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Photodegradation of Hexythiazox in Different Solvent Systems under the Influence of Ultraviolet Light and Sunlight in the Presence of TiO_2, H_2O_2, and KNO_3 and Identification of the Photometabolites

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ABSTRACT: The photodegradation of the carboxamide acaricide hexythiazox in three different solvent systems (aqueous methanolic, aqueous isopropanolic, and aqueous acetonitrilic solutions) in the presence of H_2O_2, KNO_3, and TiO_2 under ultraviolet (UV) light ($\lambda_{max} \geq 250$ nm) and sunlight ($\lambda_{max} \geq 290$ nm) has been assessed in this work. The kinetics of photodecomposition of hexythiazox and the identification of photoproducts were carried out using liquid chromatography−mass spectrometry. The rate of photodecomposition of hexythiazox in different solvents followed first-order kinetics in both UV radiation and natural sunlight, and the degradation rates were faster under UV light than under sunlight. Hexythiazox was found to be more efficiently photodegraded in the presence of TiO_2 than in the presence of H_2O_2 and KNO_3. Two major photoproducts were separated in pure form using column chromatography and identified according to IR, ^{1}H NMR, and mass spectral information as cyclohexylamine and 5-(4-chlorophenyl)-4-methylthiazolidin-2-one. Another nine photoproducts were identified according to LC-MS/MS spectral information. The plausible photodegradation pathways of hexythiazox were proposed according to the structures of the photoproducts.

KEYWORDS: hexythiazox, photodegradation, UV light, sunlight, sensitizer, kinetics, photoproduct,

INTRODUCTION

Hexythiazox is the common name of [(4*RS*,5*RS*)-5-(4-chlorophenyl)-*N*-cyclohexyl-4-methyl-2-oxo-1,3-thiazolidine-3-carboxamide and is an effective carboxamide acaricide for controlling various mites. It is intended for use as a contact or stomach poison against the eggs and larvae of tetranychids on apple, strawberry, cucumber, pepper, soybean, and cultivated flowering plants.[1,2] On the basis of all available data, hexythiazox poses little acute risk to freshwater fish, freshwater invertebrates, birds, and mammals.

Residual pesticides are known to be decomposed by various natural conditions in which hydrolysis in water[3,4] and photodegradation [5−11] are the most important factors involved in the decomposition of pesticides in the environment. The investigations and understanding of the photochemical stability and transformations of hexythiazox in the environment can provide better knowledge on transformations and degradation processes in the environment, degradation rate, and development of efficient methods for detoxification of the compound. Hexythiazox has low solubility in water. Increasing the solubility of a pesticide in water necessitats the use of high concentrations of organic solvents (methanol, acetonitrile, and isopropanol).[12]

Numerous chemical contaminants of concern absorb UV at below 300 nm wavelengths and, hence, can undergo efficient direct photolysis. Indirect photolysis or photosensitization is important, especially for the pesticide molecules having no chromophoric groups. The extent of sunlight photolysis is highly dependent on UV absorption profiles of the pesticide, the surrounding medium, and the emission spectrum of sunlight, because the energy to break chemical bonds in pesticide molecules usually ranges from 70 to 120 kcal mol^{-1}, corresponding to light at wavelengths of 250−400 nm.[13] Nelieu et al.[14] stated that sunlight irradiation of nitrate ions, which are often present in natural waters, gives rise to the reactive $^{\bullet}$OH radicals, $^{\bullet}NO_2$, and N_2O_4. The use of TiO_2 as a medium for environmental cleanup of organic pollutants through the activation of photo-oxidation has received much attention due to its low cost, photostability, and low toxicity to humans and the environment.[15] The phototransformation of organic compounds by UV/TiO_2 is presumably initiated by the hydroxyl radical ($^{\bullet}$OH), which is formed by reacting electron holes on the excited TiO_2 surface and OH^- (or H_2O) from the surrounding water.[16,17] Efficient degradation takes place in the presence of H_2O_2 used as oxidizing agent under UV light. The mechanism most commonly accepted for the photolysis of H_2O_2 is the cleavage of the molecules into hydroxyl radical with a quantum yield of two OH radicals formed per quantum of radiation absorbed.[18]

However, the fate and transformation pathways of hexythiazox in different photochemical environments in the presence TiO_2, H_2O_2, and KNO_3 in this context have not yet been systematically carried out in any laboratory. Therefore, the present experiment was conducted to understand the nature of photodegradation of hexythiazox under the influence of UV and sunlight, to determine the kinetics and formation of photometabolites, and to determine the probable mechanism of formation of photoproducts. We also optimized and validated a LC-MS/MS method for trace level quantification of hexythiazox in different solvent media.

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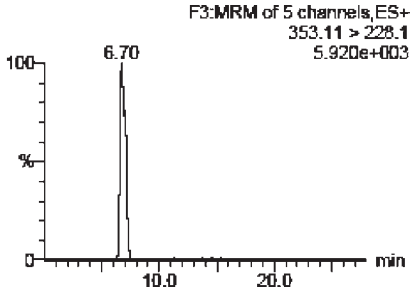

Figure 1. LC-MS/MS chromatogram of standard hexythiazox (50 μg mL^{-1}).

MATERIALS AND METHODS

Chemicals and Solvents. An analytical grade of hexythiazox (purity = 99.90%) was supplied by M/s Biostadt India Ltd., Mumbai, India. Anhydrous sodium sulfate (E. Merck), silica gel for column chromatography, 100−200 mesh (Rankem), TiO_2 (Sigma Chemical Co.), KNO_3 (Sigma Chemical Co.), and H_2O_2 (Sigma Chemical Co.) were used without further purification. All of the solvents (acetonitrile, dichloromethane, methanol, hexane, ethyl acetate, chloroform, and isopropanol) are of HPLC grade and purchased from E. Merck. Purified water was prepared by using a Milli-Q (Millipore, Bedford, MA) water purification system.

Standard Solutions. Stock solutions of hexythiazox standard were prepared by weighing 10 ± 0.02 mg in volumetric flasks (certified "A" class) and dissolving each in 100 mL of methanol. Five levels of calibration concentration containing 0.01, 0.025, 0.05, 0.1, and 0.5 μg mL^{-1} and three levels of fortification concentration containing 0.025, 0.05, and 0.1 μgmL^{-1} of hexythiazox were prepared by serial dilution of stock solution with methanol.

Apparatus and Chromatography. The kinetics study and the characterization of the photoproducts were carried out with an Alliance 2695 separations module (Waters, Milford, MA), coupled to a Micromass Quattro Micro triple-quadrupole mass spectrometer (Micromass, Manchester, U.K.) with MassLynx V4.1 software. IR spectra was taken on 1.0 mm KBr pellets by using a Perkin Elemer (Spectrum One, model L 120-000A) infrared spectrophotometer. ^{1}H nuclear magnetic resonance spectra were recorded on a Bruker DRX-300 spectrometer (300 MHz) using tetramethylsilane (TMS) as an internal standard. A rotary vacuum evaporator of Eyela (SB-1000) and a Beckman Coulter (Avanti J-30I) were used for sample preparation in this study.

Irradiation Experiment. In the present investigation hexythiazox was irradiated separately in three different solvent systems of isopropanol and water (1:1, v/v), acetonitrile and water (1:1, v/v), and methanol and water (1:1, v/v) in the absence or presence of sensitizers (H_2O_2, KNO_3, TiO_2) under the influence of both UV light and sunlight. The concentration of the solution irradiated was 250 μg mL^{-1} and was prepared by dissolving 250 mg of hexythiazox in 1000 mL of mixed solvent. A dark control (without sensitizer) was kept under both cases (UV and sunlight), and no reaction was observed during the entire irradiation period.

Photolysis under UV Light. Then the solutions were irradiated for 100 h under the UV lamp in the presence or absence of sensitizers (H_2O_2, KNO_3, TiO_2, 50 mg/L). For irradiation under UV light, the solution was placed inside a borosilicate photoreactor fitted with a high-pressure mercury lamp (125 W, HPK, Philips) to achieve maximum intensity of UV light at >280 nm. The reactor was equipped with a water-cooled Pyrex filter to maintain a constant solution temperature (25 °C) with continuous stirring by a magnetic stirrer.

Photolysis under Sunlight. An irradiation experiment in the sunlight was performed at Kalyani (West Bengal, India, 22° 59′ N latitude and 13 m altitude) for 100 h (6 h per day from January 2008 to February 2008) under clear skies, at temperatures of 15 ± 5 °C in the wavelength range ≥250 nm.

Sample Analysis for Kinetic Study. The progress of the reaction was followed by successive sampling (100 μL) at intervals of 0, 5, 15, 25, 40, 60, and 75 h from both the different irradiated and control matrices in the presence and absence of sensitizers (TiO_2, H_2O_2, and KNO_3). Then each sample was made 0.2 μg mL^{-1} obtained by serial dilution with the respective solvent mixture. Then the sample was vortexed, centrifuged, and analyzed by LC-MS/MS for kinetics study.

Analytical Methods. The LC-MS/MS analysis was done with an Alliance 2695 separations module (Waters) coupled to a Micromass Quattro triple-quadrupole mass spectrometer (Micromass) with MassLynx 4.0 software. The HPLC separation was carried out using a Symmetry C18 column (100 × 2.1 mm i.d., 5 μm). The mobile phase was isocratic (solvent A/solvent B 50:50 v/v) and was composed of (A) methanol/water 90:10 (v/v) with 5 mM ammonium acetate and (B) methanol/water 10/:90 (v/v) with 5 mM ammonium acetate. Hexythiazox was eluted at retention times of 6.70 min. The column oven temperature was maintained at 24 °C, and the flow rate was maintained at 0.3 mL min^{-1}. An aliquot of 10 μL was injected in the LC-MS/MS. The estimation was performed in positive mode by multiple reaction monitoring (MRM) with mass transitions 353.11 → 228.1 and 353.11 → 168.1 with a scan time of 100 ms. The cone voltage for hexythiazox was 29 V with collision energies of 14 and 26 V for the first and second mass transitions, respectively. The first mass transition was used for quantification, whereas the second mass transition was used for confirmation of the residues. The optimized MS instrument parameters obtained by the tuning were as follows: capillary voltage, 1.20 kV; cone voltage, 46 V; source temperature, 120 °C; desolvation temperature, 350 °C; desolvation gas flow, 650 L h^{-1} nitrogen; cone gas flow, 25 L h^{-1}; argon collision gas (argon) pressure to 3.5 e^{-3} psi for MS/MS. In the MRM transitions the dwell and interscan times were 0.3 and 0.1 s, respectively. The LC-MS/MS run time was 10 min per sample.

Validation of the Proposed Method. The analytical method was validated as per the single-laboratory validation approach.[19] The performance of the method was evaluated considering different validation parameters that include the following items: calibration range, sensitivity, precision, and accuracy-recovery experiments.

Extraction, Isolation, and Identification of Intermediate Photoproducts from Solution. For the identification and isolation of reaction products, 2 g of hexythiazox was irradiated in eight different batches each containing 250 mg of hexythiazox (purity = 99.90%) dissolved in 1 L of water containing TiO_2 (50 mg/L) as photosensitizer. The solution mixture was homogenized by shaking and then irradiated by UV light for 100 h. After photolysis, each batch was combined, dried over anhydrous sodium sulfate, and concentrated using a rotary vacuum evaporator. The combined crude was subjected to column chromatography (60 × 1 cm i.d. glass column) over activated silica gel (100−200 mesh), and the column was eluted with solvents of increasing polarity (hexane to ethyl acetate, in increasing ratio) to isolate the photolytic products in pure form. Volumes of 50 mL of eluting solvent were collected, and each aliquot was subjected to thin layer chromatography (TLC) analysis, which was performed on Merck silica gel F_{254} plates as a stationary phase to determine if any metabolite of hexythiazox was eluting from the crude mixture from the column. Fractions showing similar chromatographic features were grouped and evaporated to dryness, the details of which have been depicted in Table 2. The details of the column chromatography and identification of the two photometabolites are described under Results and Discussion.

As a very small amount of hexythiazox was irradiated in each case, there was a little chance to get a good amount of each photometabolite in pure form by glass column chromatography separation from the crude mixture after 100 h of irradiation. Hence, most of the photometabolites

Table 1. Kinetics Study of Hexythiazox in Different Solvent Systems under the Influence of UV Light or Sunlight without and with Sensitizers (H_2O_2, KNO_3, and TiO_2)

	residue (μg mL^{-1}, mean ± SD)							
	UV light				sunlight			
time (h)	blank	H_2O_2	KNO_3	TiO_2	blank	H_2O_2	KNO_3	TiO_2
				Hexythiazox in Aqueous Isopropanol				
0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0
5	9.8 ± 0.03	9.7 ± 0.09	9.6 ± 0.08	9.5 ± 0.1	9.8 ± 0.08	9.6 ± 0.06	9.4 ± 0.06	9.3 ± 0.05
15	9.0 ± 0.04	8.8 ± 0.08	8.7 ± 0.09	8.6 ± 0.06	9.3 ± 0.06	9.1 ± 0.05	9.0 ± 0.05	8.8 ± 0.04
25	8.2 ± 0.03	8.1 ± 0.06	7.9 ± 0.05	7.8 ± 0.05	9.0 ± 0.05	8.8 ± 0.04	8.6 ± 0.07	8.5 ± 0.03
40	7.4 ± 0.05	7.2 ± 0.07	7.1 ± 0.07	6.8 ± 0.05	7.6 ± 0.05	7.3 ± 0.06	7.2 ± 0.05	7.1 ± 0.02
60	6.2 ± 0.07	5.8 ± 0.04	5.9 ± 0.05	5.7 ± 0.04	7.2 ± 0.04	6.9 ± 0.05	6.7 ± 0.06	6.6 ± 0.04
75	5.7 ± 0.04	5.5 ± 0.06	5.4 ± 0.04	5.2 ± 0.08	6.6 ± 0.04	6.3 ± 0.04	6.2 ± 0.06	6.0 ± 0.05
100	4.9 ± 0.03	4.6 ± 0.04	4.5 ± 0.04	4.2 ± 0.04	6.1 ± 0.03	5.8 ± 0.03	5.6 ± 0.03	5.5 ± 0.01
$t_{1/2}$ (h)	94.07	88.54	86.01	81.36	130.88	125.43	120.41	115.78
				Hexythiazox in Aqueous Acetonitrile				
0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.	10.0 ± 0.0	10.0 ± 0.
5	9.5 ± 0.05	9.3 ± 0.08	9.2 ± 0.05	9.2 ± 0.03	9.5 ± 0.05	9.2 ± 0.04	9.1 ± 0.04	9.1 ± 0.07
15	8.6 ± 0.03	8.3 ± 0.06	8.1 ± 0.06	8.0 ± 0.07	9.1 ± 0.05	8.9 ± 0.03	8.7 ± 0.07	8.5 ± 0.04
25	7.7 ± 0.02	7.1 ± 0.04	7.0 ± 0.05	6.9 ± 0.02	8.6 ± 0.04	8.4 ± 0.04	8.3 ± 0.08	8.1 ± 0.05
40	7.1 ± 0.04	6.5 ± 0.02	6.4 ± 0.04	6.3 ± 0.01	7.3 ± 0.03	7.0 ± 0.02	6.8 ± 0.05	6.6 ± 0.05
60	5.8 ± 0.03	5.5 ± 0.07	5.3 ± 0.03	5.2 ± 0.04	6.8 ± 0.06	6.2 ± 0.04	6.1 ± 0.06	5.9 ± 0.06
75	5.0 ± 0.02	4.8 ± 0.05	4.7 ± 0.03	4.6 ± 0.04	6.2 ± 0.04	5.8 ± 0.03	5.7 ± 0.01	5.5 ± 0.04
100	4.3 ± 0.02	4.1 ± 0.02	4.0 ± 0.01	3.8 ± 0.03	5.4 ± 0.02	5.2 ± 0.02	5.1 ± 0.05	4.9 ± 0.01
$t_{1/2}$ (h)	81.36	79.22	77.19	73.42	115.78	107.51	103.80	97.11
				Hexythiazox in Aqueous Methanol				
0	10.00 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.0	10.0 ± 0.04	10.0 ± 0.0
5	9.6 ± 0.08	9.4 ± 0.08	9.3 ± 0.06	9.2 ± 0.04	9.7 ± 0.04	9.5 ± 0.06	9.4 ± 0.05	9.4 ± 0.07
15	8.8 ± 0.05	8.5 ± 0.04	8.4 ± 0.05	8.3 ± 0.05	9.2 ± 0.05	8.9 ± 0.04	8.7 ± 0.06	8.7 ± 0.05
25	7.8 ± 0.02	7.3 ± 0.06	7.2 ± 0.04	7.1 ± 0.04	8.8 ± 0.06	8.6 ± 0.03	8.5 ± 0.04	8.5 ± 0.06
40	7.2 ± 0.02	6.8 ± 0.03	6.6 ± 0.02	6.5 ± 0.03	7.5 ± 0.05	7.1 ± 0.02	7.0 ± 0.03	7.0 ± 0.07
60	6.1 ± 0.08	5.7 ± 0.06	5.5 ± 0.03	5.4 ± 0.02	7.1 ± 0.04	6.6 ± 0.07	6.5 ± 0.02	6.5 ± 0.02
75	5.2 ± 0.02	5.0 ± 0.03	4.9 ± 0.04	4.7 ± 0.01	6.5 ± 0.03	6.1 ± 0.05	6.0 ± 0.03	6.0 ± 0.03
100	4.5 ± 0.01	4.2 ± 0.01	4.1 ± 0.02	4.0 ± 0.02	5.8 ± 0.02	5.5 ± 0.03	5.3 ± 0.03	5.3 ± 0.04
$t_{1/2}$ (h)	86.01	81.36	79.22	77.19	125.43	115.78	111.49	103.80

Table 2. Column Chromatographic Separation of a Photoirradiated Solution of Hexythiazox

eluting solvent	no. of flasks (50 mL each)	observation after evaporation
hexane	1−31	brownish liquid
hexane/ethyl acetate (9.7:0.3)	32−36	no significant observation
hexane/ethyl acetate (9.5:0.5)	37−51	brownish liquid, single spot in TLC
hexane/ethyl acetate (9:1)	52−55	no significant observation
hexane/ethyl acetate (8.5:1.5)	56−96	no significant observation
hexane/ethyl acetate (8:2)	97−102	no significant observation
hexane/ethyl acetate (7.5:2.5)	102−106	white solid, single spot in TLC
hexane/ethyl acetate (7:3)	107−138	no significant observation
hexane/ethyl acetate (6.5:3.5)	139−147	no significant observation
hexane/ethyl acetate (4:6)	231−238	no significant observation
hexane/ethyl acetate (3:7)	239−245	no significant observation

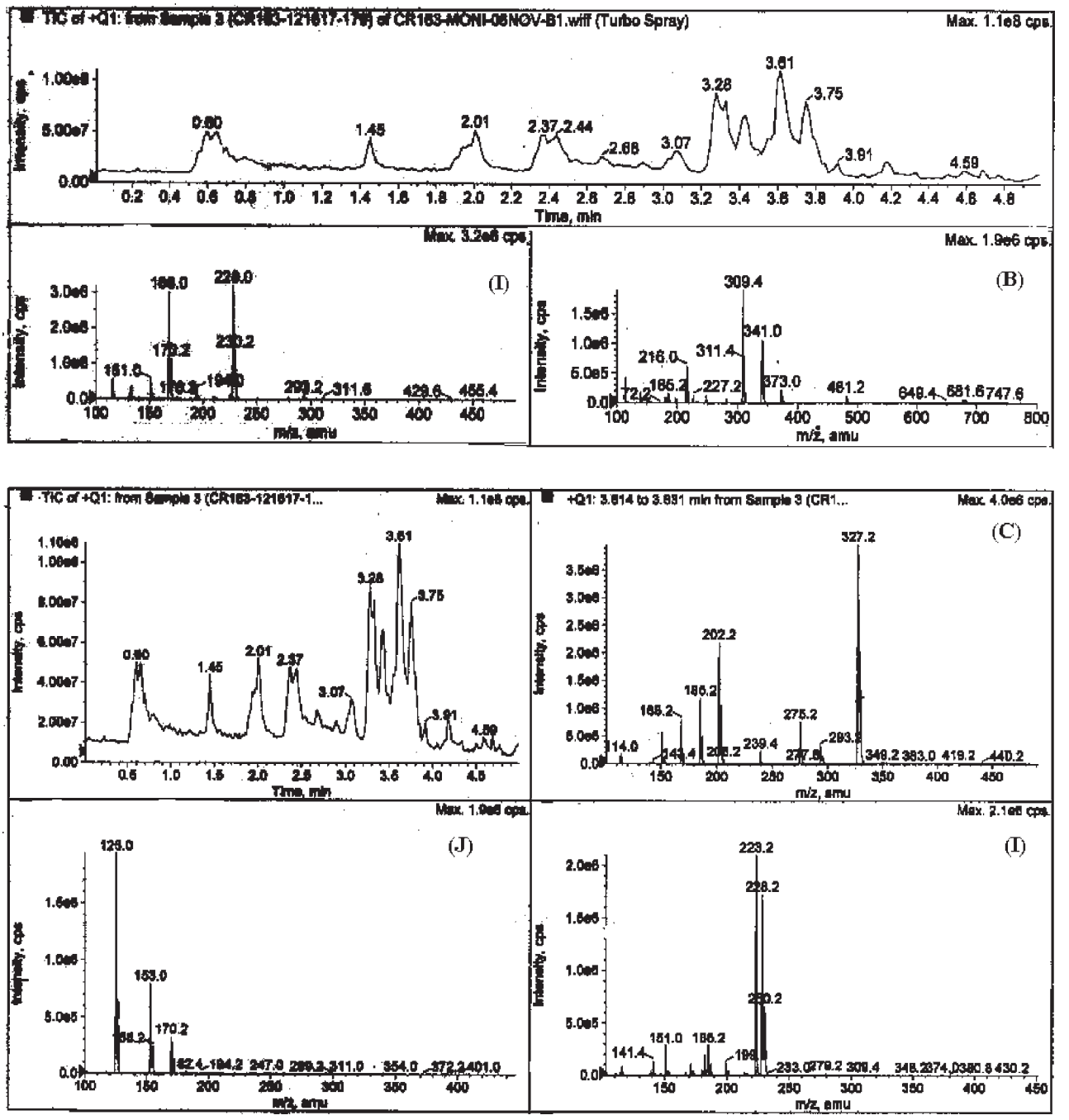

Figure 2. Mass spectra of intermediates formed during the photodegradation of hexythiazox after 50 h of irradiation with UV light in the presence of TiO_2.

and major intermediates from the crude mixture (after 100 h of irradiation of hexythiazox) were identified and confirmed by LC-MS/MS technique.

RESULTS AND DISCUSSION

Validation of the Proposed Analytical Method. The linearity in the response was studied using three different solvent systems prepared by spiking hexythiazox at five concentration levels, ranging from 0.005 to 5 μg mL^{-1}. The calibration curves were obtained by plotting the peak area against the concentration of the corresponding calibration standards in all matrices. Good linearity was observed in the studied range with R^2 values >0.99. It can be seen that the mean recoveries ranged from 98 to 99% for the three different solvent systems, and the relative standard deviation (RSD) values obtained from run to run (RSDr) and from day to day (RSDR) were <6%. From the results obtained, the developed method was found to be precise[20] fr quantitative purposes (Figure 1). An estimated value of LOD was 0.002 μg mL^{-1}, whereas LOQ values were in the range of 0.005 μg mL^{-1}.

Photodegradation Kinetics. We presented different approaches of photodissipation of 10 μg mL^{-1} hexythiazox under UV light and sunlight in Table 1 in different solvent systems after 0, 5, 15, 25, 40, 60, 75, and 100 h of photoirradiation. All of the samples were processed and analyzed by LC-MS/MS followed

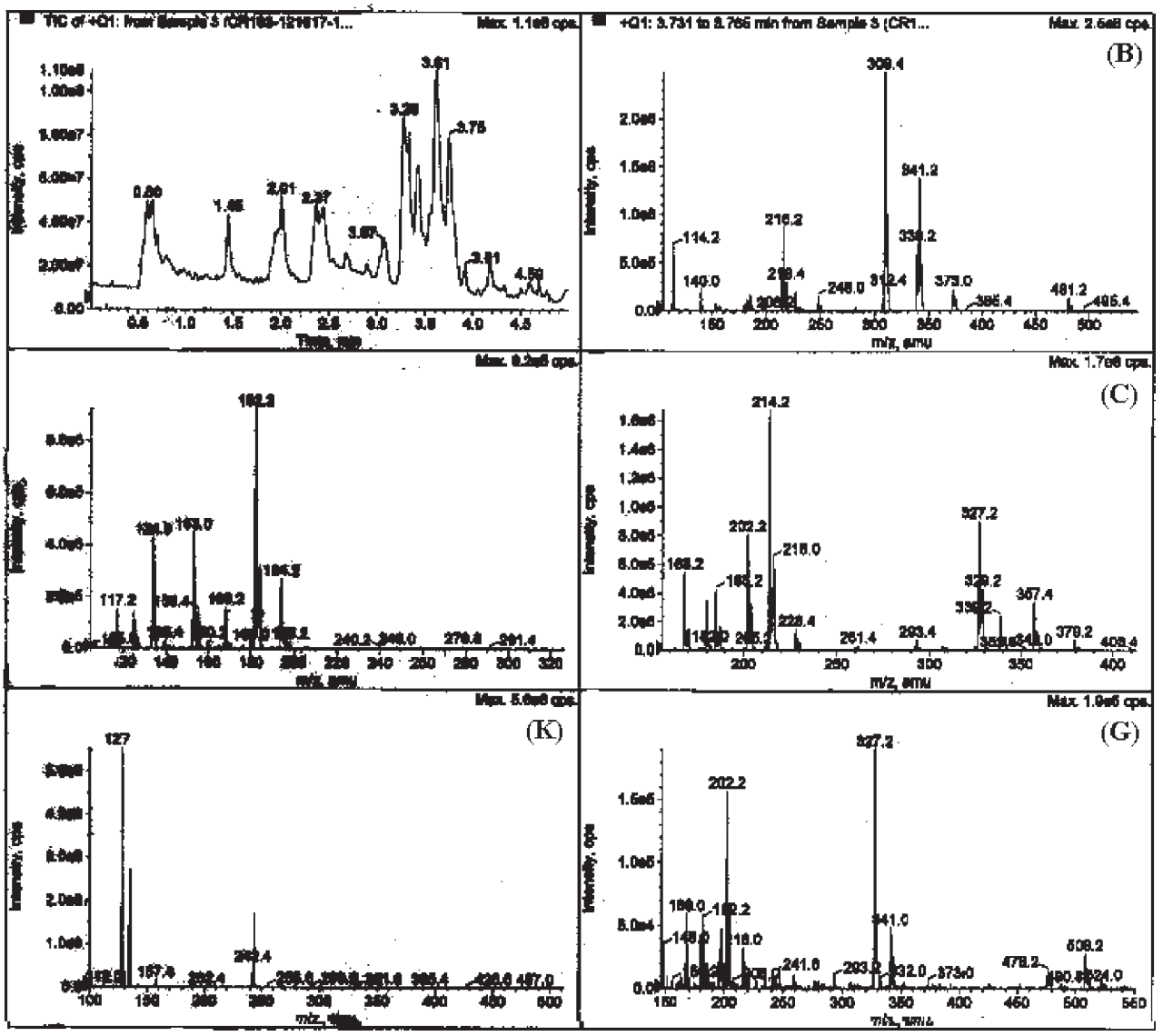

Figure 3. Mass spectra of intermediates formed during the photodegradation of hexythiazox after 100 h of irradiation with UV light in the presence of TiO_2.

by calculation of the data in micrograms per milliliter. From Table 1, it can be observed that the rate of disappearance of hexythiazox was decreased with time of irradiation in all cases. The results revealed that the degradation of hexythiazox in different solvent systems followed first-order kinetics. The half-life values were calculated from the corresponding regression equations.

Aqueous isopropanolic solution of hexythiazox in the absence of sensitizer under UV irradiation showed 25.1% degradation of the initial concentration after 40 h, whereas the corresponding values were 27.2, 28.5, and 31.1% in the presence of H_2O_2, KNO_3, and TiO_2, respectively. The concentration of the parent compound after 100 h of irradiation was found to be 4.9 μg mL^{-1} and 4.6−4.2 μg mL^{-1} under UV light in the absence and in the presence of sensitizer (H_2O_2, KNO_3, and TiO_2), respectively. The half-life value was 94.07 h in the absence of sensitizer and 88.54−81.36 h in the presence of sensitizer. For irradiation under sunlight, the aqueous isopropanolic solution of hexythiazox after 100 h of irradiation under direct sunlight the corresponding values of degradation were 39 and 41−44% in the absence and presence of sensitizer, respectively. The half-life value was 130.88 h in the absence of sensitizer and 125.43−115.78 h in the presence of sensitizer (H_2O_2, KNO_3, and TiO_2).

Aqueous acetonitrile solution of hexythiazox in the absence of sensitizer under UV irradiation showed 28.9% degradation of the initial concentration after 40 h, whereas the corresponding values were 34, 37, and 36% in the presence of H_2O_2, KNO_3, and TiO_2, respectively. The concentration of the compound remaining at the end of the irradiation period (100 h) was found to be 4.37 μg mL^{-1} and 4.1−3.85 μg mL^{-1} under UV light in the absence and presence of sensitizer (H_2O_2, KNO_3, and TiO_2), respectively. The half-life value was 81.36 h in the absence of sensitizer and 79.22−73.42 h in the presence of sensitizer. For the sunlight-irradiated aqueous acetonitrile solution of hexythiazox after 100 h of irradiation under direct sunlight the corresponding values of degradation were 45 and 47−51% in the absence and presence of sensitizer, respectively. The half-life value was 115.78 h in the absence of sensitizer and 97.11−107.51 h in the presence of sensitizer (TiO_2, KNO_3, and H_2O_2).

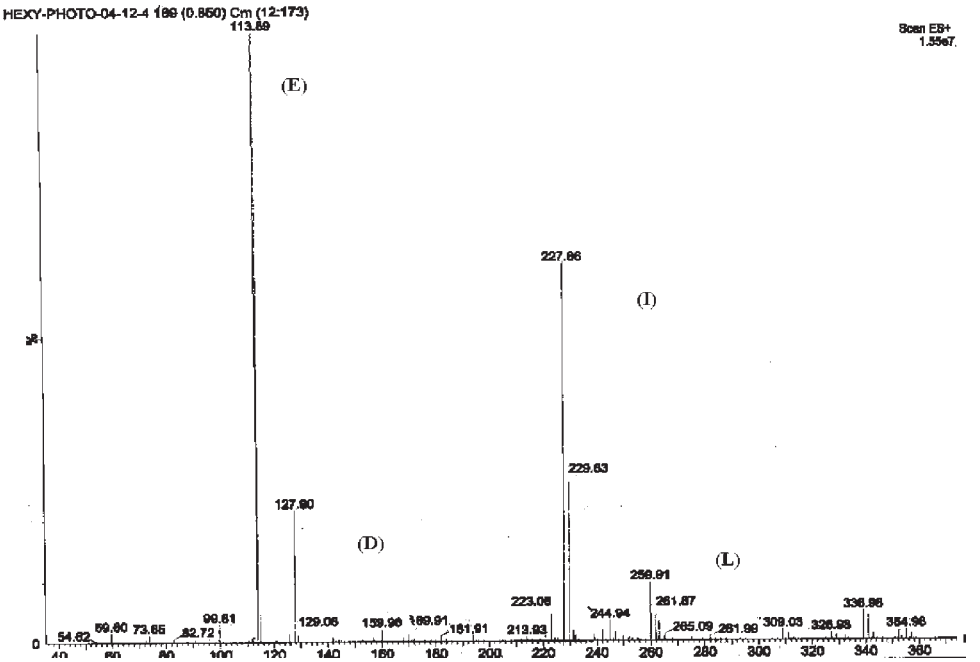

Figure 4. LC-MS chromatogram (MS scan) obtained for hexythiazox solution after 50 h of irradiation with UV light in the presence of TiO_2.

On the other hand, the aqueous methanolic solution of hexythiazox in the absence of sensitizer under UV irradiation showed 27.9% degradation of the initial concentration after 40 h, whereas the corresponding values were 31, 34, and 33% in the presence of H_2O_2, KNO_3, and TiO_2, respectively. The concentrations of the compound remaining at the end of the irradiation period (100 h) were found to be 54 and 60−57% under UV light in the absence and in the presence of sensitizer (H_2O_2, KNO_3, and TiO_2), respectively. The half-life value was 86.01 h in the absence of sensitizer and 81.36−77.19 h in the presence of sensitizer. For irradiation under sunlight, the aqueous methanolic solution of hexythiazox in the absence of sensitizer dissipated to 25% of the initial concentration after 40 h of irradiation, whereas the corresponding values were 31, 33, and 34% in the presence of H_2O_2, KNO_3, and TiO_2, respectively. After 100 h of irradiation under direct sunlight, the corresponding values were 41 and 45−49% in the absence and in the presence of sensitizer, respectively. The half-life value was 125.43 h in the absence of sensitizer and 115.78−103.80 h in the presence of sensitizer (H_2O_2, KNO_3, and TiO_2).

Table 1 reveals that the rate of degradation of hexythiazox in three solvent systems is faster under UV irradiation compared to sunlight irradiation. Sensitizer H_2O_2 in both solvent systems had less of an effect on the rate of degradation in UV light and sunlight irradiation than the other sensitizers (KNO_3 and TiO_2). The greatest degradation rate was observed in the presence of TiO_2 (Table 1). It was also observed that the rate of disappearance of hexythiazox in the aqueous acetonitrile system was faster than in the aqueous methanolic system and that the degradation is slowest in aqueous isopropanolic system. In all cases a dark control was kept, and no reaction was observed during the entire irradiation period.

Column Chromatographic Isolation and Characterization of Photometabolites. From the kinetic experiment it was found that the half-life of hexythiazox was lowest under UV irradiation in solution containing TiO_2 as sensitizer. Thus, it was expected that the quantitative yield of photometabolites will be maximum under this condition. With this basic information this system was chosen for column chromatographic study. Two products were isolated in column chromatography. The fraction 37−51 obtained from the above column chromatography (Table 2) yielded a light brownish liquid (R_f = 0.4 (ethyl acetate/hexane = 1:9)); the IR spectrum of this compound exhibited two absorption bands at 3319 and 2932 cm^{-1} due to the presence of a primary amine group. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.44 (m, 3H), 1.78 (m, 2H), 2 (m, 2H), 2.67 (m, 1H); MS (EI) 98.86 (M^+). IR, ^1H NMR, and mass spectra evidence conclusively established the structure of M1 as cyclohexylamine (**F**). Concentration of the fraction 102−106 obtained from the above column chromatography (Table 2) yielded a light white solid (R_f = 0.3 (ethyl acetate/hexane = 1:9)); the IR spectrum of this compound exhibited only a single weak band at 3184 cm^{-1} due to the presence of a secondary amine group. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.41−7.43 (m, 4H), 5.75(t, 1H), 4.54 (d, 1H), 3.88 (d, 1H), 1.30 (d, 3H). IR, ^1H NMR, and mass spectra evidence conclusively established the structure of M1 as 5-(4-chlorophenyl)-4-methylthiazolidin-2-one (**I**).

Identification of Major Intermediates. The photodegradation of hexythiazox in different sources of solvent medium under UV light and sunlight exposure in the presence or absence of sensitizers results in a total of 11 photoproducts. In the present investigation the 11 photometabolites of hexythiazox (**A**−**K**) were identified from final solvent mixtures. Only two photometabolites (**I** and **F**) were separated out in pure form by following the above column chromatographic method. From the different spectral data (IR, ^1H NMR, mass) the structures of these two metabolites were assigned as cyclohexylamine (**F**) and 5-(4-chlorophenyl)-4-methylthiazolidin-2-one (**I**). The remaining 9 photometabolites (A−E, G, H, J, and K) were identified from the different irradiation systems on the basis of LC-MS/MS analysis (Figures 2−4). On the basis of MS/MS data analysis, the structures of these 9 photometabolites were assigned as 5-(4-chlorophenyl)-4-methyl-2-oxothiazolidine-3-carboxylic acid

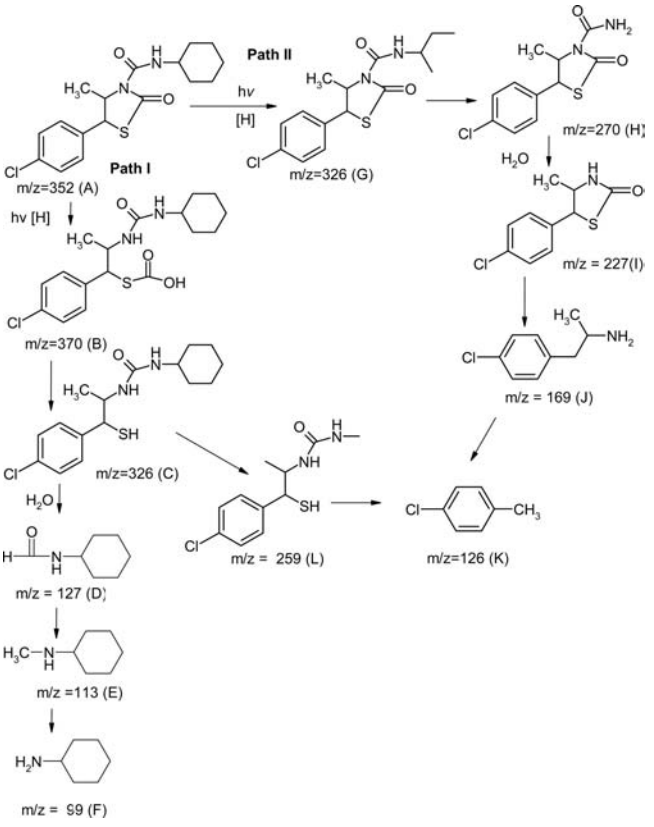

Figure 5. Proposed photodegradation pathway for hexythiazox on the basis of metabolites identified.

cyclohexylamide (**A**), thiocarbonylic acid 1-(4-chlorophenyl)-2-(3-cyclohexylureido)propyl ester (**B**), 1-[2-(4-chlorophenyl)-2-mercapto-1-methylethyl]-3-cyclohexylurea (**C**), *N*-cyclohexylformamide (**D**), cyclohexylmethylamine (**E**), 5-(4-chlorophenyl)-4-methyl-2-oxothiazolidine-3-carboxylic acid *sec*-butylamide (**G**), 5-(4-chlorophenyl)-4-methyl-2-oxothiazolidine-3-carboxylic acid amide (**H**), 2-(4-chlorophenyl)-1-methylethylamine (**J**), and 1-chloro-4-methylbenzene (**K**).

A possible reaction mechanism of photodegradation pathways of hexythiazox in aqueous isopropanol in the presence of TiO_2 is portrayed in Figure 5. The photolysis is explained by a radical mechanism wherein the initial step is homolytic cleavage of the C−C bond and C−N bond in path I and path II, respectively, which could undergo further reactions. The photolysis of **A** results in **B** and **G** by hydrogen transfer from the organic solvent. In aquous medium a subsequent hydrolysis of **C** leads to the formation of **D** and hydrolysis of **H** leads to the formation of **I**. A possible intermediate in the formation of **F** is **E**. **K** is described as the final photoproduct of hexythiazox. In conclusion, hexythiazox is rather susceptible to photodegradation independent of the chemical environment, resulting in **K** and **F** as main products in organic solvents. However, photoproduct **H** is quite stable toward photodegradation. Further research is needed to transfer the results from model systems to field condition.

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REFERENCES

(1) Muccinelli, M. New active principles in plant protection: heythiazox (an acaricide). *Inf.-Fitopatol.* **1987**, *37*, 64.

(2) Graham Thwaite, W. Resistance to clofentezine and hexythiazox in *Panonychus ulmi* from apples in Australia. *Exp. Appl. Acarol.* **1991**, *11*, 73–80.

(3) Robinson, D. E.; Mansingh, A.; Dasgupta, T. P. Fate and transport of ethoprophos in the Jamaican environment. *Sci. Total Environ.* **1999**, *30*, 373–379.

(4) Kaur, I.; Mathur, R. P.; Tandon, S. N.; Dureja, P. Identification of metabolites of malathion in plant, water and solid by GC-MS. *Biomed. Chromatogr.* **1997**, *11*, 352–355.

(5) Lin, Y. J.; Karuppiah, M.; Shaw, A.; Gupta, G. Effect of simulated sunlight on atrazine and metolachlor toxicity of surface waters. *Ecotoxicol. Environ. Saf.* **1999**, *43*, 35–37.

(6) Grover, R.; Wolt, J. D.; Cessna, A. J.; Schiefer, H. B. Environmental fate of trifluralin. *Rev. Environ. Contam. Toxicol.* **1997**, *153*, 1–64.

(7) Nivedita, S.; Srikumar, P.; Hemanta, B.; Narayan, A.; Anjan, B. Photodegradation of fenarimol. *Pest Manag. Sci.* **2000**, *56*, 289–292.

(8) Won, H. B.; Wong, M. K.; Mok, C. Y. Comparative study on quantum yields of direct photolysis of organophosphorus pesticides in aqueous solution. *J. Agric. Food Chem.* **1994**, *42*, 2625–2630.

(9) Nojima, K.; Isogami, C. Photolysis of aldrin in the presence of benzaldehyde in solid vapor−air system. *Chem. Pharm. Bull.* **1996**, *44*, 1580–1584.

(10) Cosby, P. G.; Moilanen, K. W.; Nakagawa, M.; Wong, A. S. *Environmental Toxicology of Pesticides*; Academic Press: New York, 1972; p 423.

(11) Kanrar, B; Anjan Bhattacharyya, S. Photolysis of the herbicide bispyribac sodium in aqueous medium under the influence of UV and sunlight in presence or absence of sensitizers. *J. Environ. Sci. Health., Part B* **2009**, *44*, 788–797.

(12) Pramanik, S. K.; Das, S.; Bhattacharyya, A. Photodegradation of the herbicide penoxsulam in aqueous methanol and acetonitrile. *J. Environ. Sci. Health., Part B* **2008**, *43*, 569−575.

(13) Watkins, D. A. M. Some implications of the photochemical decomposition of pesticides. *Chem. Ind.* **1974**, 185–190.

(14) Nelieu, S.; Shankar, M. V.; Kerhoas, L.; Einhorn, J. Phototransformation of Monuron induced by nitrate and nitrite ions in water: contribution of photonitration. *J. Photochem. Photobiol. A: Chem.* **2008**, *193*, 1–9.

(15) Fujishima, A.; Rao, T. N.; Tryk, D. A. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C* **2000**, *1*, 1–21.

(16) Ollis, D. F.; Hsiao, C.; Budiman, L.; Lee, C. Heterogeneous photoassisted catalysis: conversions of perchloroethylene, dichloroethane, chloroacetic acids, and chlorobenzenes. *J. Catal.* **1984**, *88*, 89–95.

(17) Graetzel, M. In *Energy Resources through Photochemistry and Catalysis*; Graetzel, M., Ed.; Academic Press: New York, 1983.

(18) Bolton, J. R.; Bircger, K. G.; Tumas, W.; Tolman, C. A. Figure of Merit for technical developmnmt and application of advanced oxidation technologies for both electric and solar derived systems. *Pure Appl. Chem.* **2001**, *73*, 627–637.

(19) Thompson, M.; Ellison, S. L.; Wood, R. Harmonized guidelines for single laboratory validation of method of analysis. *Pure Appl. Chem.* **2002**, *74*, 835–855.

(20) Commission of the European Union. Quality Control Procedures for Pesticide Residues Analysis, Document SANCO/3131/2007, 2007.