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Research Article

Photocatalytic Degradation of Trifluralin, Clodinafop-Propargyl, and 1,2-Dichloro-4-Nitrobenzene As Determined by Gas Chromatography Coupled with Mass Spectrometry

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Phototransformation is considered one of the most key factors affecting the fate of pesticides. Therefore, our study focused on photocatalytic degradation of three selected pesticide derivatives: trifluralin (**1**), clodinafop-propargyl (**2**), and 1,2-dichloro-4-nitrobenzene (**3**). The degradation was carried out in acetonitrile/water medium in the presence of titanium dioxide (TiO_2) under continuous purging of atmospheric air. The course of degradation was followed by thin-layer chromatography and gas chromatography-mass spectrometry techniques. Electron ionization mass spectrometry was used to identify the degradation species. GC-MS analysis indicates the formation of several intermediate products which have been characterized on the basis of molecular ion, mass fragmentation pattern, and comparison with NIST library. The photocatalytic degradation of pesticides of different chemical structures manifested distinctly different degradation mechanism. The major routes for the degradation of pesticides were found to be (a) dealkylation, dehalogenation, and decarboxylation, (b) hydroxylation, (c) oxidation of side chain, if present, (d) isomerization and cyclization, (e) cleavage of alkoxy bond, and (f) reduction of triple bond to double bond and nitro group to amino.

1. Introduction

The contamination of water bodies due to the presence of pesticides constitutes a pervasive problem and therefore advanced methods are in demand for the effective treatment of these pesticide polluted ground and surface waters. Advanced oxidation processes have proven effective for the removal of organic pollutants. During the last two decades, photocatalytic processes involving semiconductor particles under UV light illumination have been shown to be potentially advantageous and useful in the degradation of organic pollutants [1–3]. The process occurs as a result of the interaction of a semiconductor photocatalyst and UV radiation that yields highly reactive hydroxyl and superoxide radical anions, which are believed to be the main species responsible for the oxidation of organic substrates. The most commonly used photocatalyst is TiO_2, which is inexpensive, abundant, photostable, and nontoxic [4]. The mechanism of photocatalysis is well documented in the literature [4, 5]. Briefly, when a semiconductor such as TiO_2 absorbs a photon of energy equal to or greater than its band gap energy, an electron may be promoted from the valence band to the conduction band (e^-) leaving behind an electron vacancy or "hole" in the valence band (h^+), as shown in (1). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species [6, 7]. In particular, h^+ may react with surface-bound H_2O to produce the hydroxyl radical and e^- is picked up by oxygen to generate superoxide radical anion (O_2^{-}), as indicated in (2) and (3):

$$TiO_2 + h\nu \longrightarrow TiO_2^{*}\left(e^- + h^+\right) \quad (1)$$

$$e^- + O_2 \longrightarrow O_2^{\bullet -} \quad (2)$$

$$H_2O + h^+ \longrightarrow OH^{\bullet} + H^+ \quad (3)$$

The photocatalyzed degradation of pesticides does not occur directly to release inorganic species but through the formation of prolonged intermediates or degradation products which can themselves be toxic and, in some cases, more persistent than the original substrate [8–10].

Therefore detection and identification of the degradation products during photocatalytic treatment are important to optimize and increase the overall efficiency of the process. However, the intricacy of the reaction pathways, formation of numerous by-products, and the broad range of concentration and polarity of intermediated products are some of the problems faced during analytical determination of degradation products. Therefore careful analytical screening using diverse techniques is essential to examine the various possible transformation routes and to understand and propose the reaction pathways [11].

Due to the complexity of the electron/radical induced reactions occurring during the photocatalytic processes, it is difficult to suggest a comprehensive reaction pathway explaining the formation of all detected intermediates. However, a comparatively adequate number of fairly abundant degradation products have been recognized during the process, so that a probable scheme can be suggested considering the common transformation processes of other organic compounds [11]. Gas chromatography coupled with mass spectrometry is one of the most frequent analytical tools used for the detection of degradation products [12–14].

Trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl) aniline) (**1**), a dinitroaniline herbicide, is one of the most common herbicides used to control many annual grasses and broadleaf weeds for agricultural crops [15]. Trifluralin is currently registered in more than 50 countries for use on over 80 crops [16]. It is currently the 3rd and 4th most commonly used herbicide on cotton and soybean, respectively. Due to its hydrophobic nature, it strongly sorbs to soil and therefore its transport to the surface and ground water in the dissolved-phase is very limited. Offsite transport mainly takes place by soil erosion and subsequent deposition into streams and lakes or by volatilization losses following field applications [17–20]. Trifluralin has been classified as group C possible human carcinogen and possesses relatively high toxicity for aquatic organisms. Moreover, trifluralin is suspected to be an endocrine disruptor [21].

Clodinafop-propargyl (2-propynyl (R)-2-[4-(5-chloro-3-fluoro-2-pyridinyloxy)phenoxy]propionate) (**2**) is a systemic, postemergence herbicide that effectively controls isoproturon-resistant little seed canary grass biotypes (*Phalaris minor* Retz.) along with other broad-leaved weeds of wheat (*Triticum aestivum*) [22–26]. This herbicide is used in combination with a safener, cloquintocet-mexyl, but has an antagonistic effect with auxin-type herbicides [27]. It interferes with the production of fatty acids needed for plant growth in susceptible grassy weeds [28]. This herbicide breaks down rapidly in soil and is mobile in soil. The toxicity data indicates that clodinafop-propargyl has low acute oral, dermal, and inhalation toxicity. It has been classified as "likely to be carcinogenic to human" causing developmental and fetotoxicity in rats. This product has been found to be moderately toxic to aquatic organisms (human health risk assessment for the use of the new active ingredient, clodinafop-propargyl, on wheat, United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Washington, DC).

Chloronitrobenzenes are important chemical intermediates in the manufacture of dyes and agricultural, pharmaceutical, and industrial agents [29–33]. The toxicity induced by chloronitrobenzenes includes hematoxicity, sphenotoxicity, hepatotoxicity [34–36], and immunotoxicity [37, 38].

Therefore in this paper we report the photocatalytic transformation of three selected pesticide derivatives: trifluralin (**1**), clodinafop-propargyl (**2**), and 1,2-dichloro-4-nitrobenzene (**3**) in acetonitrile/water medium catalyzed by TiO_2 in the presence of atmospheric oxygen and UV light.

2. Experimental

2.1. Reagents and Chemicals. The analytical standard trifluralin (**1**), clodinafop-propargyl (**2**), and 1,2-dichloro-4-nitrobenzene (**3**) were purchased from Sigma-Aldrich, India, and were used without further purification. Heterogeneous photocatalytic transformation experiments were carried out using Degussa P-25 TiO_2 (Degussa AG). Degussa P25 consists of 80% anatase and 20% rutile with a specific BET-surface area of 50 $m^2\,g^{-1}$ and primary particle size of 20 nm [39]. All other chemicals used in this study like acetonitrile (CH_3CN), sodium sulphite (Na_2SO_3), chloroform ($CHCl_3$), and so forth were of analytical grade and obtained from Merck.

2.2. Procedure. Experiments were carried out in an immersion well photoreactor made of Pyrex glass equipped with a magnetic bar, a water circulating jacket, and an opening for molecular oxygen. A detailed description of photocatalytic reactor was documented in our previous paper [40]. In a typical run, TiO_2 (Degussa, P25 1.5 gL^{-1}) was added to acetonitrile/water (1 : 6) solution of trifluralin (1.22 mM; 180 mL) or clodinafop-propargyl (1.22 mM; 180 mL) or 1,2-dichloro-4-nitrobenzene (1.24 mM; 180 mL). The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips) placed at the centre of the inner jacket. The light intensity was measured at the inner wall of the annular reactor using UV-light intensity detector (Lutron UV-340) and was found in between 1.92 and 1.95 mW/cm^2. IR-radiations were eliminated by a water jacket. Aliquots (10 mL) were withdrawn at different time intervals and filtered using Whatman grade number 1 filter paper to remove the TiO_2 particles. The filtrate was extracted at least thrice with chloroform (10 mL) and dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure to give a residual mass. The formation of products was followed using thin-layer chromatography technique and then finally analyzed by GC-MS analysis technique. $CHCl_3$ was used to reconstitute the sample of trifluralin and clodinafop-propargyl for GC-MS analysis whereas CH_3CN was used as solvent for 1,2-dichloro-4-nitrobenzene.

Table 1: Probable products formed during the photocatalytic degradation of trifluralin (**1**) along with their retention time and corresponding mass fragmentation.

Retention time (min)	Name	Confirmed by	Mass fragmentation
9.4	2,6-Dinitro-N,N-dipropyl-4-(trifluoromethyl)aniline (**1**)	NIST	335.142 (M^+), 318.138, 306.136/307.105, 290.105, 264.076/265.053, 248.054, 206.051, 160.049, 145.035
9.9	2-Ethyl-7-nitro-5-(trifluoromethyl)-1H-benzo[d]imidazole (**12**)	NIST	259.157 (M^+), 241.123, 227.105, 213.095, 207.014, 199.073, 186.098, 158.187, 147.827, 114.459, 99.536, 54.368
11.0	2-Ethyl-7-nitro-1-propyl-5-(trifluoromethyl)-1H-benzo[d]imidazole (**9**)	NIST	301.134 (M^+)/302.143, 282.140, 272.098, 258.078, 243.087/244.094, 212.077/213.083, 159.043, 145.037
12.7	7-Amino-2-ethyl-1-propyl-5-(trifluoromethyl)-1H-benzo[d]imidazole 3-oxide (**7**)	MS	287.150 (M^+)/288.159, 258.113/259.124, 245.103, 230.82, 217.069, 202.083
12.9	3-(2-(Hydroxyamino)-6-nitro-4-(trifluoromethyl)phenylamino)propan-1-ol (**10**)	MS	295.164 (M^+)/296.177, 280.140, 266.123, 252.111/23.111, 239.112, 225.095
13.0	2-Ethyl-1-propyl-5-(trifluoromethyl)-1H-benzo[d]imidazol-7-amine (**11**)	MS	271.155 (M^+)/272.160, 256.131, 242.113, 229.104/228.097
15.2	3-(2,6-Dinitro-4-(trifluoromethyl)phenylamino)propan-1-ol (**6**)	MS	310.171 (M^+), 295.153, 283.159/284.162, 268.134, 254.116, 240.101, 227.102, 213.089/214.091, 185.057

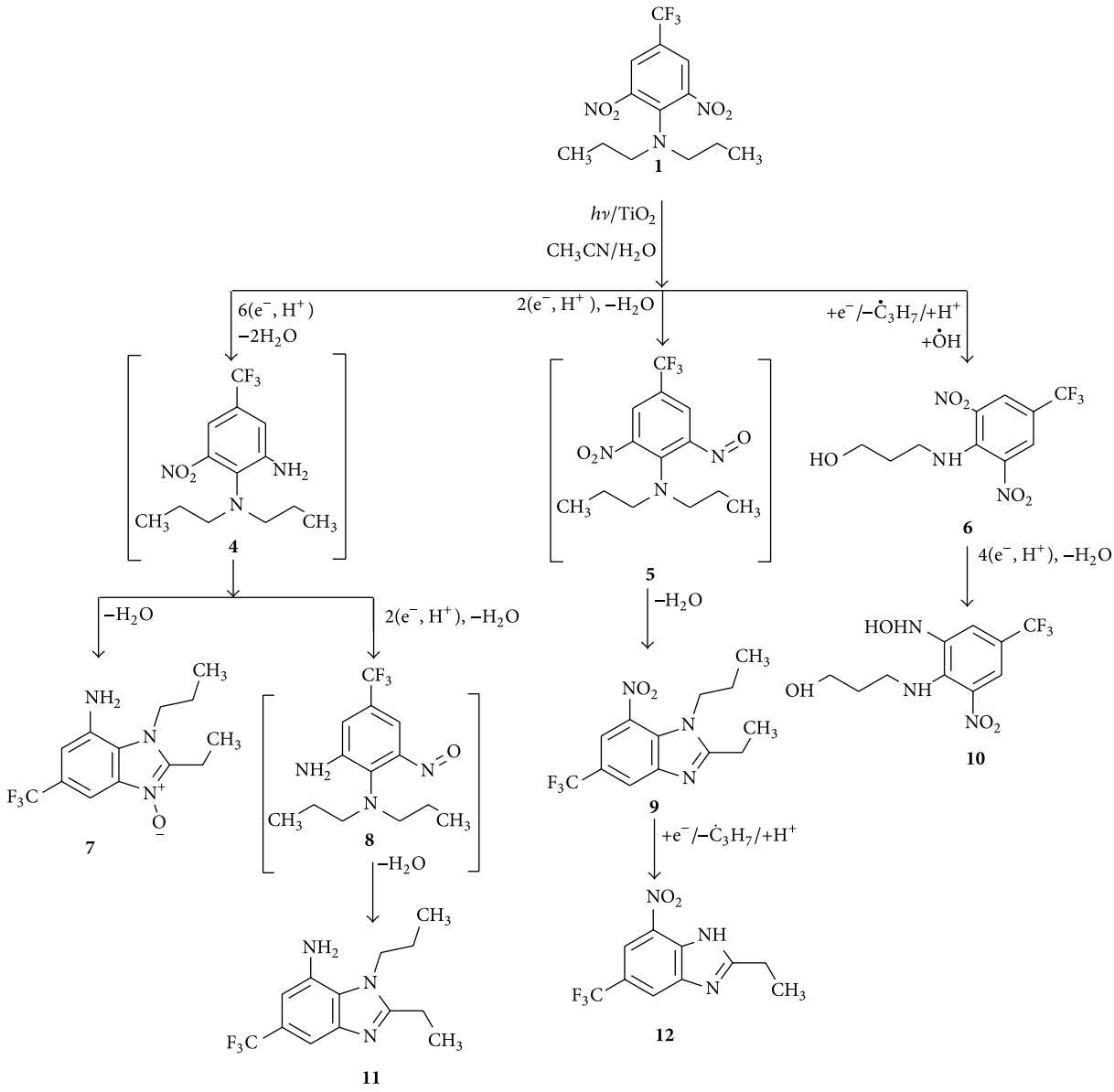
Note that the number in the parenthesis corresponds to the number of the compound in the degradation scheme.

2.3. Analysis. For GC-MS analysis, AccuTOF-GCv (JMS-T100GCv) system from Jeol Asia equipped with Agilent 7690 GC was used. The GC column for separation was a HP-5, 30 m long, and 0.25 mm internal diameter. The film thickness was 0.25 μm. The column temperature programme used was 100°C initially with an isothermal hold time for 5 min and then rose to 280°C at a ramp of 10°C/min. The injector temperature was 250°C and the injection volume was 0.4 μL, with a split ratio of 1 : 50. The interface temperature was maintained at 280°C. The carrier gas was helium with a flow rate of 1 mL/min. The positive electron ionization mode was used at 70-electron volt.

3. Results and Discussion

3.1. Photocatalytic Transformation of Trifluralin (1). GC-MS analysis of unirradiated and irradiated samples (6 hr and 9 hr) of trifluralin (**1**) is shown in Figures 1(a), 1(b), and 1(c), respectively. Figure 1(a) indicates a single peak at retention time (R_t) 9.4 corresponding to trifluralin confirmed by comparing molecular ion and mass fragmentation pattern with NIST library. Figures 1(b) and 1(c) indicate formation of several intermediate products on irradiation of trifluralin in the presence of TiO_2. It is interesting to note that, on prolonged irradiation of trifluralin for 9 hours, concentration of few intermediates decreases whereas some additional intermediates are formed. Few products that were characterized based on molecular ion, on mass fragmentation patterns, and also on comparison with NIST library are shown in Table 1.

The probable degradation pathway of trifluralin (**1**) under photocatalytic conditions showing the formation of various products is shown in Scheme 1. The complete reduction of one of the nitro groups of **1** to amino group leads to the formation of **4**. Partial reduction of nitro group of **4** gives nitroso derivative **8** which upon cyclization and subsequent loss of water molecule leads to the formation of product **11**. Cyclization of **4**, prior to reduction of nitro group, leads to N-oxide derivative **7**. Similarly, partial reduction of one of the nitro groups of **1** leads to intermediate **5** which upon further loss of water molecule gives benzimidazole derivative **9**. Loss of N-propyl group of **9** leads to the formation of **12**. The formation of benzimidazoles (**9**, **11,** and **12**) and benzimidazole-N-oxide derivative **7** was not unexpected. Previous studies have shown that N-alkyl-o-nitroanilines are readily cyclised to form benzimidazoles and benzimidazole-N-oxides upon irradiation at 2537 Å and upon irradiation through Pyrex [41, 42]. The entire aspects of chemical interaction between aromatic nitro groups and ortho side chains had been the subject of a review by Preston and Tennant [43]. Alternatively loss of one of the propyl groups and hydroxylation of another alkyl group of **1** may lead to **6**. Partial reduction of one of the nitro groups of **6** gives **10**. It is worth mentioning that dealkylation and reduction of nitro group to amino via nitroso under photocatalytic conditions are well documented in the literature [7, 11, 44–46].



Scheme 1: Probable pathway for the degradation of trifluralin (**1**) catalyzed by TiO_2 in the presence of UV light.

3.2. Photocatalytic Transformation of Clodinafop-Propargyl (2). Figures 2(a) and 2(b) show the gas chromatogram of unirradiated and irradiated sample (3 hr) of clodinafop-propargyl (**2**), respectively. The single peak at retention time (R_t) of 22.9 min in Figure 2(a) corresponds to clodinafop-propargyl confirmed by comparing its molecular ion and mass fragmentation pattern with those in NIST library. Figure 2(b) shows the gas chromatogram of clodinafop-propargyl after irradiation for three hours indicating the formation of several intermediate products along with some unchanged starting material. The structures of eight degradation products have been confirmed on the basis of their molecular ion and mass fragmentation patterns shown in Table 2.

The formation of these products during photocatalytic degradation of clodinafop-propargyl **2** can be understood in terms of the pathway shown in Scheme 2. The main reaction routes for the degradation involve dehalogenation, aromatic ring substitution, reduction of triple bond to double bond, and cleavage of ether linkage.

Loss of fluorine in **2** followed by hydroxylation may lead to the formation of **13** which in turn may form product **16** by the loss of pyridyl moiety via cleavage of the ether linkage. Alternatively, demethylation and the loss of propargyl alcohol radical followed by hydroxylation lead to product **14**. Cleavage of the ether linkage in **14** may lead to the formation of 5-chloro-3-fluoropyridin-2-ol (**17**) and 2-phenoxyacetic acid (**18**). Loss of acetic acid moiety of **14** may give product **19**

Table 2: Probable products formed during the photocatalytic degradation of clodinafop-propargyl (**2**) along with their retention time and corresponding mass fragmentation.

Retention Time (min)	Name	Confirmed By	Mass fragmentation
24.1	Prop-2-ynyl 2-(4-(5-chloro-3-hydroxypyridin-2-yloxy)phenoxy)propanoate (**13**)	MS	346.934 (M^+)/348.926, 310.977, 281.030, 264.022/266.022, 235.985, 219.987, 207.977, 179.996, 172.055, 146.055, 127.986, 99.903, 90.983, 72.570, 62.376
24.0	Allyl 2-(4-(5-chloro-3-fluoropyridin-2-yloxy)-2-hydroxyphenoxy)propanoate (**20**)	MS	366.986 (M^+)/368.852, 266.016/268.014, 237.979/238.985, 221.978, 209.977, 176.026, 159.034, 129.981, 90.894
23.9	Allyl 2-(4-(3-fluoro-5-hydroxypyridin-2-yloxy)phenoxy)propanoate (**21**)	MS	333.962 (M^+), 226.014/228.012, 198.932, 183.971, 170.949, 154.030, 138.009, 124.974, 110.962, 92.868
22.9	2-Propynyl (R)-2-[4-(5-chloro-3-fluoro-2-pyridinyloxy)phenoxy]propionate (clodinafop-propargyl) (**2**)	NIST	348.943 (M^+)/350.912/351.911, 310.992, 266.32/268.014, 251.997, 237.995/239.977, 221.978, 209.976, 204.010, 181.988, 176.025, 159.034, 129.980, 109.936, 90.894, 75.672, 62.374
17.6	2-(4-(5-Chloro-3-fluoropyridin-2-yloxy)phenoxy)acetaldehyde (**14**)	MS	281.083 (M^+), 237.977/238.996/240.983, 210.984, 176.025/177.028, 149.033, 129.982, 80.755, 62.375
16.2	4-(5-Chloro-3-fluoropyridin-2-yloxy)phenol (**19**)	MS	237.979 (M^+)/238.996/240.983, 210.984, 204.010, 176.029/177.028, 156.031, 149.032, 129.980, 108.982, 93.875, 80.755, 75.660, 64.444
13.9	Prop-2-ynyl 2-(4-hydroxyphenoxy)propanoate (**16**)	MS	220.039 (M^+)/221.043, 137.056/138.060, 109.994/111.003, 80.755, 64.444
5.9	2-Phenoxyacetic acid (**18**)	MS	152.038 (M^+), 109.994, 80.755
3.8	5-Chloro-3-fluoropyridin-2-ol (**17**)	MS	146.983 (M^+)/148.979, 118.976/120.986, 91.831, 56.180

Note that the number in the parenthesis corresponds to the number of the compound in the degradation scheme.

Table 3: Probable products formed during the photocatalytic degradation of 1,2-dichloro-4-nitrobenzene (**3**) along with their retention time and corresponding mass fragmentation.

Retention time (min)	Name	Confirmed By	Mass fragmentation
16.6	1,2-Bis(3,4-dichlorophenyl)diazene (**27**)	NIST	318 (M^+)/319.947, 172.975/174.9, 144.963/146.9, 108.984, 75.021
8.3	Dichloronitrophenol (**22**)	NIST	206.957 (M^+)/208.9/210.970, 176.991/178.9, 160.969, 148.969, 132.969/134.967, 124.989, 112.989, 96.986, 86.969, 72.986, 62.016
6.7	2-Chloro-5-nitrophenol (**23**)	NIST	172.990 (M^+)/174.990, 142.992/144.992, 126.995, 107.011, 98.994, 91.012, 72.979, 63.018, 53.001
6.6	3,4-Dichloroaniline (**25**)	NIST	160.98 (M^+)/162.9/164.979, 126.008, 98.995, 90.027
6.3	3,4-Dichlorophenol (**24**)	NIST	161.967 (M^+)/163.9/165.962, 144.707, 98.995, 63.020
6.2	1,2-Dichloro-4-nitrobenzene (**3**)	NIST	190.987 (M^+)/192.978/194.970, 160.974/162.971, 144.983/146.974, 132.972/133.9, 108.995/110.987, 83.978, 74.016/75.024/73.001, 50.017

Note that the number in the parenthesis corresponds to the number of the compound in the degradation scheme.

which in turn may form **17** by the expulsion of phenoxide radical. The difference of **18** mass units between **20** (m/z 367) and **2** (m/z 349) suggests that, before hydroxylation, precursor compound **15** is formed via the partial reduction of triple bond to double bond. Alternatively, dechlorination of **15** followed by hydroxylation may lead to the formation of product **21**. It is interesting to note that compounds **13** and **17** have also been reported to be formed during the direct photolysis of **2** on glass surface under sunlight and UV light [47].

3.3. Photocatalytic Transformation of 1,2-Dichloro-4-Nitrobenzene (3). Gas chromatograms of unirradiated and irradiated samples (3 and 9 hr) of 1,2-dichloro-4-nitrobenzene (**3**) are shown in Figures 3(a), 3(b), and 3(c), respectively. It is obvious from Figure 3(a) that unirradiated

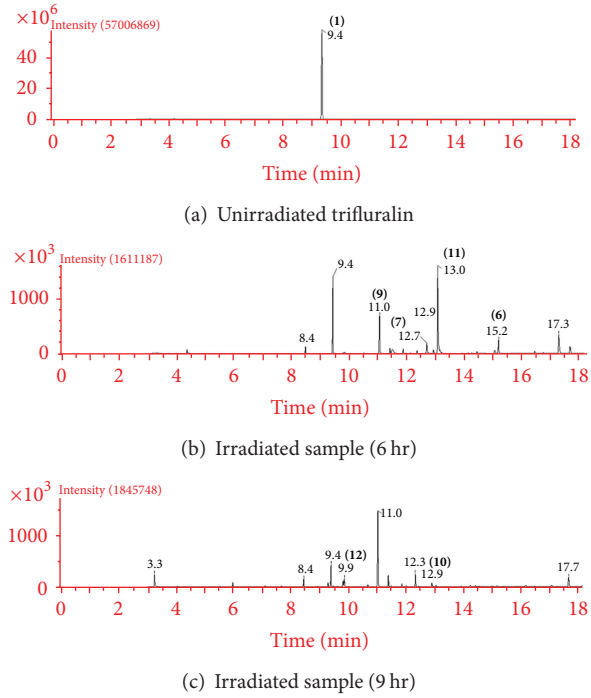


Figure 1: Gas chromatogram of trifluralin (**1**): (a) unirradiated trifluralin, (b) irradiated mixture (6 hr), and (c) irradiated mixture (9 hr).

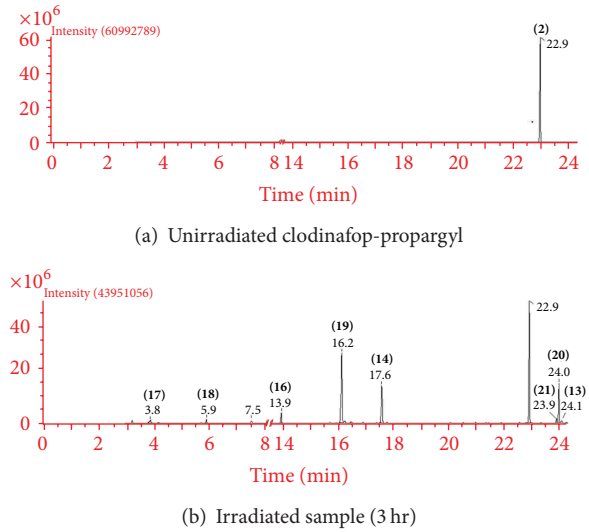


Figure 2: Gas chromatogram of clodinafop-propargyl (**2**): (a) unirradiated clodinafop-propargyl, (b) irradiated sample (3 hr).

sample of compound **3** shows a single peak at a retention time (R_t) of 6.2 minutes corresponding to 1,2-dichloro-4-nitrobenzene confirmed by comparing its molecular ion and mass fragmentation pattern with those in NIST library. Gas chromatogram of the irradiated sample (3 hours) indicates the formation of several degradation products along with some unchanged starting material. The prolonged irradiation for nine hours shows increase in the concentration of few

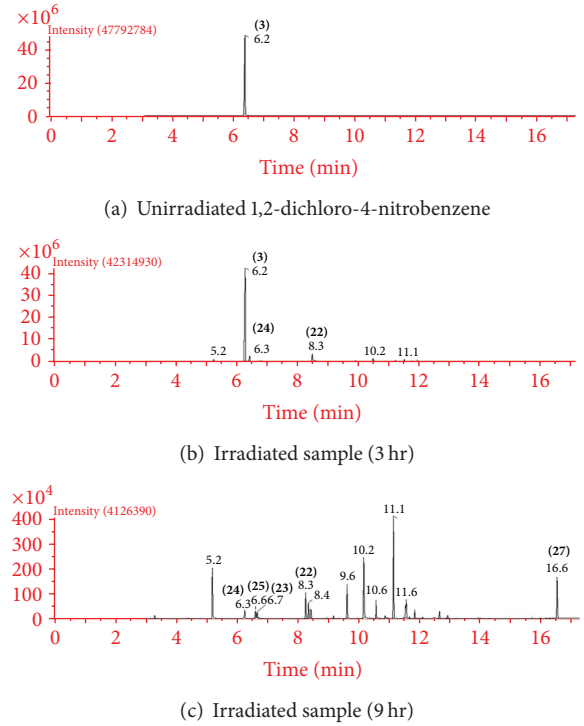
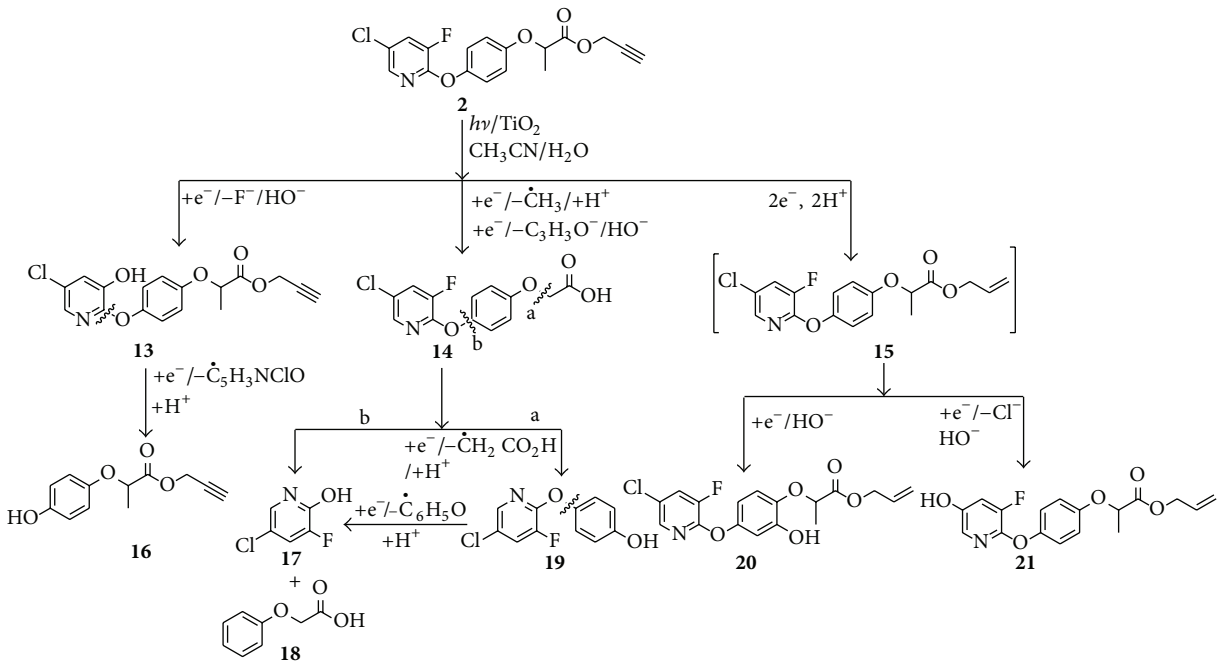


Figure 3: Gas chromatogram of 1,2-dichloro-4-nitrobenzene (**3**): (a) unirradiated 1,2-dichloro-4-nitrobenzene, (b) irradiated sample (3 hr), and (c) irradiated sample (9 hr).

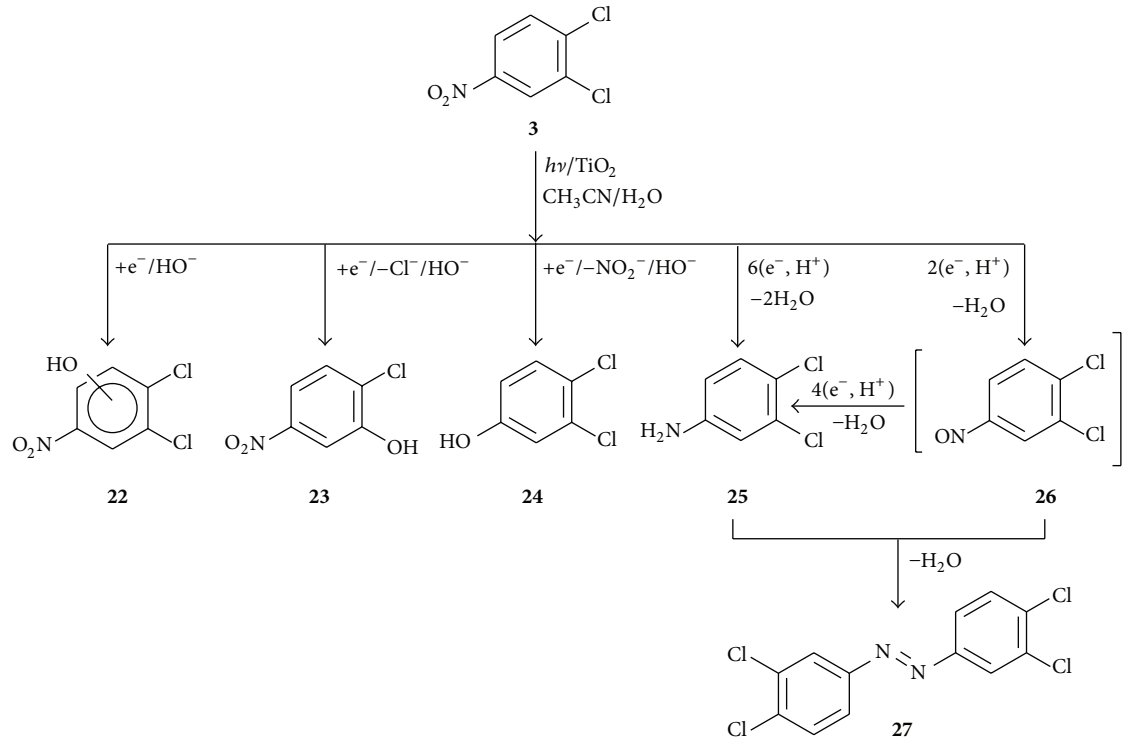
products as well as formation of several new products. The structure of few products corresponding to peaks at retention times (R_t) of 6.3 min, 6.6 min, 6.7 min, 8.3 min, and 16.6 min has been confirmed on the basis of their molecular ion, on mass fragmentation pattern, and also on comparison of their mass fragmentation data with that in NIST library. The molecular ion and mass fragmentation pattern of 1,2-dichloro-4-nitrobenzene and its different degradation products are shown in Table 3. The probable pathway showing the transformation of 1,2-dichloro-4-nitrobenzene into various intermediate products in the presence of TiO_2 in acetonitrile water mixture is shown in Scheme 3.

The main routes of transformation of 1,2-dichloro-4-nitrobenzene under photocatalytic conditions were found to be dehalogenation, denitration, hydroxylation, and dimerization. Thus the direct hydroxylation of **3** may give **22** whereas substitution of one of the chlorines by hydroxyl group leads to **23**.

Alternatively denitration of **3** followed by hydroxylation may give dichlorophenol **24**. Complete reduction of nitro group of **3** to amino group via nitroso derivative **26** gives dichloroaniline derivative **25**. Reaction of **25** with nitroso derivative **26** followed by loss of water gives diazene derivative **27**. It is interesting to note that reduction of nitro group to amino via nitroso under photocatalytic conditions is well documented in the literature [11, 44–46].



Scheme 2: Possible route for the degradation of clodinafop-propargyl (**4**) in CH_3CN/H_2O medium catalyzed by TiO_2 in the presence of UV light.



Scheme 3: Probable phototransformation of 1,2-dichloro-4-nitrobenzene (**3**) in CH_3CN/H_2O medium catalyzed by TiO_2 in the presence of UV light.

4. Conclusion

Photocatalytic transformation of organic pollutants is an important factor to understand their fate and environmental behavior. The three pesticide derivatives studied underwent photocatalytic degradation and comprehensive pathways of transformation were proposed by identification of intermediate products. The GC-MS technique proved efficient for the detection and identification of the formed degradation products. The photocatalytic degradation of pesticides of different chemical structures demonstrated markedly different degradation pathways. Loss of alkyl groups, halogen(s), cleavage of alkoxy and ester bonds, denitration, oxidation of side chain, cyclization, and reduction of alkyne to alkene and nitro to amino group were found to be the typical degradation routes. The study is essential in revealing the extent of photostability and the precise reaction mechanisms of photocatalytic transformation of pesticides and contributes to the apt understanding of environmental behavior of pesticides.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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