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Photostabilization of the Herbicide Norflurazon by Using Organoclays

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Photostable formulations of the herbicide norflurazon [4-chloro-5-(methylamino)-2-(α,α,α -trifluoro-*m*-tolyl)pyridazin-3-(2*H*)-one] were achieved by adsorbing it on pillared clay or on montmorillonite preadsorbed with the organic cation thioflavin T (TFT). Diffuse reflectance Fourier transform infrared spectra showed the existence of strong interactions between the aromatic moieties of preadsorbed TFT and the herbicide, particularly after irradiation. The photostabilization of norflurazon obtained with TFT-clay was mainly due to energy transfer from the herbicide to the organic cation via π – π^* interactions. An additional mechanism is the lower production of radicals from the clay when the clay mineral surface is covered with the organic cation. These radicals are responsible for the enhanced photodegradation observed when norflurazon was irradiated in the presence of untreated montmorillonite.

Keywords: Norflurazon; thioflavin T; montmorillonite; pillared clay; photostabilization

INTRODUCTION

Photochemical degradation is an important mechanism of dissipation of herbicides in soils. On dry, sunlight-exposed surfaces photolysis may dominate other transformation pathways that are favored under conditions found in the bulk soil (Misra et al., 1997). In the case of soil, direct photolysis is assumed to be operable only on or within 0.1–0.5 mm of the surface, and thus its potential contribution as a dissipation mechanism could be limited once a precipitation event has flushed the herbicide into the soil. However, the upward movement of the herbicides with capillary rise of the water front to the surface can occur in the field under conditions of net negative water balance (Shepard et al., 1987; Streck, 1998). Indirect photochemical processes can also be an important route for the degradation of the herbicide because a variety of oxidants are formed on the sunlight-exposed soil surface that can potentially transform herbicides (Herbert and Miller, 1990; Katagi, 1992, 1993).

Norflurazon is a widely used soil-applied herbicide labeled for grass and broadleaf weed control in several crops, such as cotton, soybean, and citrus (Ahrens, 1994; Wilcut et al., 1997). Its primary mode of action involves blocking carotenoid biosynthesis by inhibition of phytoene desaturase. Hubbs and Lavy (1990) reported that photodegradation contributes significantly to its field dissipation.

In general, several approaches have been used to decrease the loss of herbicides by photodegradation, for

example, chemical modification of the herbicide molecule to obtain new photostable herbicides and the use of UV-absorbing molecules in commercial formulations (Elliot et al., 1974; Bridges et al., 1992; Jordan and Johnson, 1998). Margulies et al. (1985, 1993) suggested the use of clay minerals in the design of new photostable formulations of herbicides. This method is based on the sorption of the photolabile bioactive compound on the surface of clays to which a selected organic chromophore has been previously attached. The chromophore can absorb the excess of energy from the photoexcited molecule of the herbicide by energy-transfer or charge-transfer mechanisms, which lengthens the lifetime of the herbicide. Some degree of photostabilization was achieved by using the unmodified clay (Margulies et al., 1992; El-Nahal et al., 1999). The dose rate of this herbicide applied in the field could be increased to compensate for its photodegradation. However, new environmental issues would arise from increasing the amount of herbicide applied because norflurazon has been reported to leach in porous soils with low organic matter content (Reddy et al., 1992).

The aim of the current study is to develop organoclay formulations of the herbicide norflurazon, which would provide effective photoprotection of the herbicide. Thus, the amount of active ingredient applied to the soil would be lowered, and the economic and environmental costs will decrease. We also focus on the use of a polyoxoaluminum pillared clay as a potential photostabilizer.

MATERIALS AND METHODS

Materials. The clays used were a standard montmorillonite (SWy-1) (van Olphen and Fripiat, 1979) supplied by the Clay Minerals Society and an alumina pillared montmorillonite (ALFULCAT 2C) (Jones et al., 1997; Mishaal et al., 1999) supplied by the National Technical University of Athens, Greece. Analytical and technical grade norflurazon, 99.9 and 97.8% purities, respectively, were kindly supplied by Novartis

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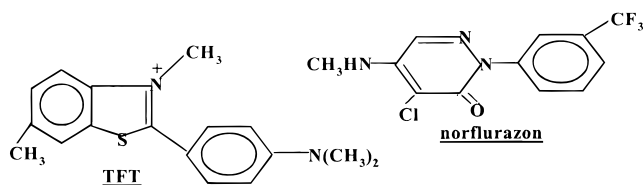


Figure 1. Structural formulas of the herbicide and the organic cation thioflavin T.

A.G. (Basel, Switzerland). Thioflavin T (TFT), 2,5-dimethylfuran, *p*-nitroacetophenone, and *N,N*-dimethylformamide were purchased from Sigma-Aldrich-Fluka (Sigma Chemical Co., St Louis, MO); 2-propanone and hydrogen peroxide were from Frutarom Laboratory Chemicals (Haifa, Israel); pyridine was from BDH Laboratory Supplies (Poole, U.K.); and HPLC grade acetonitrile and HPLC grade water were from Merck (Darmstadt, Germany). The structural formulas of norflurazon and TFT are shown in Figure 1.

Preparation of the Organomontmorillonite Complexes. These complexes were prepared by dropwise addition of aliquots of 10^{-2} M TFT to an aqueous suspension of montmorillonite under continuous stirring. The final suspension was 1% (w/v). After 24 h of stirring, the suspensions were centrifuged at 20000*g* for 20 min, the supernatant was discarded, and the samples were freeze-dried. The final loads of TFT were 0.2 and 0.5 mmol/g (denoted TFT 0.2 or 0.5, respectively).

Preparation of Formulations. Formulations from herbicide dissolved in water (denoted by "w") were prepared by dissolving technical norflurazon up to the solubility limit; the solutions were filtered through a 0.45 μ m Millipore filter and mixed with pillared clay or organoclay, the final suspension being 0.5% (w/w). The suspensions were stirred for 24 h and thereafter centrifuged. The supernatant was discarded, and the pellets were freeze-dried. The active ingredient (ai) content (w/w) was 0.42% for montmorillonite-TFT 0.2, 0.35% for montmorillonite-TFT 0.5, and 0.70% for pillared clay. Formulations from herbicide dissolved in 2-propanone (denoted by "a") were also prepared for pillared clay and montmorillonite preadsorbed with TFT at 0.2 and 0.5 mmol/g by dissolving the herbicide in 2-propanone and mixing the solution with the clay, the suspension being 3% (w/w). The solvent was evaporated using a rotavapor, and the same procedure was repeated five times to enhance the interactions between the herbicide and the clay surface. The final ai content (w/w) for the formulations prepared from 2-propanone was 15%. The rotavapor was used during each cycle for a very long time to ensure that no 2-propanone was remained; IR spectra recorded of the formulations did not show any characteristic absorption bands of 2-propanone.

Irradiation Procedures. Photolysis was carried out within a Rayonet photoreactor (The New England Ultraviolet Co.) equipped with 14 RPR 3500 lamps, having a peak output at 350 nm. The power was 24 W per lamp. The reactor was placed horizontally, and samples were in sealed quartz tubes (10 \times 130 mm) containing 8 mL of norflurazon solutions and suspensions of clay/organoclay formulations of the herbicide, the initial ai content for the irradiation experiments being 65.85 μ M. The tubes were also held in a horizontal position in a merry-go-round arrangement and secured at both ends, rotating to ensure equal exposure of the samples. Photolysis runs were carried out in duplicate for irradiation times from 15 to 120 min. No norflurazon degradation was detected in dark controls.

Photoproducts and remaining norflurazon were extracted from the clay matrix by transferring the solution/suspensions to polycarbonate tubes, adding ethanol (8 mL), and mixing for 2 min using a vortex mixer (model K-550-G) operating at the highest speed. The tubes were centrifuged and the supernatants analyzed. Preliminary experiments indicated that norflurazon was completely recovered from the formulations. Norflurazon was determined by using a Merck-Hitachi HPLC equipped with a fluorescence detector as described by William and Mueller (1994).

Photolysis experiments were also carried out under natural light conditions. Quartz tubes with solutions of norflurazon and suspensions of norflurazon in the presence of clay were exposed to full sunlight at an angle of $\sim 30^\circ$ from vertical. The remaining norflurazon was determined after exposure times from 30 min to 5 days as described above.

Chloride release from photolysis of norflurazon was followed as a function of the irradiation time. Chloride was determined by using a DX-300 ion chromatograph (Dionex Corp., Sunnyvale, CA), using an AS9 analytical column and guard column together with an anion micromembrane suppressor and carbonate/bicarbonate buffer as eluent.

Assay of Active Oxygen Species. The possible involvement of oxygen species in photolysis was examined. The production of singlet oxygen was followed by the rate of disappearance of aliquots of 2,5-dimethylfuran added to the solutions under study and formation of its photoproduct. After irradiation for an appropriate period, the reaction was quenched by the addition of methanol (4 mL), and the supernatants were analyzed by HPLC equipped with a diode array detector. The mobile phase was acetonitrile/water (70:30) at 1 mL/min flow, and the detection wavelength was 225 nm. The involvement of hydroxyl radicals was examined by using Fenton's reagent. Ferrous sulfate (0.138 mg, 0.62 mL) was added to 8 mL of norflurazon formulations (65.85 μ M) containing 30 μ M hydrogen peroxide and shaken for 15 min. The oxidation was repeated twice by readdition of oxidant, followed by addition of ferrous sulfate.

Spectroscopic Measurements. UV-vis spectra were recorded by using a Hewlett-Packard 8452A spectrophotometer. Diffuse reflectance Fourier transform infrared (DRIFT) spectra were obtained with a Nicolet Magna-IR-550. The spectra were recorded at room temperature in the range of 400–4000 cm^{-1} . The emission spectrum of norflurazon was recorded with an SLM OP450 fluorometer.

Bioassays. The herbicidal activity of irradiated and non-irradiated samples was tested in bioassays by using magenta vessels containing 1.63 g of the aquatic plant *Lemna minor* in 200 mL of water. The activity of the formulations was followed by measuring their bleaching effect on *Lemna* plants after 1 week, in comparison to a control that did not receive any application of the herbicide. For this purpose a dose-response curve was established by using the commercial formulation (Zorial, 80% w/w, Novartis). An inhibition percentage of 35% was obtained for a solution concentration of 0.8 mg/L, which was used as the effective initial concentration for all of the experiments with clay formulations. The water loss by evaporation was replenished every day. Chlorophyll of *L. minor* plants was extracted with 4 mL of *N,N*-dimethylformamide; the solutions were incubated for 48 h, and the chlorophyll content was measured by visible spectroscopy at 664 and 647 nm and related to the fresh weight of the plants. The experiment was carried out four times for each formulation. Blanks indicated no release of the organic cation TFT.

RESULTS AND DISCUSSION

Photolysis of Norflurazon. Irradiation of norflurazon solutions produces deschloronorflurazon as the main photoproduct (Ahrens, 1994). We observed a very good agreement between the amounts of chloride released and degraded norflurazon (data not shown).

Irradiation of Clay Formulations. The half-life time of irradiated norflurazon in its organoclay formulations produced from water is ~ 4 -fold larger than that from its analytical solutions (Table 1). The photostabilization is less efficient when clay formulations in which norflurazon was added from 2-propanone are irradiated, which could be attributed to the presence of herbicide molecules loosely adsorbed and not interacting with the organic cation.

Table 1. Photodegradation of Norflurazon and Its Organoclay Formulations: Half-Life Times ($t_{1/2}$), Kinetic Constants, and Regression Coefficients of Analytical Norflurazon (NFZ), Organoclay Formulations, and the Herbicide in the Presence of Montmorillonite (SWy, 3.125 g L⁻¹ Clay Concentration)

system	$t_{1/2}$ (min)	$k \times 10^3$ (min ⁻¹)	R^2
NFZ	54.2	12b	0.94
SWy-TFT 0.2-NFZ (w)	200.9	3c	0.97
SWy-TFT 0.2-NFZ (a)	136.4	5d	0.92
SWy-TFT 0.5-NFZ (w)	194.1	4c	0.92
SWy-TFT 0.5-NFZ (a)	126.4	5d	0.95
PC-NFZ (w)	292.4	2e	0.82
PC-NFZ (a)	134.3	5d	0.98
SWy	37.3	19a	0.95

^a Means with the same letter are not significantly different at the 5% level as determined by Student's multiple-range test. The notations "(w)" and "(a)" indicate formulations prepared in water and 2-propanone, respectively, as described under Materials and Methods. The kinetic parameters were obtained by fitting the experimental data to a first-order kinetic reaction.

Photostabilization of norflurazon in organoclay formulations might be due to energy- or charge-transfer processes from the herbicide to the organic cation. On the other hand, competitive absorption of UV by the organic cation is not expected because of the low absorbance of TFT at ~ 350 nm (Margulies et al., 1988a). Table 1 shows a somewhat unexpected result that in the presence of clay suspensions of montmorillonite, the rate of norflurazon photodegradation is enhanced.

The highest degree of photostabilization of norflurazon was obtained with the pillared clay formulation (Table 1). In the case of the herbicide metolachlor (Nennemann et al., 2000), its high adsorption on pillared clay was attributed to the formation of hydrogen bonds between the strong donor sites of the acid-activated pillared clay and the acceptor sites of the herbicide molecule. Spectroscopic evidence by IR of isolated O-H groups of the pillared clay interacting with norflurazon was not possible (spectra not shown) due to the background of H-bonded hydroxyls interacting strongly with water molecules. Thus, we are not sure which mechanisms are involved in the photostabilization of norflurazon by pillared clays.

The efficiency of energy-transfer processes depends on the matching of energy levels of donor and acceptor chromophores, on the distance between them, and on their relative orientations (Margulies et al., 1993). The feasibility of energy-transfer processes from norflurazon to TFT is shown in Figure 2, which indicates an overlap between the emission spectrum of norflurazon and the absorption spectrum of the organic cation adsorbed on the clay. Energy transfer would involve $\pi-\pi^*$ transitions between triplet states, because the absorption band of the organoclay complex centered at 418 nm is essentially of $\pi-\pi^*$ character ($\epsilon = 26138$ M⁻¹ cm⁻¹, the peak shifts to longer wavelengths when solvent polarity increases). This is in agreement with the suggestion by Nir et al. (2000) that the adsorption of several hydrophobic herbicides, such as alachlor and norflurazon, on organomontmorillonite is due to $\pi-\pi^*$ interactions between the phenyl ring of the herbicide and the aromatic moieties of the organic cation.

Information regarding intermolecular interactions can be obtained by using infrared spectroscopy. In Figure 3, the spectrum of norflurazon shows absorption bands due to the vibration modes of the pyridazinone ring at 1410 and 1530 cm⁻¹ (Sánchez-Martín and Sánchez-

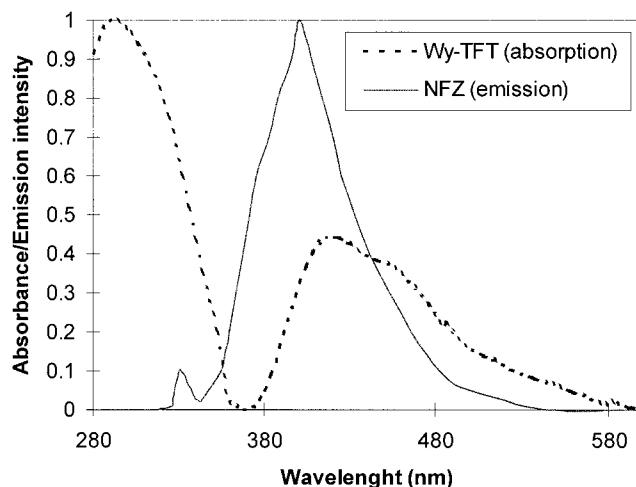


Figure 2. Normalized emission spectrum of norflurazon and absorption spectrum of TFT adsorbed on the clay at a loading of 0.2 mmol/g of clay.

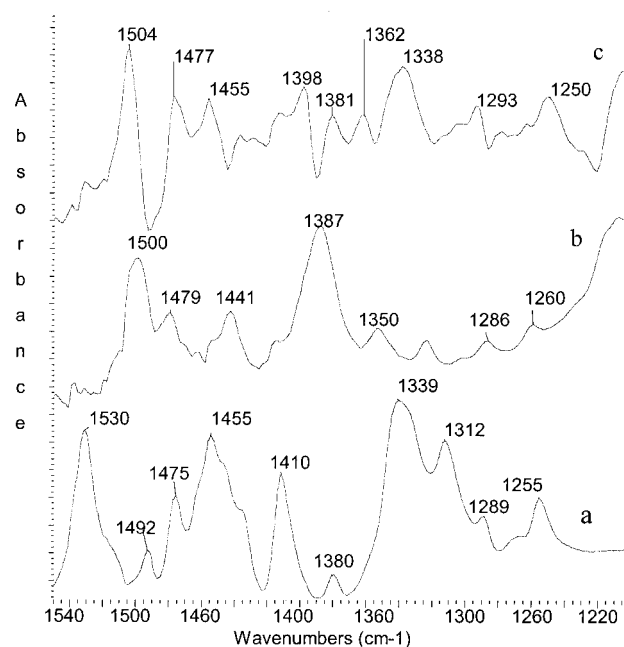


Figure 3. DRIFT spectra of analytical norflurazon (a) and montmorillonite preadsorbed with TFT (0.2 mmol/g of clay) (b) and the spectrum of norflurazon adsorbed on the organoclay complex after 2 h of irradiation, from which its spectrum without irradiation was subtracted (c).

Camazano, 1987), the breathing modes of the phenyl ring at 1475 and 1455 cm⁻¹, the C aromatic-N stretching frequency at 1339 cm⁻¹, the C-N stretching vibrations of the enamine group at 1289 cm⁻¹ (Margulies et al., 1988a), the C-F stretching frequency at 1312 cm⁻¹, and the C aliphatic-N stretching at 1255 cm⁻¹. The most important absorption bands for the organoclay are those due to the thiazol ring at 1500 and 1387 cm⁻¹ (Pouchert, 1981), the C-H deformation band of methyl attached to N at 1441 cm⁻¹, the breathing modes of the phenyl ring at 1479 cm⁻¹, and the C aliphatic-N and C aromatic-N stretching frequencies at 1260 and 1350 cm⁻¹, respectively.

Specific absorption bands due to the photoproducts could not be resolved in the norflurazon spectrum after subtraction of the spectrum of the organoclay formulation irradiated from the one corresponding to the nonirradiated organoclay (Figure 3c). Previous infrared

Table 2. Remaining Herbicidal Activity in Norflurazon Formulations after Irradiation for 2 h As Determined by Using *L. minor* Bioassays

formulation	inhibition ^a (% of control)	formulation	inhibition ^a (% of control)
commercial	0 (±3.6)	TFT 0.2 (w)	49.8 (±2.2)
PC (w)	71.0 (±1.6)	TFT 0.5 (w)	49.2 (±1.7)
		TFT 0.5 (a)	35.6 (±2.3)

^a The standard error is indicated in parentheses.

results showed that molecular interactions between TFT and norflurazon were occurring without irradiation (T. Undabeytia, S. Nir, and B. Rubin, unpublished data). After 2 h of irradiation, new changes are observed. The most relevant features are the shifts of the absorption bands of TFT from 1387 to 1398 cm⁻¹ and from 1350 to 1362 cm⁻¹ and the appearance of a negative peak at 1385 cm⁻¹. The possibility that this negative peak might be due to an incorrect normalization factor used in the subtraction is unlikely because the TFT peak at 1500 cm⁻¹ appears. These changes in the spectrum indicate that specific intermolecular interactions between the two adsorbed organic molecules, TFT and norflurazon, occur following irradiation. These changes in the aromatic moieties of TFT are suggested to arise from the donation of π electrons from the herbicide, which would produce a shift to higher frequencies of stretching ring vibrations (Nakanishi and Solomon, 1977). These results are consistent with an energy-transfer mechanism.

We ruled out charge-transfer processes that have been reported for flavin and analogues (Draper and Crosby, 1983). They are able to undergo photochemical reactions to a semiquinoid form in the presence of an electron donor. No absorption bands due to reduced TFT were detected in the infrared spectra, which can be due to a spontaneous oxidation of the reduced dye with ground-state oxygen. The possibility that this mechanism prevails was tested by using the electron donor EDTA as a quencher for electron-transfer reactions. The rate of norflurazon degradation was not affected by the presence of 600 μ M EDTA (10:1 EDTA/norflurazon ratio) (results not shown).

The degree of photostabilization of clay formulations of norflurazon was compared with the commercial formulation by using a bioassay (Table 2). After 2 h of irradiation, some of the clay "w" formulations showed ~50% herbicidal activity, in contrast to the commercial formulation, which lost all of its activity. Photostabilization is reduced for the TFT 0.5 "a" formulation, indicating that an increase of the loading of the herbicide on the organoclay will decrease its herbicidal activity. This can be due to either larger amounts of loosely adsorbed molecules on the organoclay that are more susceptible to photodegradation or a larger number of impaired interactions between the herbicide molecules and the organoclay, because energy-transfer processes will be dependent on the geometry and distances between the interacting chromophores. The bioassay results parallel those of Table 1; the lowest rate constant of degradation was obtained for the formulation showing the largest herbicidal activity, PC (w).

Irradiation of Norflurazon in the Presence of Montmorillonite. As stated before, the irradiation of norflurazon solutions in the presence of montmorillonite suspensions enhances its photodegradation. This may be caused by the formation of active oxygen species as

a result of the irradiation of oxygen or water associated with the clays (Katagi, 1990). Singlet oxygen is formed on soil surfaces irradiated (Gohre and Miller, 1983). Katagi (1993) observed the generation of hydroxyl radicals by exposure of suspended clays to UV light, which accelerated the photodegradation of the insecticide esfenvalerate.

The involvement of singlet oxygen species was determined by the consumption of 2,5-dimethylfuran and formation of its photoproduct. Singlet oxygen reacts with 2,5-dimethylfuran by a cycloaddition to form an ozonide that decomposes in water to give *cis*-diacetylene, which isomerizes to the more stable *trans* compound (Gohre and Miller, 1983). The singlet oxygen species is not responsible for the enhanced photodegradation of norflurazon in montmorillonite suspensions, because the amount of norflurazon degraded after irradiation of the herbicide solutions in the presence of 200 μ M 2,5-dimethylfuran was not affected by the presence of the trapping agent (results not shown). At the same time, production of singlet oxygen was confirmed by the consumption of 2,5-dimethylfuran and formation of its photoproduct. Efficient charge-transfer processes can take place between adsorbed molecules and lattice iron of clay minerals (Bergaya and Van Damme, 1983; Rozen and Margulies, 1991).

Photoinduced electron transfer from aluminosilicates to adsorbed molecular oxygen was reported by Che and Tench (1983). On this basis, Katagi (1990) proposed the generation of hydroxyl and hydroperoxyl radicals by reaction of water with O₂⁻ formed on clays by irradiation. This author measured the amount of hydrogen peroxide produced by autooxidation of these radicals after irradiation of clay mineral surfaces. The amount determined for montmorillonite after 4 h of irradiation was 0.9 ppb on a dry weight basis, which should be expected to be considerably larger when aqueous suspensions of this clay mineral are irradiated.

The involvement of these radicals was followed by the addition of Fenton's reagent, which is a well-established system to generate hydroxyl radicals. In addition, oxidation of ferrous ion in the presence of oxygen would generate O₂⁻ (Larson et al., 1991). The addition of Fenton's reagent to norflurazon in the presence of the clay resulted in a complete degradation of the herbicide, indicating the involvement of these radicals in the enhanced photodegradation of the herbicide. The opposite trend obtained with organoclay formulations, that is, photostabilization, could be due to the more efficient competition of energy-transfer processes, in addition to lower levels of production of radicals when the clay mineral surface is covered with the organic cation.

Under natural conditions (37° N latitude, summer), we observed a half-life time of 1.07 days for norflurazon in contrast to its lower half-life in the presence of the clay (0.66 day). These data are in good agreement with those presented in Table 1, which indicate a 1.5-fold enhancement in the rate of herbicide degradation in the presence of the clay. This extremely low half-life time of norflurazon contrasts with that of the herbicide metolachlor, for which Kochany and Maguire (1994) reported half-lives of 22 days under similar conditions.

CONCLUDING REMARKS

Photostabilization of the herbicide norflurazon was achieved by the development of organoclay formulations.

A bioassay based on the response of the aquatic plant *L. minor* showed photostabilizations of norflurazon up to 50% for formulations prepared from montmorillonite and up to 70% for that from pillared clay, under irradiation which completely inactivated the commercial formulation. These data demonstrate the potential of pillared clays and organoclays in the development of photostable formulations of norflurazon. Pillared clays have been the subject of research for the past two decades due to the fact that they are cheap materials with physicochemical properties that render them suitable for applications such as filters for detoxifying water or as heterogeneous catalysts for shape selective processes. Formulations based on the organic cation TFT are more expensive. The development of new formulations of other hydrophobic herbicides based on cation, such as TFT, would emphasize its importance and, consequently, its economic viability. The introduction of an additional organic cation such as TFT in herbicide formulations is not expected to cause new environmental issues due to the extremely strong and irreversible binding of TFT on montmorillonite (Margulies et al., 1988b; present work).

Photodegradation of norflurazon was enhanced in the presence of montmorillonite and was attributed to the attack of hydroxyl radicals produced by the clay under irradiation. The results indicate this mechanism as a possible route for degradation of the herbicide in soils and natural waters. However, the importance of this mechanism is limited because of the presence of organic substances. In intact soils, Katagi (1990) reported that partial coverage of clay minerals with humic substances inhibits efficient electron transfer from clay minerals to adsorbed water and to dissolved oxygen-impeding formation of radicals.

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