil. All experiments were performed in triplicate.

2.6. Analysis of norflurazon and its main metabolite

NFZ samples were analysed by HPLC under the following conditions: mobile phase, 50:50 acetonitrile/water; flow $0.5\,mL\,min^{-1}$; chromatographic column, Kromasil C18 (15×0.40 i.d.) (Teknokroma, Spain); fluorescence detector (Shimadzu RF-10 A XL) at excitation wavelength of 310 and emission 405 nm. The retention time for norflurazon under these conditions was 6.5 min. Limit of detection was $0.01\,mg\,L^{-1}$.

NFL metabolite was determined by employing a HPLC/MS instrument (Waters) under the following conditions: mobile phase, Milli-Q water with formic acid 0.1% (60%) and acetonitrile (40%); a flow rate of $0.3\,mL\,min^{-1}$; a C18 silica-based analytical column, Xterra TM MS 2.1 mm $\times$ 150 mm $\times$ 5 µm. Column effluent was directly input into the electrospray ionization (ESI) interface operating in the positive ion mode. The characteristic ion used for analysis was m/z 304, corresponding to the molecular weight of the herbicide protonated form. A Waters ZQ 2000 Detector (single quadrupole) mass spectrometer (Waters, Milford, MA) with a Z-spray–electrospray interface was used. Desolvation and cone gas was nitrogen which flow was set to approximately 200 and $50\,L\,h^{-1}$, respectively. Capillary voltage of 3.5 kV was used in positive ionization mode. The source temperature was set to 80 °C and the desolvation temperature to 200 °C. Dwell times of $0.20\,s\,scan^{-1}$ were chosen. Data station operating software was MassLynx v4.0.

2.7. Statistical analysis

Photodegradation data were subjected to ANOVA analysis and significant differences ($p < 0.05$) determined by least significant differences (LSD) comparisons to identify if photoprotective effect of ECF was significantly different from CF as well as to test how the presence of soil colloidal components can provide any significant differences on the NFZ photostability observed from ECF.

Stepwise multiple linear regression analysis was used to identify predictive equations for the herbicide photodegradation from ECF based on soil components variables, in order to see which variable made a more significant contribution to norflurazon photodegradation in aqueous solution. Parameters were added to the model in order of significance, non-significant ($p > 0.05$) variables were eliminated, leaving only significant variables at $p \leq 0.05$ in the final model.

All statistical analyses were performed using the statistical analysis program SPSS® version 16 (SPSS Inc., Somers, NY 10589, USA).

3. Results and discussion

3.1. Photodegradation of norflurazon

As shown in Fig. 1a, the commercial form of NFZ provided an exponential decay in the amounts of the herbicide remaining in solution under irradiated conditions (CF exposed), whereas the NFZ kept almost unaltered in dark experiments (CF dark), which provides a clear evidence of the great degradative effect of the light on NFZ stability in both water and soil (Fig. 1b), with almost 100% and 60% degraded, respectively. The irradiation of NFZ in both soil and aqueous solution produced desmethylnorflurazon (DM-NFZ) as main photodegradation product, observed by the mass fragment of 289.60 (m/z) obtained by HPLC/MS. A very good agreement was observed between the amount of DM-NFZ detected and NFZ degraded (data not shown). It has been previously reported that the major photodegradation pathway of NFZ involves the loss of methyl group (demethylation) and the chloro group (dechlorination), resulting in the formation of desmethylnorflurazon (DMNFZ) and deschloronorflurazon (DCMNFZ) [35,36].

3.2. Photostability of NFZ formulations in water and soil

As shown in Fig. 1a, the herbicide release from the microencapsulated formulation to the aqueous solution (ECF dark) was greatly delayed in comparison with that from the commercial formulation (CF dark), in which almost 100% of the herbicide was kept in solution throughout the experiment, and consequently available to be photodegraded. The reason is that the herbicide is entrapped in the polymer and has to diffuse out from EC microspheres into the outside sink solution [22]. The herbicide releasing from ECF was
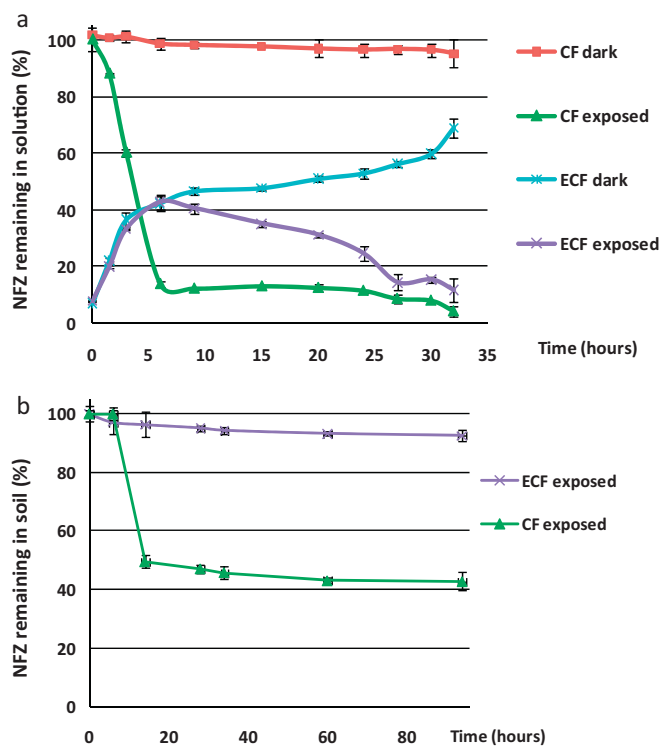

Fig. 1. Norflurazon‡ in solution from microencapsulated (ECF) and commercial (CF) formulations in water (a) and soil (b) during the photodegradation study [‡Values are mean of three replicated].

Table 1
Norflurazon in solution and residual[a] (%) after photodegradation experiments in aqueous solution.[b]

|	Dark experiments		Irradiated experiments	
	NFZ In solution	NFZ Residual	NFZ In solution	NFZ Residual
CF	94.9 (±4.9)	94.9 (±4.9)	4.02 (±1.8)	4.02 (±1.8)
ECF	68.3 (±3.4)	97.2 (±7.8)	11.6 (±3.9)	43.3 (±6.0)
ECF + FA	57.6 (±5.9)	93.8 (±7.4)	3.2 (±3.9)	45.6 (±9.6)
ECF + Mo	53.3 (±4.4)	98.5 (±8.0)	2.4 (±3.9)	49.0 (±6.6)
ECF + HA	63.1 (±3.1)	94.5 (±8.2)	22.4 (±3.9)	59.2 (±8.6)
ECF + Go	72.1 (±2.5)	98.7 (±6.4)	70.3 (±3.9)	96.2 (±8.2)

[a] NFZ in solution plus NFZ encapsulated.
[b] Values are mean of three replicated (±standard deviation).

nonlinear (ECF dark), characterized by an initial fast release in the first few hours. This initial rapid discharge results from the NFZ located in surface of the particles [22,37]. Afterwards, lower constant concentrations of NFZ were released over a longer period of time, which is due to the lengthening of the diffusional pathway of the herbicide through the polymer [38]. When the formulation ECF is exposed to the light (ECF exposed), this sustained release compensates the losses by photodegradation of NFZ in aqueous solution, and even no NFZ photodegradation was observed during the first 6 h of light exposition (Fig. 1a). On the contrary, only 12% of the NFZ applied as CF was detected in solution after 6 h (CF exposed), since the herbicide is immediately released to the media and thus completely available for its degradation. This is the reason why the residual NFZ applied as ECF was approximately a 40% higher than that applied as CF at the end of the experiment (Table 1). The residual NFZ results from the NFZ in solution under irradiation plus NFZ that remains encapsulated.

When NFZ microspheres are applied to the soil (Fig. 1b), almost 100% of the initially applied NFZ was detected all over the experiment (ECF exposed). In contrast, 60% of the initially applied NFZ as CF was photodegraded at the end of the experiment (CF exposed). This fact shows the photoprotective effect provided by the microencapsulation. Dark controls for both ECF and CF were not shown, since they kept unaltered after 96 h. The slower NFZ photodegradation of CF formulation observed in soil compared to that in water can be explained by the screening effect of the soil matrix, which slows down the dissipation process [5,39].

The encapsulation in ethylcellulose itself acts as a physical barrier, in which the encapsulated NFZ is protected against the action of the light for some period of time. This could explain that the residual NFZ (NFZ in solution plus NFZ encapsulated) in the irradiated samples was much higher when it was applied as ECF (43.3%) than that obtained from CF (4.02%) after 32 h (Table 1). Considering the results shown in Fig. 1a, curves from dark control and irradiated samples are overlapped for first 6 h, suggesting that the light had not degradative effect until this time. This would imply that EC could exhibit a protective effect on NFZ photodegradation, even when the herbicide is not encapsulated. After 6 h, the released NFZ from ECF in the exposed samples begins to be degraded. To confirm this hypothesis a simple test was made by using the same photoreactor conditions, but a blank of microspheres without NFZ encapsulated were suspended in 250 mL of an aqueous solution of commercial NFZ (20 ppm). After 6 h, 97% of the initially dissolved NFZ was unaltered in presence of EC empty microspheres (Fig. 2b). This could be explained by a screening effect of the EC particles (physical action) coupled with a competition between NFZ and EC for the available photons, and an energy transfer processes between both herbicide and polymer (chemical action). Demchak and Dybas [15] studied the photostability of abamectin in protein zein microspheres, which was enhanced due to retarded reaction between oxygen and the diene chromophore of abamectin in presence of
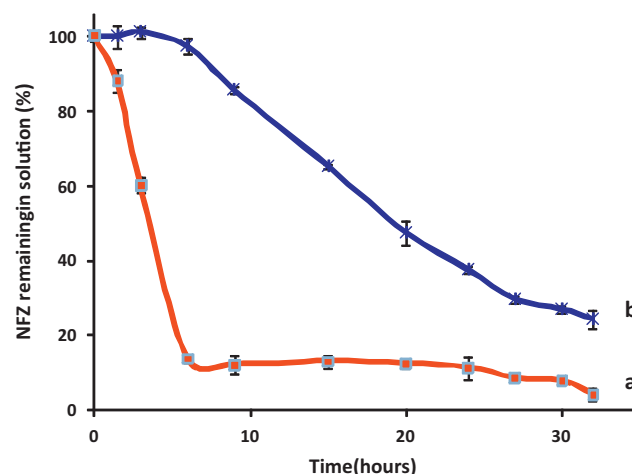
Fig. 2. Irradiation of commercial NFZ aqueous solution (20 mg L^{-1}) (a) and in the presence of empty EC microspheres (non-encapsulated NFZ) (b) [‡Values are mean of three replicated].

light. These authors stated that zein could act as a quencher of singlet oxygen (chemical action) and/or oxygen barrier (physical action).

3.3. Influence of soil components and microencapsulation on NFZ photodegradation in aqueous solution

In order to know which of soil colloidal components are involved in the NFZ photodegradation process, experiments were carried out in the presence of goethite, fulvic acid, montmonillonite (Mo) and humic acid (HA). The percentages of NFZ remaining in solution in the presence of different soil colloidal components are shown in Fig. 3 and greatly varied for each soil component considered. On the other hand, the percentages of residual NFZ in the system (not degraded NFZ, in solution + encapsulated) were plotted versus irradiation time, fitting the data to a simple first order model (Fig. 4). Degradation constants (k) and DT$_{50}$ values obtained ranged from 0.002 to 0.22 h^{-1} and from 260 to 3 h, respectively. The mean scores and deviations for the NFZ in solution and residual for each soil component after photodegradation experiments were presented in Table 1.

In the case of Go, although previous studies have reported that the photodegradation rate of some organic molecules is related to their sorption ability to the oxide surface, NFZ has not been found to be adsorbed on Go [31,40], which obstruct the action of photons on the herbicide molecule. In the present work, the 70.3% of the applied NFZ remained in solution in the presence of Go, which is quite similar to the percentage obtained in the corresponding dark experiment (72.1%) that shows the released NFZ (Table 1). This fact indicates that practically all the NFZ released into aqueous media has kept unaltered, but not adsorbed on the oxide surface, and thus greatly protected against its photo-descomposition (97.5% of the NFZ initially applied has not been degraded) (Table 1). In fact, exposed and dark profiles of the NFZ remaining in solution were almost coincident (Fig. 3a), which provides a visual evidence of this. This high photo-protection can be explained by the combination of both the screening effect of Go and the slower gradual release provided by EC microspheres. The high photoprotective effect of Go is observed also in Fig. 4c, since the DT$_{50}$ value obtained was the highest (260 h).

In the absence of soil components, the final residual NFZ from ECF formulations was 43.2% under irradiation, whereas this value enhanced to 59.2% in the presence of HA. Similarly, DT$_{50}$ values increased from 35 to 53 h when HA were present in the
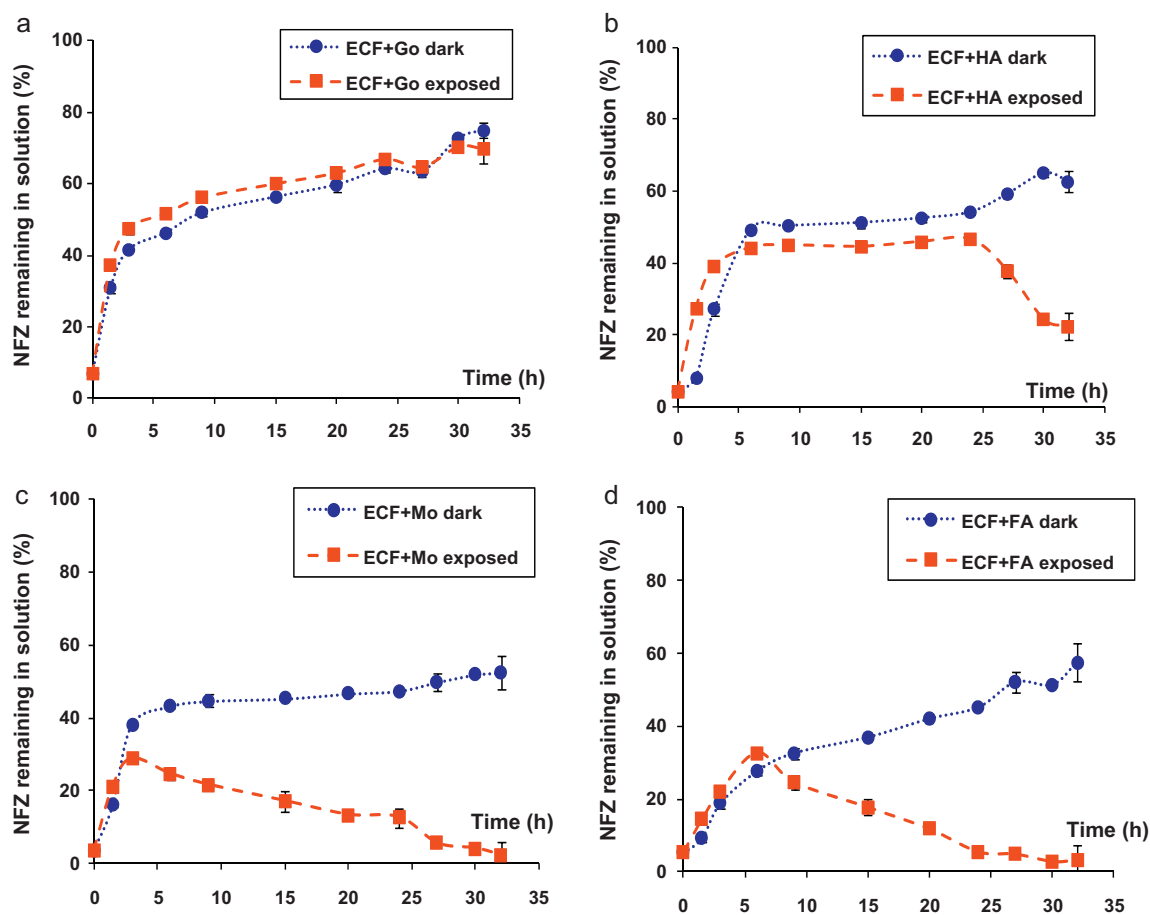
Fig. 3. Norflurazon remaining in solution from microencapsulated (ECF) formulations during photodegradation studies in aqueous suspensions of different soil components [‡Values are mean of three replicated].

NFZ-microspheres suspension. This indicates that this soil component also provided a high photo-protective effect, but lower than Go did (Table 1, Fig. 4d). In some previous studies, it has been shown that HA act as photo-sensibilizer by photo-induced radical generation [41], but this effect has been demonstrated to depend on the pesticide affinity for the generated free radicals [42]. Conversely to Go, HA protection can be attributed to the NFZ adsorption on this component, which would cause a deactivation of the excited herbicide molecule [40], although only a small percentage of NFZ (about 5%) seems to be adsorbed on HA (Table 1) comparing ECF dark controls in water and in the presence of HA. Additionally, a screening effect of HA can also contribute to explain its photoprotective effect, as reported with certain pesticides in aqueous solution [43,44]. Graphically (Fig. 3b), HA clearly protected NFZ against decomposition for 24 h, afterwards the amount of herbicide remaining in solution under light conditions progressively declined, being lower than that detected in the absence of light. Other authors have also reported a decreasing of the pesticide photodegradation in presence of HA [8,45].

In presence of Mo, only 49% of the applied herbicide remained in the system at the end of the irradiated experiment versus 43.3% in absence of the clay mineral (Table 1). It indicates that Mo slightly protected the herbicide against photodegradation. However, this is contradictory with DT_{50} and k-values for ECF and ECF in the presence of Mo, which are quite similar (Table 1, Fig. 4b and 4e). No statistical differences ($p > 0.05$) were found in the rate of NFZ-photolysis in both cases. As shown in Fig. 3c, no photodegradation was observed during the first 2 h. Afterwards the amounts of NFZ were progressively declining to 13% after 24 h and finally

dropped off at the end of the experiment, that is, almost all the released NFZ (53.3%) was degraded (Table 1). Some authors have reported the photostabilization of bensulfuron-methyl after being adsorbed in clay minerals [9], whereas other authors have reported that clay minerals enhance the photolysis of metolachlor in water [46]. Undabeytia et al. [12] observed increased photodegradation of norflurazon when the herbicide was irradiated in an aqueous suspension containing Mo. It was attributed to the attack of hydroxyl radicals produced by the clay under irradiation. However, it has been previously found to be dependent on the concentration of Mo in the aqueous media. In this sense, Villaverde et al. [31] observed an increase of NFZ photo-degradation rate as Mo concentration increased. It was because of higher concentration of the clay yielded higher amounts of NFZ absorbed and available to be attacked by reactive species formed at the clays surface. The results found here support this, although in the present work the NFZ concentration in the aqueous media was gradually increasing with time and Mo concentration was fixed (80 mg L^{-1}). The Mo concentration used here coincides with the lowest concentration used by Villaverde et al. [31], which had provided a light photostabilization of the herbicide. During the first 2 h, NFZ released into aqueous suspension was very low to be susceptible to be absorbed and attacked by active radicals on the Mo surface. At this time, the screening effect provided by Mo protects the herbicide against its photodegradation. However, longer periods of irradiation rendered a higher number of reactive species attacking NFZ on the clay mineral. The adsorption of NFZ on Mo is supported by the decrease in the amount of NFZ remaining in solution (15%) observed when compared the ECF dark controls in water and in the presence of Mo after 32 h (Table 1).
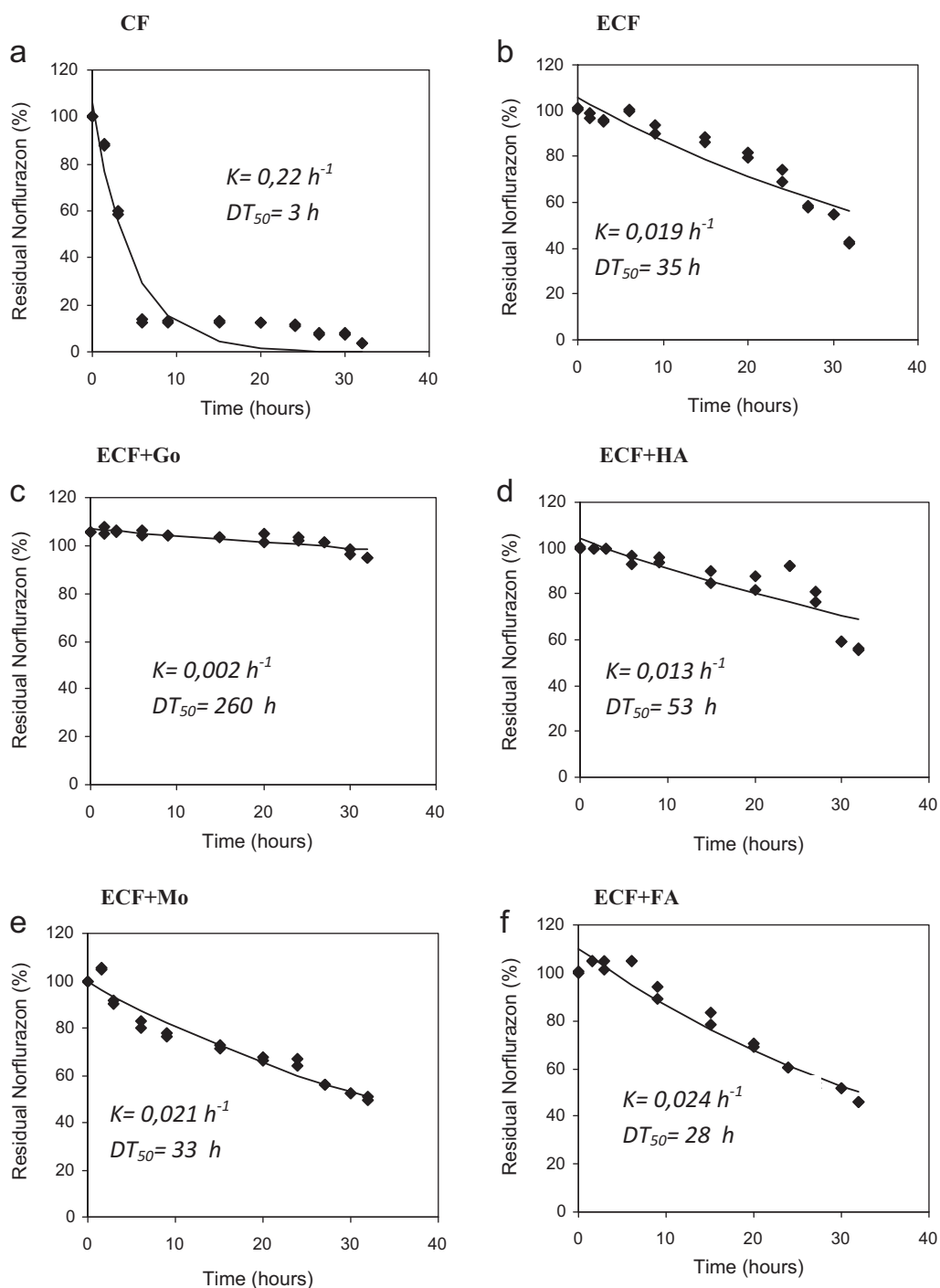
Fig. 4. NFZ photodegradation profiles in aqueous solution of commercial (CF) (a) and microencapsulated (ECF) formulation (b), and ECF in the presence of gohetite (ECF + Go) (c), humic acids (ECF + HA) (d), montmorillonite (ECF + Mo) (e), and fulvic-acids (ECF + FA) (f), and the corresponding kinetic parameters after their adjustment to simple first-order kinetics: photodegradation constants (k) and DT_{50} values. Model (dash line); measured (symbol, ♦).

This suggests that the concentration of the released herbicide was fair enough to be absorbed by the clay, and thus a great part is available to be degraded by hydroxyl radicals. This fact would become more important than the screening effect from Mo after the first 2 h, making that all the released NFZ was photo-decomposed at the end of the experiment under irradiation.

FA did not protect to NFZ from its photodecomposition, and the residual herbicide at the end of the experiment was comparable to that observed for ECF (Table 1). As shown in Fig. 4b and f, DT_{50} value was even lower than that for ECF (28 and 35 h^{-1}, respectively).

This result is in agreement with that from Villaverde et al. [31] using water solutions of NFZ and cyclodextrins. The iron content in natural-metal–fulvic acid complex is 22.2% and has been attributed to have an attenuation effect on its herbicide photostabilization capability. The luminescence of humic substances can be attenuated by complex formation with paramagnetic metals, decreasing their photochemically excited states. A slight adsorption of NFZ on FA was shown by the decrease in the NFZ remaining in solution from the dark controls (Table 1, Fig. 3d in comparison to Fig. 1). However, it should be noticed that this fact did not provide a NFZ

Table 2
Standardized regression coefficients of the soil component predictors in the multiple linear regression analysis for the photodegradation of microencapsulated norflurazon in aqueous solution.

	Standardized coefficient	t	p
Constant		112.973	0.000
Go	−1.101	−72.618	0.000
HA	−0.286	−18.850	0.000
Mo	−0.162	−10.684	0.000
FA	−0.073	−4.789	0.005

photostabilization by energy transfer from the herbicide to the FA. The presence of the ferrous ions counteracted the photoprotective effect of the herbicide adsorption to FA.

ANOVA analysis was performed and LSD comparisons were used to identify if the presence of soil colloidal components can provide any significant differences ($p < 0.05$) on the NFZ photostability observed from ECF. The NFZ photodegraded (NFZD) was calculated from the difference between the herbicide detected in aqueous solution under dark and irradiated conditions. The ANOVA showed all the soil components have a great effect on NFZD, as it was significant beyond the 0.01 level [$F(4,5) = 1939.2$, $p < 0.01$, $R^2 = 0.999$]. To see which soil variable made a more significant contribution into NFZD aqueous solution, a stepwise multiple linear regression analysis was also used. The resultant predictive equation for herbicide photodegradation based on soil variables is as follows: NFZD = 57.71 (± 0.51)–52.47 (± 0.72) Go–13.62 (± 0.72) HA–7.72 (± 0.72) Mo–3.46 (± 0.72) FA. Table 2 shows the standardized coefficients of the soil predictors and their significance. The p-values of all predictors indicate their significant influence on NFZD in aqueous solution at a 95% confidence level. The results agree what observed above. Go was the most significant variable, followed by HA, Mo and FA. Although Mo and FA had a weak influence on NFZD, they were still significant ($p < 0.01$).

4. Conclusions

The present work extends the knowledge about ethylcellulose-microencapsulated formulations. The findings found here clearly demonstrate that EC-microspheres provided a gradual and sustained release of NFZ, which considerably counteracts the herbicide photolysis in comparison to the commercial formulation. ECF protected against photodegradation in both aqueous solution and soil. The gradual release of the herbicide from ECF reduces the amount of herbicide available to be photodegraded.

Moreover, an additional reduction in the rate of NFZ-photodecomposition in aqueous solution was observed in the presence of colloidal soil components such as goethite and humic acids, but not in the cases of montmorillonite of fulvic acids, that was similar to that of ECF alone. UV screening effect was mainly responsible for the photoprotective effect of goethite and humic acids. Adsorption of NFZ to humic acids also contributed to the photoprotective effect.

NFZ photodegradation in aqueous suspensions were well explained by a simple first order model. DT_{50} value from CF (3 h) was really lower than those obtained from (ECF): 35 h for ECF; 260 h for ECF–goethite; 53 h for ECF–humic acids; 33 h for ECF–montmorillonite; and 28 h for ECF–fulvic acids.

These lab-scale findings prove that the use of ethylcellulose-microencapsulated formulations could reduce the herbicide dosage, since they can minimize the pesticide losses by photolysis. These facts would be especially advantageous during the first hours after foliar and soil application, besides the reduced losses of the herbicide due to leaching and dissipation observed in previous papers.

References

[1] D.V. Sojic, V.N. Despotovic, N.D. Abazovic, M.I. Comor, B.F. Abramovic, Photo-catalytic degradation of selected herbicides in aqueous suspensions of doped titania under visible light irradiation, J. Hazard. Mater. 179 (2010) 49–56.
[2] A. Kiss, D. Virag, Photostability and photodegradation pathways of distinctive pesticides, J. Environ. Qual. 38 (2009) 157–163.
[3] S. Chiron, L. Comoretto, E. Rinaldi, V. Maurino, C. Minero, D. Vione, Pesticide by products in the Rhone delta (Southern France). The case of 4-chloro-2-methylphenol and of its nitroderivative, Chemosphere 74 (2009) 599–604.
[4] T. Katagi, Photodegradation of pesticides on plant and soil surfaces, Rev. Environ. Contam. Toxicol. 182 (2004) 1–189.
[5] S. Gupta, V.T. Gajbhiye, R.K. Gupta, Effect of light on the degradation of two neonicotinoides viz acetamiprid and thiacloprid, Bull. Environ. Contam. Toxicol. 81 (2008) 185–189.
[6] B. Eyheraguibel, A. Ter Halle, C. Richard, Photodegradation of bentazon, clopyralid, and triclopyr on model leaves: importance of a systematic evaluation of pesticide photostability on crops, J. Agric. Food. Chem. 57 (2009) 1960–1966.
[7] J. Thomas, A. Bejjani, B. Nsouli, A. Gardon, J.M. Chovelon, In situ studies of pesticides photodegradation on soils using PD-TOFMS technique: application to norflurazon and oxyfluorfen, Int. J. Mass Spectrom. 279 (2009) 59–68.
[8] J.P. Da Silva, L.F.V. Ferreira, I. Osipov, I.F. Machado, Surface photochemistry of pesticides containing 4-chlorophenoxyl chromophore, J. Hazard. Mater. 179 (2010) 187–191.
[9] P. Graebing, J.S. Chib, Soil photolysis in a moisture- and temperature-controlled environment. 2. Insecticides, J. Agric. Food Chem. 52 (2004) 2606–2614.
[10] Y. Si, J. Zhou, H. Chen, D. Zhou, Y. Yue, Effects of humic substances on photodegradation of bensulfuron-methyl on dry soil surfaces, Chemosphere 56 (2004) 967–972.
[11] V.R. Herbert, G.C. Miller, Depth dependence of direct and indirect photolysis on soil surfaces, J. Agric. Food Chem. 38 (1990) 913–918.
[12] T. Undabeytia, S. Nir, E. Tel-Or, B. Rubin, Photostabilization of the herbicide norflurazon by using organoclays, J. Agric. Food Chem. 48 (2000) 4774–7479.
[13] Y. El-Nahhal, T. Undabeytia, T. Polubesova, Y.G. Mishael, S. Nir, L. Marguiles, B. Rubin, Organo-clay formulations of pesticides: reduced leaching and photodegradation, J. Appl. Clay Sci. 18 (2001) 309–326.
[14] M. Kamiya, K. Nakamura, Cyclodextrin inclusion effects on photodegradation rates of organophosphorous pesticides, Environ. Int. 21 (1995) 299–304.
[15] R.J. Demchak, R.A. Dybas, Photostability of abamectin/zein microspheres, J. Agric. Food Chem. 45 (1997) 260–262.
[16] P.L. Huston, J.J. Pignatello, Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction, Water Res. 33 (1999) 1238–1246.
[17] W. Ahrens, Norflurazon, in: Herbicide Handbook, 7th ed., Weed Sci. Soc. Am., Champaign, IL, 1994, pp. 9–11.
[18] E. Morillo, C. Maqueda, R. Reinoso, T. Undabeytia, Effect of two organic amendments on norflurazon retention and release by soils of different characteristics, Environ. Sci. Technol. 36 (2002) 4319–4325.
[19] M. Singh, S. Tan, D. Sharma, Leaching and sorption of norflurazon in soils as affected by cationic surfactants, Bull. Environ. Contam. Toxicol. 68 (2002) 901–907.
[20] E. Morillo, T. Undabeytia, A. Cabrera, J. Villaverde, C. Maqueda, Effect of soil type on adsorption–desorption, mobility and activity of the herbicide norflurazon, J. Agric. Food Chem. 52 (2004) 884–890.
[21] R. Fernández-Urrusuno, J.M. Ginés, E. Morillo, Development of controlled release formulations of alachlor in Ethylcellulose, J. Microencapsul. 17 (2000) 331–342.
[22] F. Sopeña, A. Cabrera, C. Maqueda, E. Morillo, Controlled release of the herbicide norflurazon into water from Ethylcellulose, J. Agric. Food Chem. 53 (2005) 3540–3547.
[23] F. Sopeña, C. Maqueda, E. Morillo, Norflurazon mobility, dissipation, activity and persistence in a sandy soil as influenced by formulation, J. Agric. Food Chem. 55 (2007) 3561–3567.
[24] F. Sopeña, A. Cabrera, C. Maqueda, E. Morillo, Ethylcellulose formulations for controlled release of the herbicide alachlor in a sandy soil, J. Agric. Food Chem. 55 (2007) 8200–8205.
[25] F. Sopeña, C. Maqueda, E. Morillo, Influence of soil characteristics and formulation on alachlor dissipation in soil, Soil Sci. Soc. Am. J. 72 (2008) 767–774.
[26] F. Sopeña, C. Maqueda, E. Morillo, Formulation affecting alachlor efficacy and persistence in sandy soils, Pest Manag. Sci. 65 (2009) 761–768.
[27] T. Undabeytia, F. Sopeña, T. Sánchez-Verdejo, J. Villaverde, S. Nir, E. Morillo, C. Maqueda, Performance of slow release of formulations of alachlor, Soil Sci. Soc. Am. J. 74 (2010) 898–905.

[28] C.W. Hubbs, T. Lavy, Dissipation of norflurazon and other persistent herbicides in soil, Weed Sci. 38 (1990) 81–88.

[29] C. Maqueda, E. Morillo, T. Undabeytia, F. Martin, Sorption of glyphosate and Cu (II) on a natural fulvic acid complex: mutual influence, Chemosphere 37 (1998) 1063–1072.

[30] L.A. Perez-Maqueda, J.M. Criado, J. Subrt, C. Real, Synthesis of acicular hematite catalyst with tailored porosity, Catal. Lett. 60 (1999) 151–156.

[31] J. Villaverde, C. Maqueda, T. Undabeytia, E. Morillo, Effect of various cyclodextrins on the photodegradation of a hydrophobic herbicide in aqueous suspensions of different soil coloidal components, Chemosphere 69 (2007) 575–584.

[32] Guidance document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 2006.

[33] J. Villaverde, W. van Beinum, S. Beulke, C.D. Brown, The kinetics of sorption by retarded diffusion into soil aggregate pores, Environ. Sci. Technol. 43 (2009) 8227–8232.

[34] M.P. Frank, P.G. Graebing, J.S. Chib, Effect of soil moisture content and sample depth on photolysis, J. Agric. Food. Chem. 50 (2002) 2607–2614.

[35] R. Roberts, H.D. Huston, in: Royal Soc. of Chem. (Ed.), Metabolic Pathways of Agrochemicals: Herbicides and Plant Growth Regulators, Royal Soc. of Chem., Cambridge, UK, 1998, p. p. 411.

[36] G.-G. Ying, B. Williams, Photodegradation of norflurazon in water, Toxicol. Environ. Chem. 71 (1999) 261–269.

[37] J. Zhao, R. Wilkins, Controlled release of a herbicide from matrix granules based on solvent-fractionated organosolv lignins, J. Agric. Food Chem. 48 (2000) 3651–3661.

[38] K. Papadokostaki, S. Amarantos, J. Petropoulos, Kinetics of release of particulate solutes incorporated in cellulosic polymer matrices as a function of solute solubility and polymer swellability. I. Sparingly soluble solutes, J. Appl. Pol. Sci. 67 (1998) 277–287.

[39] S. Gupta, V.T. Gajbhiye, R.K. Gupta, Effect of ultraviolet and sunlight on persistence of thiamethoxam in soil, Pest. Res. J. 18 (2006) 211–214.

[40] J. He, W. Ma, W. Song, J. Zhao, X. Qian, S. Zhang, J. Yu, Photoreaction of aromatic compounds at α-FeOOH/H$_2$O interface in the presence of H$_2$O$_2$: evidence for organic-goethite surface complex formation, Water Res. 39 (2005) 119–128.

[41] X. Zhao, M. Quan, H. Zhao, S. Chen, Y. Zhao, J. Chen, Different effects of humic substances on photodegradation of p,p′-DDT on soil surfaces in the presence of TiO$_2$ under UV and visible light, J. Photochem. Photobiol. A 167 (2004) 177–183.

[42] M. Kamiya, K. Kameyama, Photochemical effects of humic substances on the degradation of organophosphorous pesticides, Chemosphere 36 (1998) 2337–2344.

[43] M. Elazzouzi, A. Bensaoud, A. Bouhaouss, A. Dahchour, P. Meallier, A. Piccolo, Photodegradation of imazapyr in the presence of humic substances, Fresen. Environ. Bull. 8 (1999) 478–485.

[44] C. Zamy, P. Mazellier, B. Legube, Phototransformation of selected organophosphorous pesticides in dilute aqueous solutions, Water Res. 38 (2004) 2305–2314.

[45] J.R. Gabin, D.M.P. Milori, M.L. Simoes, W.T. da Silva, L.M. Neto, Influence of humic substances on the photolysis of aqueous pesticide residues, Chemosphere 66 (2007) 1692–1698.

[46] R. Mathew, S. Khan, Photodegradation of metolachlor in water in the presence of soil mineral and organic constituents, J. Agric. Food Chem. 44 (1996) 3996–4000.