

ISOLATION AND CHARACTERIZATION OF PHOTO-CATALYTICALLY DEGRADED PRODUCTS OF PYROXASULFONE USING MYRIAD ANALYTICAL TECHNIQUES

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ABSTRACT

Photocatalytic degradation of pyroxasulfone was carried out in presence of artificial sunlight. Effect of time, sample concentration, catalyst concentration, light intensity and pH was observed on degradation process. Various solvent systems and catalysts were also tried. MgO was found to be the most effective catalyst for degradation of pyroxasulfone, while Methanol: Water (50:50) was found to be the most compatible solvent system for this degradation process. Two degraded products (Degradant-1 and Degradant-2) were isolated and characterized using various analytical techniques. On the basis of experimental findings, a tentative degradation scheme has been proposed.

KEY WORDS : Artificial Sunlight, MgO, Pyroxasulfone, Photodegradation, Photocatalytic

INTRODUCTION

Agriculture is essential for survival and development of a country, and therefore, increase in crop production and protection is needed. Agrochemicals played a very important role in solving this issue but the excessive use of agrochemicals in agricultural lands and urban green areas to save crops as well as plants from various diseases is also causing a large number of adverse effects on various ecosystems (especially humans) (Nicolopoulou-Stamati *et al.*, 2016).

The misuse of agrochemicals is a major source of pollution in potable water, reservoirs, and watersheds. The majority of the misuses are due to irresponsible behavior of farmers and agrochemical sellers, as well as large Government fertilizer subsidies that acts as an incentive use of fertilizer (overuse).

Acephate is an organophosphate pesticide, which is been commonly used to control insect and pests in agricultural fields. Degradation of acephate and

methamidophos has been attempted using photo-Fenton and photocatalysis using (UV/TiO₂) systems (Lin *et al.*, 2020). Mandal *et al.* (2011) investigated photodegradation of hexythiazox in three different solvent systems in the presence of H₂O₂, KNO₃, and TiO₂ under ultraviolet light as well as sunlight. It was reported that hexythiazox was found to photodegrade more efficiently in the presence of TiO₂ as compared to H₂O and KNO₃. Two major photoproducts were identified as cyclohexylamine and 5-(4-chlorophenyl)-4-methylthiazolidin-2-one.

Kanrar and Bhattacharys (2009) studied photolysis of a rice herbicide, bispyribac sodium (Sodium 2, 6-bis [(4, 6-dimethoxypyrimidin-2-yl)oxy]benzoate) in aqueous media (distilled water, irrigation water and pond water) in presence of UV light and sunlight and TiO₂ and KNO₃. It was observed that photodegradation process followed order kinetics. They could isolate five photo metabolites using column chromatographic method. The structures of these five metabolites were identified as (Phenol), [2, 6-Dihydroxy benzoic acid],

[2, 6-bis [(4, 6 dimethoxypyrimidin-2yl) oxy] benzoic acid], [2-(3-Hydroxy-phenoxy)-pyrimidine-4, 6-diol] and as [2,4-Dihydroxy-3, 5-dimethoxy-6-(4-methoxy pyrimidine-2-yloxy)-benzoic acid]. A tentative photodegradation mechanism of bispyribac sodium has been proposed, which involves hydrolysis, O-dealkylation, hydrolytic cleavage, dehydroxylation, decarboxylation, hydroxylation, and O-alkylation.

The effect of modified metallic nanoparticles (Au, Cu and Ni) as co-catalysts of Degussa-P25 TiO₂ for the photocatalytic degradation and mineralization of the herbicide 6-chloro-N2-ethyl-N4-isopropyl-1,3,5-triazine-2,4-diamine (atrazine) has been studied. It was reported that gold particles retain their metallic state, while copper and nickel particles were initially in the metallic state, but these are oxidized during the reaction. It was revealed that bare TiO₂-P25 could achieve a mineralization of 48% only after 5 h. The superficially modified TiO₂ with gold nanoparticles could achieve a mineralization more than 60% (Santacruz-Chávez *et al.*, 2015).

McMurray *et al.* (2006) investigated photocatalytic removal of atrazine from water using immobilised TiO₂ films. The degradation of atrazine was there with a number of intermediates products identified but the stable end product was cyanuric acid only. The process was monitored using different techniques like total organic carbon analysis (TOC) high performance liquid chromatography (HPLC), and liquid chromatography-mass spectrometry (LC-MS). A decrease in TOC was observed, which was attributed to the oxidative degradation of side chains of atrazine. Seven intermediates identified as 2-chloro-4-ethylamino-6-(1-methyl-1-ethanol) amino-1,3,5-triazine, 2-chloro-4-acetamido-6-isopropylamino-1,3,5-triazine, 2-chloro-4-ethylamino-6-(2-propanol)amino-1,3,5-triazine, deisopropylatrazine, 2-hydroxyatrazine, desethylatrazine, and 2-hydroxydesethyl atrazine. The effect of operational parameters such as UV source, oxygen concentration, catalyst loading, and initial pollutant concentration was investigated. The removal of atrazine followed first order kinetics. It was revealed that use of UVB irradiation did not appear to increase the rate of degradation as compared to UVA irradiation and it was supported by the fact. The apparent quantum yield for the photocatalytic degradation was higher under UVB (0.59%) compared to UVA (0.34%).

Alkayal and Hussan (2019) used Ag@Mg₄Ta₂O₉ nanoparticles as an efficient photocatalyst for the

photocatalytic degradation of atrazine. It was observed that pore size distribution in this nanocomposite, Ag@Mg₄Ta₂O₉, was around 24nm for 2.0 wt.% nanocomposite. It was revealed that 2.0 wt.% of Ag@Mg₄Ta₂O₉ exhibited best photocatalyst efficiency for degradation of atrazine. It was found that the ability of 2.0 wt.% Ag@Mg₄Ta₂O₉ for atrazine degradation was retained and it can be reused many times with the similar efficiency. Abeish *et al.* (2014) investigated influence of ferric ions and hydrogen peroxide on the degradation of combined chlorophenols in solar/TiO₂ process. The 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) were used as model pollutants chlorophenols. Different amounts of Fe³⁺ ions were used. It was observed that optimum value was obtained for ferric ions (10 mg l⁻¹). They detected three major intermediates as phenol, hydroquinone, and 4-chlorocatechol. The concentrations of these aromatic intermediates were found to be less than TiO₂ alone and the time of degradation was also reduced to 150 min. The optimum rate of degradation was found at 3.41 mM H₂O₂.

Andreozzi *et al.* (2011) investigated the oxidation of 2,4-dichlorophenol and 3,4-dichlorophenol in aqueous solutions using Fe(III)/O₂ homogeneous photocatalysis under UV light irradiation. The optimum conditions for both these compounds was found at pH = 3.0 and initial Fe(III) concentration = 1.5 × 10⁻⁴ M. It was also reported that this oxidizing system can be used even up to pH 4.0 but with relatively slower rate. Han *et al.* (2009) prepared a series of TiO₂-Cu₂O mixed oxides via hydrolysis of titanium butoxide and reduction of copper acetate with hydrazine. They investigated photocatalytic degradation of dodecyl-benzenesulfonate (DBS) in presence of TiO₂-Cu₂O under visible irradiation. It was reported that TiO₂-Cu₂O composite oxides exhibited higher photocatalytic efficiency than TiO₂ or Cu₂O alone. It was also revealed that 5% TiO₂-Cu₂O exhibited the highest activity with degradation percentage of DBS and COD as 97.3 and 65%, respectively. It was observed that degradation of DBS followed first-order kinetics, while its adsorption followed Langmuir model. Oxygen in solution also played an important role in the elimination of COD.

Dhaka *et al.* (2018) investigated UV-C-mediated degradation of ethyl paraben (EP) in the presence of different oxidants like persulfate (PS), peroxymonosulfate (PMS), and hydrogen peroxide. It was reported that 98.1, 97.0, and 81.3%

degradation of EP could be obtained in 90/min under UV/PS, UV/H₂O₂ and UV/PMS system, respectively. The degradation rates of EP increase with increases in initial dosages of oxidant(s), but an opposite trend was observed on increasing EP concentration. It was found that degradation of EP in all these cases followed pseudo-first-order kinetics. It was also revealed that HO• radicals were the main reactive species. Szabo-Bárdos *et al.* (2011) investigated titanium dioxide-mediated photocatalyzed degradation of benzenesulfonate (BS). They monitored progress of this reaction by chemical oxygen demand (COD), and total organic carbon (TOC). Intermediates detected using liquid chromatography-mass spectrometry. It was indicated that initial step of degradation was hydroxylation of the material, which afforded two intermediates hydroxy- and dihydroxybenzenesulfonates. It was observed that there was no decay of the hydroxy species during 8 h irradiation, if dissolved oxygen is absent. Much more desulfonation and hydroxylation was there in the aerated system, accompanied by a decrease of TOC in initial stage but further hydroxylation led to cleavage of the aromatic system and polyhydroxy derivatives are formed. It was followed by ring fission, forming aldehydes and carboxylic acids.

Eslami *et al.* (2018) reported degradation of 4-chlorophenol (4-CP) by a combination of UV and MnO₂ for proxymonosulphate (PMS) activation. It was observed that highest performance for degradation of 4-CP was achieved at pH/=/4.0, PMS (1/mM) and MnO₂ (0.25 g L⁻¹). Complete degradation of 4-CP was obtained in 30/min with UV/MnO₂/PMS. It was also revealed that MnO₂ could retain its performance at least up to fourth cycle as Mn leaching was negligible. It was found that hydroxyl radical was dominant radical responsible for 4-CP degradation as evident by quenching experiments. Pyroxasulfone is used as an effective herbicide in weed management programs,

because of its high efficiency in inhibiting the elongation steps of very-long chain fatty acid (VLCFA) synthesis (Yamaji *et al.*, 2014; Nakatani *et al.*, 2016).

Pyroxasulfone is stable (hydrolytically) at all pH values because it is less susceptible to decomposition. The chemical structure of pyroxasulfone has been represented in Fig. 1.

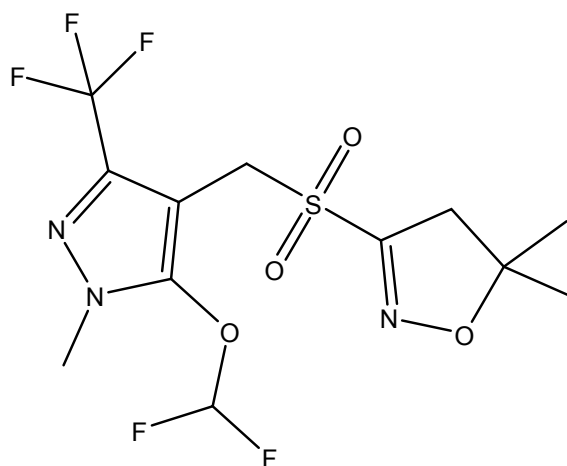


Fig. 1. Chemical structure of pyroxasulfone

MATERIALS AND METHODS

Pyroxasulfone (Technical grade) received as a gift sample from PI industries Ltd. Udaipur was used. The MgO, acetonitrile, methanol, dichloromethane, 2-propanol, NaOH, and HCl were also used as received. The HPLC grade water (Merck Millipore water of conductivity range is 2-3 $\mu\text{S cm}^{-1}$ and pH ranging between 6.5-7.0) was used in all the preparations. The specifications and mass purity of used chemicals have been provided in Table 1.

Sample preparation

Pyroxasulfone (0.020 g) and photocatalyst (MgO) (0.200 g) were taken in 100 ml volumetric flask and collectively dissolved in binary mixture of methanol

Table 1. Specifications of chemicals used

Chemical Name	Source	CAS register Number	Mass fraction purity
Pyroxasulfone	PI Industries	447399-55-5	99.5 %
Acetonitrile	Sd Fine Chemicals	75-05-8	99.5 %
Methanol	Sd Fine Chemicals	67-56-1	99.5 %
MgO	Rankem Chemicals	1309-48-4	99.0 %
Dichloromethane	Sd Fine Chemicals	75-09-2	99.5 %
NaOH	Rankem Chemicals	1310-73-2	98.0 %
HCl	Rankem Chemicals	7647-01-0	35.0 %
2-Propanol	Sd Fine Chemicals		99.5 %

and water (50:50). Then the solution was transferred in 250 ml beaker. The beaker was kept under 200 W tungsten bulb at 30 cm distance. Petri dish filled with water was used as a water filter to avoid thermal degradation. The solution was constantly mixed with the help of magnetic stirrer and monitored. The samples were drawn at several time intervals such as 1, 6, 12, 18, 24, 36, 48, 60, 72, 84, 96 and 120 h.

METHODS

Samples withdrawn from breaker were filtered using syringe filter and the degradation was monitored on Waters UPLC system.

UPLC system parameter: Column: - Acquity UPLC BEH C18, (100 mm × 2.1 mm ID, 1.7 μm). Mobile phase: - Acetonitrile: Water (0.05% H₃PO₄) :: 25:75 (gradient), Flow rate 0.4 ml /min, λ- 230 nm.

Two new peaks were observed in UPLC analysis along with pyroxasulfone. It was observed that 80 %

of pyroxasulfone peak was reduced after 120 h, which indicated degradation and two new peaks were observed due to degradants of pyroxasulfone (Fig. 2).

Isolation of compounds

Pyroxasulfone degradation products, Degradant-1 and Degradant -2 were isolated by extraction technique. Reaction mass sample of final h was taken and equal amount of dichloromethane was added. Then the mixture was shaken well and kept for some time to get bilayer mixture. Both the layers were separated using separating funnel and analyzed on UPLC system to confirm degradation product. Degradant-1 and degradant-2 were identified in aqueous layer and organic layer, respectively. Both solutions were dried separately using rota-vapour assembly so as to get solid final products. The solid was confirmed using UPLC system (Fig. 3) and other characterization techniques.

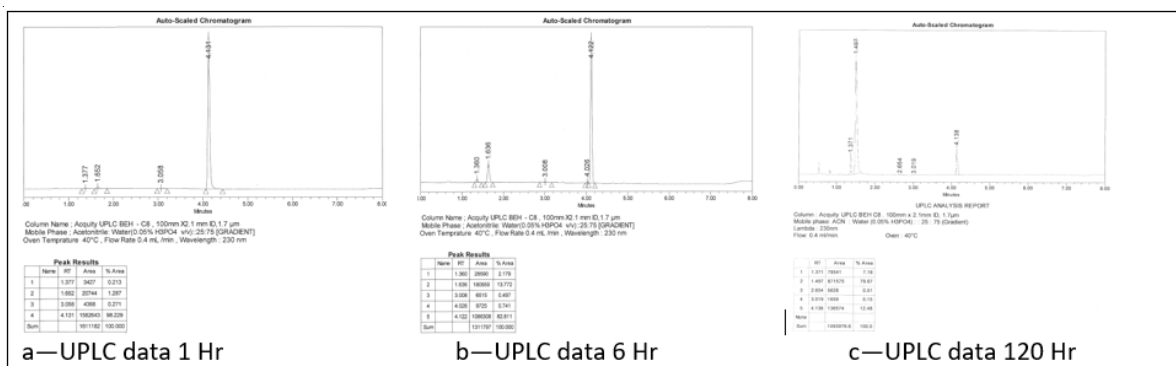


Fig. 2. Typical UPLC chromatograms showing degradation of pyroxasulfone and formation of degradation products with respect to time.

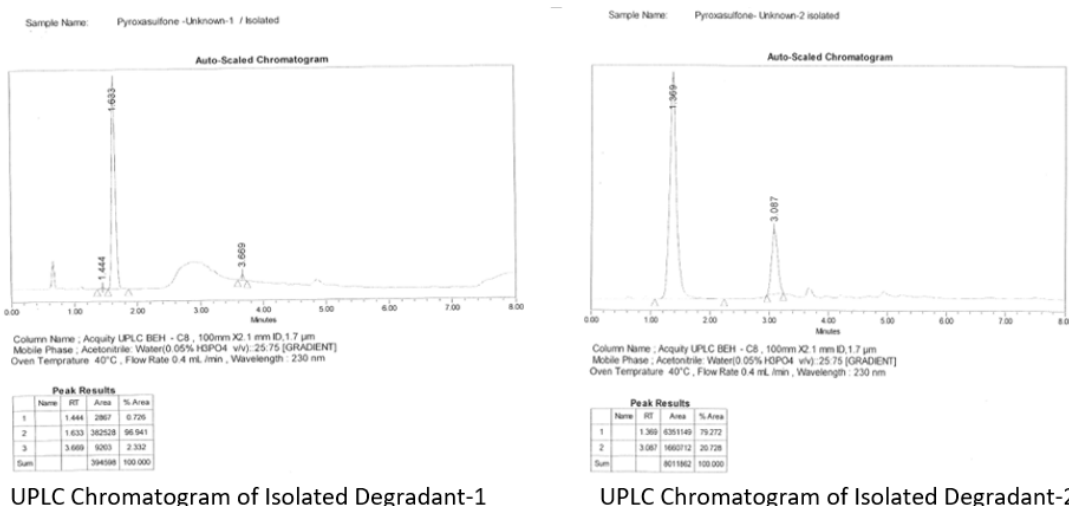


Fig. 3. UPLC Chromatogram of Isolated degradant -1 and degradant -2

Table 2. Characterization data of pyroxasulfone, degradant-1 and degradant-2

Technique	Pyroxasulfone	Degradant -1	Degradant -2
1H-NMR (δ , ppm)	1.43 (6H, s), 3.18 (2H, s), 3.84 (3H, s), 4.70 (2H, s), 7.30 (1H, t, $J_{H-F} = 73.8$ Hz)	2.89 (2H, s), 3.75 (3H, s), 8.22 (1H, t, $J_{H-F} = 73.8$ Hz)	1.41 (6H, s), 2.73 (2H, s), 3.84 (3H, s)
13C-NMR (δ , ppm)	26.58(1C,q), 36.10(1C,t), 43.68(1C,t), 47.68(1C,t), 90.56(1C,s), 94.65(1C,s), 119.82(1C,s), 121.43{d(d, $J_{C-F} = 268.4$ Hz)}, 136.71{d(q, $J_{C-F} = 35.5$ Hz)}, 144.38(1C,s), 158.46(1C,s)	36.03(1C,q), 56.11(1C,t), 102.24(1C,s), 119.82(1C,s), 121.43{d(d, $J_{C-F} = 268.4$ Hz)}, 136.71{d(q, $J_{C-F} = 35.5$ Hz)}, 144.38(1C,s)	27.25(1C,q),44.59(1C,t), 56.97(1C,q),84.91(1C,s), 167.29(1C,s)
DEPT-135- NMR	26.58(1C,q), 36.10(1C,t), 43.68(1C,t), 47.68(1C,t), 90.56(1C,t), 119.82(1C,s)	36.03(1C,q), 56.11(1C,t), 121.43{d(d, $J_{C-F} = 268.4$ Hz)}	27.25(1C,q),44.59(1C,t), 56.97(1C,q)
MS (m/z)	392[M+H] ⁺ , 433 [M+CH ₃ CN+H] ⁺	295 [M+H] ⁺ , 336 [M+CH ₃ CN+H] ⁺	130 [M+H] ⁺ , 171 [M+CH ₃ CN+H] ⁺
MS/MS (m/z)	342,308,270,229,179,145 (from 392)	230,210,179,164,123,95 (from 295)	113,98,80,74,55 (from 130)
FTIR (cm ⁻¹)	2987(-C-H-), 1572 (-C=H-), 1251(-O=S=O-), 1123 (-C-F-), 1051(-C-O-) and 752 (-C-H-)	1578(-C=C-), 1284(-O=S=O-), 1130 (-C-F-), 1054(-C-O-) and 752 (-C-H-)	2975(-C-H-), 1600 (-C=H-), 1051(-C-O-), 910(-C-H-) and 769 (-C-H-)

Characterization of compounds

The pyroxasulfone and its degradation products, degradant -1 and degradant -2 were characterized through NMR spectroscopy, Mass spectroscopy and FTIR-spectroscopy. Characterization data are provided in Table 2 and Figure 4.

RESULTS AND DISCUSSION

Effect of time

Degradation of pyroxasulfone was monitored on Waters UPLC system and the samples were analyzed at several time intervals such as 1, 6, 12, 18,

Table 3. Degradation data of pyroxasulfone, and formation of degradant-1 and degradant-2

Time (h)	Pyroxasulfone (%)	Degradant-1 (%)	Degradant -2 (%)
1	97.99	1.45	0.19
6	85.45	4.86	0.70
12	85.66	12.59	1.75
18	75.42	20.37	3.25
24	71.42	23.70	3.76
36	67.02	27.07	4.29
48	53.06	36.25	5.69
60	46.41	42.66	4.79
72	39.15	54.49	4.50
84	15.96	76.59	7.45
96	17.51	78.03	4.46
120	12.48	79.67	7.18

24, 36, 48, 60, 72, 84, 96 and 120 h. The optimum degradation was observed at 60 h, but degradation rate is almost constant after 60 h. Other parameters were also monitored up to 60 h. Effect of time on pyroxasulfone degradation has been represented in Table 3 and Fig. 5.

Effect of solvent system

The degradation reaction was carried out in absence of methanol under identical experimental conditions. No degradation was observed, when photodegradation reactions of pyroxasulfone was carried out with several solvent systems and secondly, without MgO. These results confirmed that both; MeOH/Water and photocatalyst, MgO played crucial roles in the degradation of pyroxasulfone.

Effect of concentration of pyroxasulfone

The effect of variation of the concentration of pyroxasulfone on the degradation rate has been studied at 50, 200 and 400 ppm, and the results are presented in Fig. 6a. It was observed that as the amount of pyroxasulfone was increased, the rate of photocatalytic activity increases due to availability of more molecules of pyroxasulfone. The rate of degradation was optimum at 200 ppm of the composite. Then, the rate constant decreases slightly after 200 ppm as above this concentration, the pyroxasulfone molecules will start acting as internal

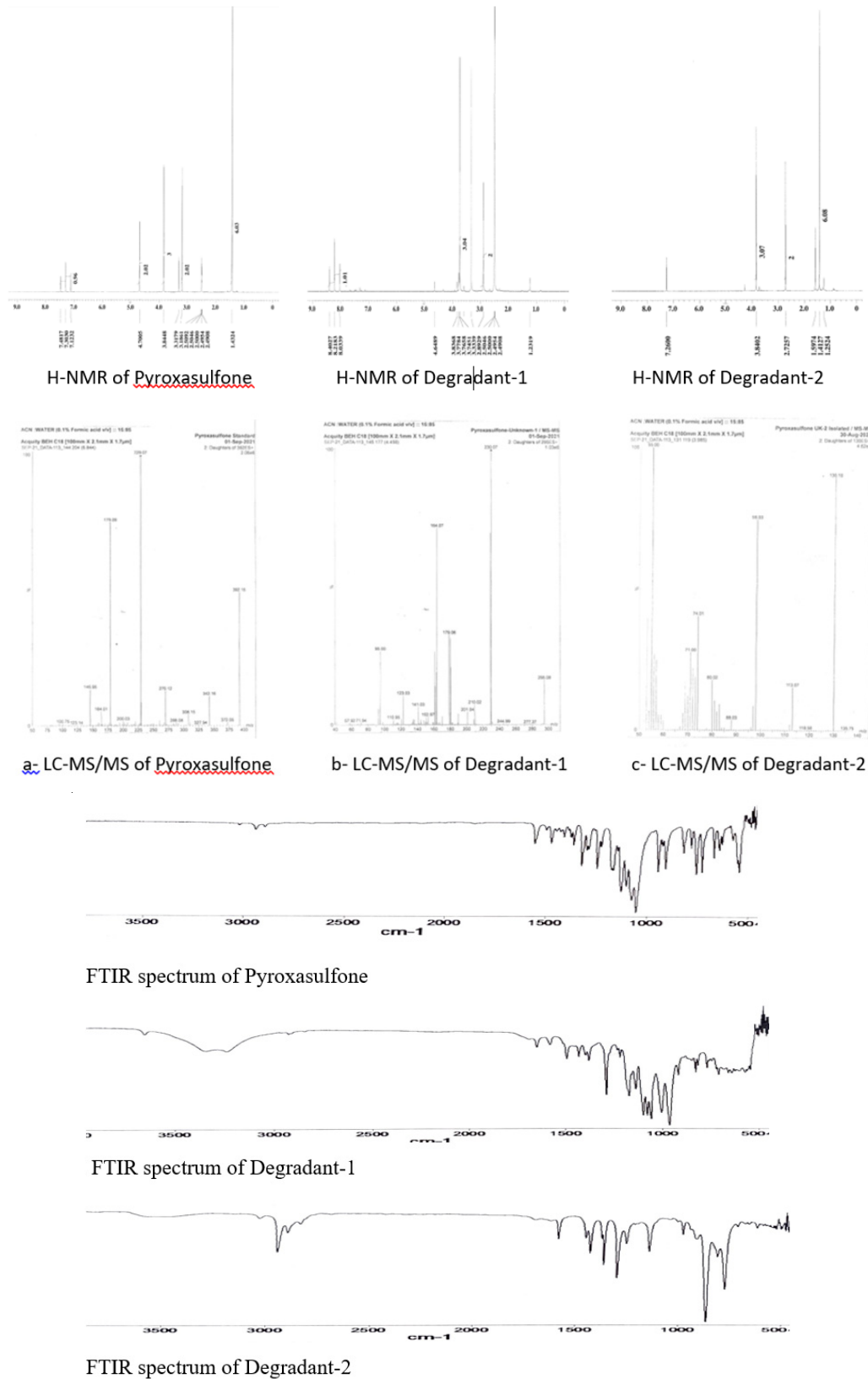


Fig. 4. Typical NMR, MS-MS spectra and FTIR spectra of (a) Pyroxasulfone, (b) Degradant-1 and (c) Degradant-2

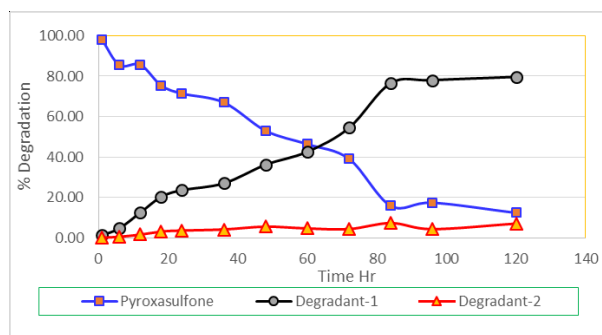


Fig. 5. Effect of time

filter for incoming radiation.

Effect of light intensity

The distance between the light source and exposed surface area of photocatalyst was varied to determine the effect of light intensity on the photocatalytic degradation. The light intensity was varied from 20.0 to 70.0 mW cm^{-2} . The results have been reported in Fig. 6 b. The results show that rate of degradation was enhanced as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit time per unit area of photocatalyst. The maximum rate for degradation of pyroxasulfone was observed at 50.0 mW cm^{-2} . On

further increasing the intensity above 60.0 mW cm^{-2} , there was a slight decrease in the rate of photodegradation.

Effect of catalyst concentration

The effect of MgO concentration on the photocatalytic degradation of pyroxasulfone was observed at 200, 2000 and 4000 ppm and the results are summarized in Fig. 6c. It was observed that as the concentration of the MgO was increased, the pyroxasulfone degradation increases but after 200 ppm (optimum condition), the rate of pyroxasulfone degradation decreases slightly or it is almost same. It was attributed to the fact that on increasing the amount of catalyst, the exposed surface area was also increased, resulting in an increase in rate of degradation. Any further increase in amount of MgO will not increase the rate, because after a certain amount, multilayers are formed, but exposed surface remained constant. As a result, the rate of degradation in also almost constant; however, there may be a slight decrease due to recombination of holes and electrons.

Effect of pH

The effect of variation of pH was studied at pH 4.0, 7.5 and 10.0 and the results are reported in Fig. 6d. It

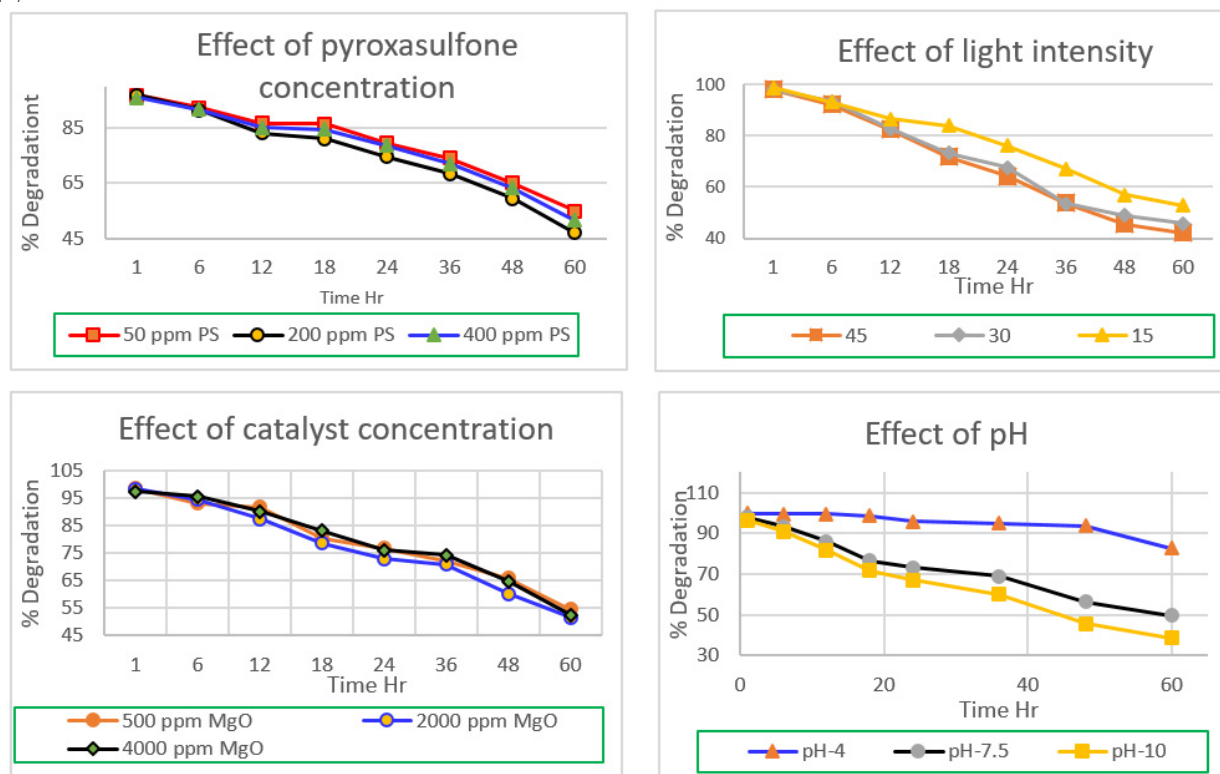


Fig. 6. The effect of (a) Pyroxasulfone concentration, (b) light intensity, (c) catalyst concentration and (d) pH

was observed that the rate increases with an increase in pH up to 10.0, but the rate of degradation decreases with a decrease in pH. Pyroxasulfone is excited in presence of light. Electrons are promoted to conduction band for valence band of MgO, leaving behind a hole. This h^+ will abstract an electron from OH^- ions to generate hydroxyl radicals, which will oxidize the pyroxasulfone to smaller fragments with two main degradants.

Effect of other parameters

The rate of photodegradation of pyroxasulfone was also studied without catalyst, steering, and light (in dark), but with scavenger (2-propanol). The results have been reported in Table 5 and Fig. 7.

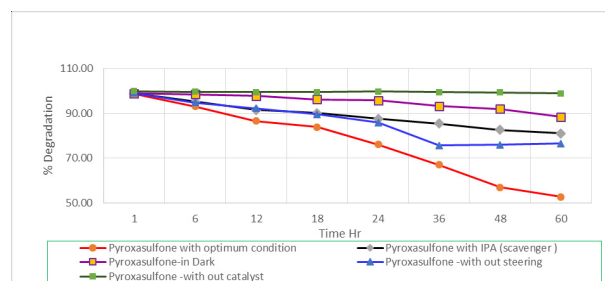


Fig. 7. Effect of without steering, without catalyst, without light and presence of scavenger on pyroxasulfone degradation

No degradation was observed without catalyst and light, but when experiment was carried out with catalyst in dark medium (absence of light), degradation rate was found to be very slow. It indicated that both; MgO and light were required for degradation of pyroxasulfone.

The experiment was also carried without steering. It was observed that even after 18 h, degradation rate was slow. It may be due to settling of MgO and compound in reaction vessel and improper exposure with light.

A scavenger (2-propanol) was added in order to confirm active oxidizing species in this photocatalytic degradation reaction. The results of this experiment showed that degradation of pyroxasulfone was slow in presence of 2-propanol (scavenger), where rate of degradation was much reduced. These results confirmed that the degradation of pyroxasulfone was primarily due to hydroxyl radicals.

Structure elucidation of degradants

The structure of two degraded products were characterized as 5-(difluoromethoxy)-4-[(dioxo- λ 6-sulfanyl)methyl]-1-methyl-3-(trifluoromethyl)-1H-pyrazole (degradant-1) and 3-methoxy-5,5-dimethyl-4,5-dihydro-1,2-oxazole (degradant-2).

Proposed Reaction Mechanism

On the basis of these experimental observations, a tentative mechanism has been proposed for the degradation of pyroxasulfone in the presence of MgO. The formation of the photodegradation products from pyroxasulfone can be explained as follows. Photocatalyst MgO activates $-SO_2-C-$ bond for cleavage and simultaneously, S_N2 type reaction takes place at 3-position of 5,5-dimethyl-4,5-dihydro-1,2-oxazole in pyroxasulfone to form 3-methoxy-5,5-dimethyl-4,5-dihydro-1,2-oxazole.

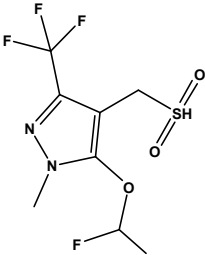
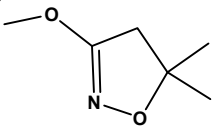
CONCLUSION

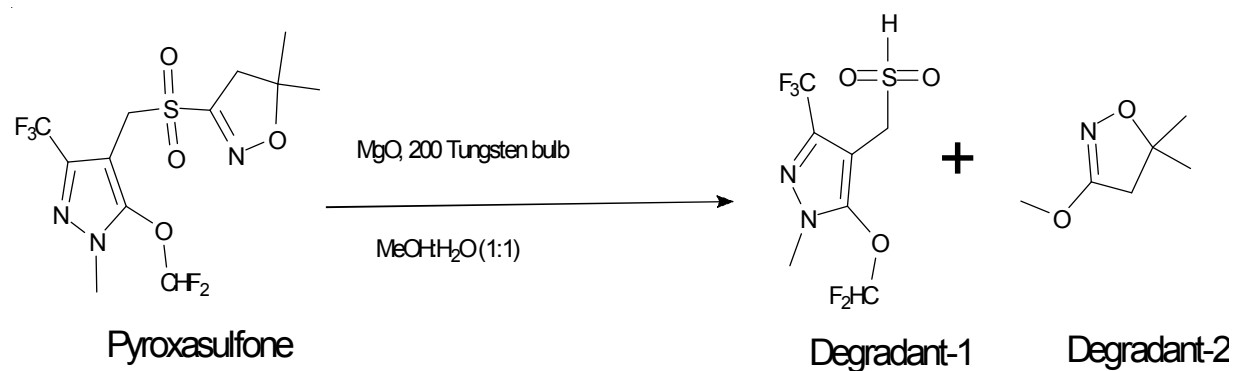
Pyroxasulfone is decomposed to afford two products 5-(difluoromethoxy)-4-[(dioxo- λ 6-sulfanyl)methyl]-1-methyl-3-(trifluoromethyl)-1H-pyrazole (degradant-1)[degradant-1] and 3-methoxy-5,5-dimethyl-4,5-dihydro-1,2-oxazole (degradant-2) [degradant-2]. Methanol, water, photocatalyst, and MgO played major role in the degradation of pyroxasulfone. The rate of degradation was

Table 5. Effect of various parameters on photodegradation of pyroxasulfone

Time (h)	Pyroxasulfone with optimum condition	Pyroxasulfone with IPA (scavenger)	Pyroxasulfone-in Dark	Pyroxasulfone -with out steering	Pyroxasulfone -with out catalyst
1	98.73	98.95	98.93	99.09	99.84
6	93.15	95.20	98.48	94.76	99.66
12	86.63	91.53	97.82	92.22	99.51
18	83.94	90.14	96.25	89.56	99.46
24	76.16	87.60	95.85	85.92	99.80
36	67.09	85.44	93.18	75.66	99.40
48	57.00	82.67	91.95	75.96	99.38
60	52.80	81.02	88.40	76.51	98.87

Table 6. Photodegradation products of pyroxasulfone

 <p>Degradant-1</p>	<p>5-(Difluoromethoxy)-4-(hydrosulfonylmethyl)-1-methyl-3-(trifluoromethyl)-1H-pyrazole Chemical Formula: $C_7H_7F_5N_2O_3S$ Molecular Weight: 294.20</p>
 <p>Degradant-2</p>	<p>3-Methoxy-5,5-dimethyl-4,5-dihydroisoxazole Chemical Formula: $C_6H_{11}NO_2$ Molecular Weight: 129.16</p>

**Scheme 1.** Photodegradation of pyroxasulfone

optimum with 200 ppm of pyroxasulfone and 2000 ppm photocatalyst. Degradation of pyroxasulfone at basic pH (10.0) was more than in acidic condition.

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