

Photocatalytic Degradation of Persistence Herbicide Fomesafen by Using ZnO/Na₂S₂O₈ as a Catalyst/Oxidant under UV radiation

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Abstract In the present investigation, the Photocatalysis of Fomesafen new class of diphenyl ether herbicide was investigated using ZnO nanoparticles at different pH 4, 7 and 9. In the present study, the optimum amount of the catalyst was used for the photocatalysis, effect of UV light, effect of aeration and effect of the addition of oxidant to the reaction mixture were studied. The ZnO nanoparticles were synthesized by Sol-gel process and characterized by SEM, TEM, and XRD. The fomesafen formulation of active strength 12.5% was used in this experiment. The rate of the reaction in this experiment was followed pseudo-first-order kinetics. The half-life values of fomesafen with ZnO/Na₂S₂O₈ in three different pH solutions were 16.03, 15.56 and 11.93 hours respectively. The optimum amount of catalyst used for this study was 100 mg L⁻¹. The rate of the reaction was rapid in basic pH than in the acidic and neutral pH values. The degradation was fast in the presence of sunlight and nanoparticles.

Keywords: Herbicide, Fomesafen, rate, oxidant, kinetics

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1. Introduction

In agro ecosystem pesticides are commonly used to bring down the infestation and to increase the crop yield. These products once sprayed are likely to enter into the natural bodies through soil by leaching. The herbicides which are mainly used in controlling grasses once applied may likely to get adsorbed in to soil surface, dissolved in runoff water or suspended as particles and carried further. The water runoff is the main significant route of transport of herbicides from their site of application to different places. In the scientific community main concern is the degradation and mineralization of herbicide contaminants. The excessive use of pesticides, by products and intermediates formed during the degradation is the main cause of pesticide pollution [1]. By conventional approaches the complete mineralization of the pesticides is not possible, such as activated sludge digestion, anaerobic digestion, and physico-chemical treatment. Therefore in recent years, studies investigations are focused on decontamination of these toxic residues in waste water by using photocatalysis methods with the support of semiconductor materials. By utilizing the UV light and semiconductors the photocatalytic treatments of waste waters has potential to mineralize the xenotoxins in to environmental friendly products [2,3,4]. There are

several methods available for the decontamination such as advanced oxidation process (AOP), photocatalytic degradation (heterogeneous catalysis), and combined photo-Fenton (homogeneous catalysis), biological oxidation (Microbial degradation) [5]. And also incineration is one of the main methods of disposal of pesticide, but it is very expensive and generally not preferred in developing nations. Thus there is need for the alternative method for complete mineralization of pesticides into environmental friendly compounds. The scientific community also realized the potential applications of the semiconducting materials [6] in solar energy generation and pollution remediation. Nano catalysts also emerged as suitable alternatives to the conventional bulk materials, due to their high surface area [7,8,9,10,11]. The contact between reactants and catalyst get enhanced, because of the high surface to volume ratio which increases the exposed surface area of the active component of the catalyst [12]. In photo catalytic activity surface area plays an important role. The contaminant molecule requires a high surface to volume ratio to be adsorbed on the surface of photocatalyst for the redox reactions to undergo complete degradation/mineralization [13,14]. The faster degradation of the contaminant molecule shall be achieved by higher catalytic surface area [15]. ZnO and TiO₂ nano particles are the found to be good photocatalysts among several others, because of biological and chemical inertness, wide band gap energy, and ease of synthesis and applicability [16]. Among the

different nano materials, zinc oxide (ZnO) is a wurtzite n-type semiconductor with a wide direct band gap of 3.37 eV and a high binding energy (60 meV) at room temperature. Fomesafen 5-(2-chloro- α,α,α -trifluoro-*p*-tolylxy)-*N*-mesyl-2-nitrobenzamide is a selective herbicide belongs to diphenyl ether class of herbicide. It is an early post-emergence of control of broad-leaved weeds in soybeans Pesticide manual, (2012). The mode of action of this compound absorbed by both leaves and roots, limited translocation in the phloem. The availability of the literature on the herbicide fomesafen was limited, so we had referred the regulatory data, pesticide manual data as a reference. So we had developed a method for the degradation of fomesafen by using ZnO/ Na₂S₂O₈ as a catalyst in different water media for eliminating the residues from water. Also the optimum amount of catalyst used for the degradation, effect of UV light, effect of aeration and effect of addition of oxidant in the photocatalysis were studied.

2. Materials and Methods

2.1. Materials

Fomesafen (purity 98.9%), analytical reference standard was purchased from Sigma- Aldrich (USA) and the herbicide formulation was purchased from the local market. Zinc Acetate dehydrate, Acetonitrile, Sodium peroxydisulphate, potassium biphthalate, Potassium phosphate monobasic, Sodium phosphate dibasic, Sodium tetra borate, Ethanol, ammonium hydroxide, and triethanol amine were purchased from Merck Limited, Mumbai. To prepare all the solutions double distilled water was used. The chemicals used in the study were reagent grade and used without further purification. The stock solutions of pesticide standards were prepared in acetonitrile. The intermediate stock solution was prepared by diluting with the acetonitrile to get the concentration of 10 mg L⁻¹.

2.2. Experimental Procedures

2.2.1. Synthesis of ZnO nano Particles

In a 100 mL beaker 20 mL of double distilled water and 30 mL of triethanolamine was taken, to this 2 mL of ethanol was added drop wise drop with a continuous stirring to get a homogenous solution and this is coded as Solution-I. Accurately 5.42 g of Zinc acetate was dissolved in 50 mL of double distilled water resulting 0.5 M of Zinc acetate di hydrate solution with continuous stirring until get a constant solution (Solution-II). In a 500 mL beaker these two solutions were mixed, to this ammonium hydroxide was added for 20 minutes with heating and continuous stirring. The formed yellow coloured gel was washed 5-7 times with water and kept in a hot air oven for 8 hours at about 200°C. The resultant powder was calcinated for four hours at 700°C [17].

2.2.2. Preparation of pH Buffers Solutions

pH 4 - 40 g of potassium dihydrogen phosphate was dissolved in 5000 mL of distilled water. By using

potassium dihydrogen phosphate the pH was adjusted to 4.0.

pH 7 - 31.5 g of disodium hydrogen orthophosphate and 25 g of potassium dihydrogen phosphate was dissolved in 5000 mL of distilled water. The pH was adjusted to 7.0 using disodium hydrogen ortho phosphate and potassium dihydrogen phosphate.

pH 9 - 62.5 g of boric acid and 75 g of potassium chloride was dissolved in 5000 mL of distilled water. By using sodium hydroxide the pH was adjusted to 9.0

2.2.3. Analytical Procedure

Agilent 1290 series High-performance Liquid Chromatography equipped with a DAD detector with Phenomenex Gemini-NX C18 of 4.6 mm i.d. and 250 mm length was used for the quantification of residues of Fomesafen. The λ_{max} was 234nm. The mobile phase used for the elution was a mixture of 800ml acetonitrile and 200ml of 0.1% of ortho phosphoric acid in Milli-Q water. The used flow rate was 0.85 mL min⁻¹; the injection volume was 10 μ L. The Fomesafen was eluted at 4.1 minutes retention time, respectively. The photocatalytic experiment of fomesafen in water was studied by spiking fomesafen formulation at 10 μ g mL⁻¹. The study was conducted under direct sunlight in the presence/absence of the catalyst. The intensity of the light during the study was noted as 20000-170000 Luxes, and temperature was 25 to 45°C. The experiment was conducted three different buffers of pH 4.0, 7.0, and 9.0. Two sets of spiked concentration are prepared for the studies. To one set of samples, the catalyst (ZnO/Na₂S₂O₈) was added, and the other set was studied without the addition of the catalyst. To attain the adsorption equilibrium and uniform distribution of the catalyst/ Oxidant particles, the solutions were sonicated (75 Hz) in the dark for about 20 min before exposure to sunlight. The samples were collected at the beginning of the experiment, and regular time intervals up to 75 hours. The sample suspensions were centrifuged using Beckman cooling centrifuge at 10000 rotations per minute at 2°C. The supernatant was transferred into the amber-colored Vials. After centrifuging the remaining ZnO nano particles were dried at 100°C and used for the catalyst reusability study following the above procedure.

3. Characterization

3.1. Scanning Electron Microscopy (SEM)

To study the morphological properties of the ZnO nano particles, the SEM technique was used. From the SEM image (Figure 1), it can clearly indicate that the ZnO nano particles are in homogeneous shape and size. From the SEM images observed that the ZnO nano particles were having the needles like morphology with size 30-60 nm in diameter. From the literature, it was revealed that as compared to spherical structures, needles or rod-like structures exhibit more photocatalytic activity [18,19].

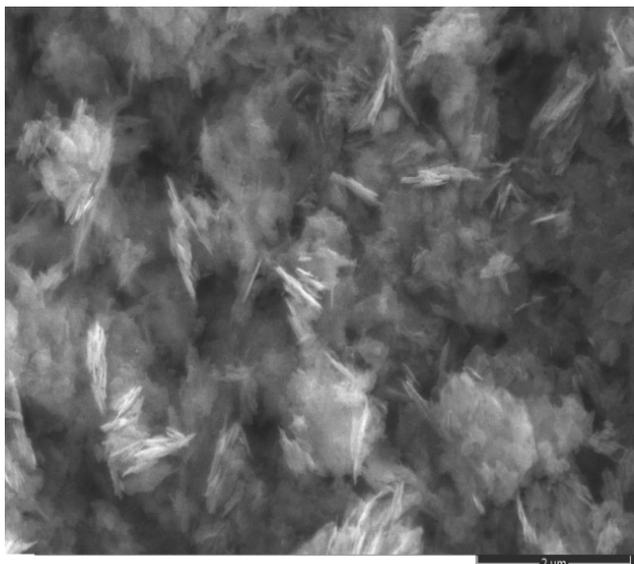


Figure 1. SEM Images of the ZnO nano particles

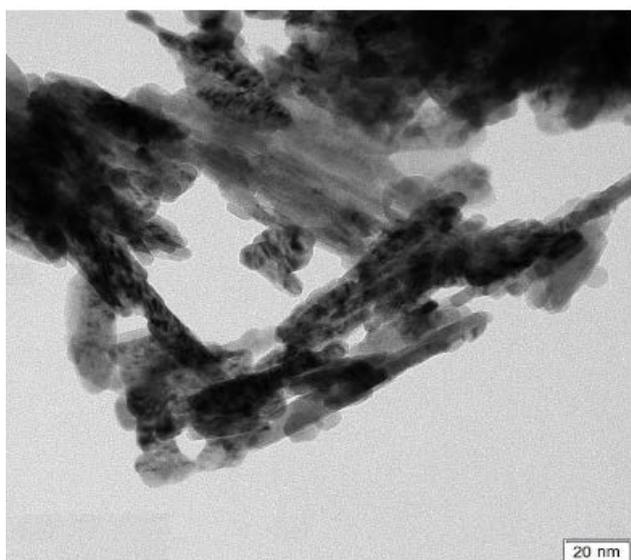


Figure 2. TEM Images of the ZnO nano particles

3.2. Transmission Electron Microscopy (TEM)

The samples were analysed by TEM microscopy to know the actual morphology and size of the particles. From the TEM images it can be identified that the synthesized ZnO nano particles in the form of needles with the dimension of ~50 nm. And also the morphology of the nano particles were confirmed as needles from the TEM images. The images were shown in (Figure 2).

3.3. X-ray Diffraction Technique (XRD)

The synthesized ZnO nano particles were characterized by using X-ray diffraction technique (XRD). There are evidence and good agreement between standard diffraction peaks and the obtained peaks, which reveals that the ZnO synthesis method was successfully done. From the (Figure 3) it was revealed that diffraction peaks which are narrow and more intensive shows good crystalline nature of the ZnO, and at the bottom, the broadening peaks were indicates that the crystalline sizes are very small [20].

4. Results and Discussion

4.1. Effect of Light Source

To Study the effect of light source on the degradation of the herbicide, the studies were conducted (i) in the dark, (ii) In dark with ZnO nano particles, and iii) Direct sunlight with ZnO nano particles. After spiking the water samples with herbicides, one set of samples was kept in dark, in another set of samples ZnO nanoparticles were added and kept in dark and in other set of samples ZnO nanoparticles were added and kept under direct sunlight. An aliquot of samples were collected at pre-determined intervals and the study was carried out with optimum amount of ZnO nanoparticles for each herbicide. The photocatalysis of Fomesafen is faster in the presence of sunlight and ZnO nano particles. There is no degradation of fomesafen was observed in dark, dark/ZnO nano particles. The degradation rate was very rapid in the presence of sunlight and catalyst. The results were presented in (Figure 4).

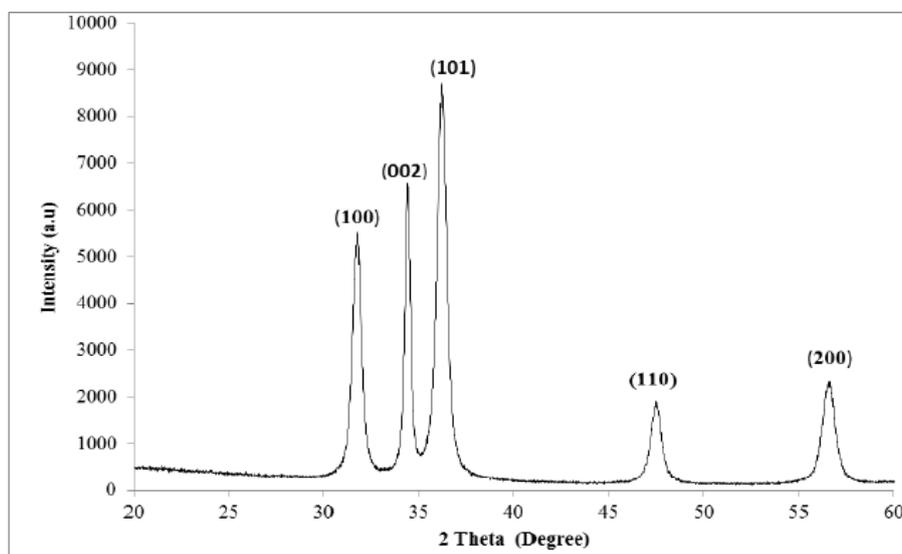


Figure 3. XRD Image of the ZnO nano particles

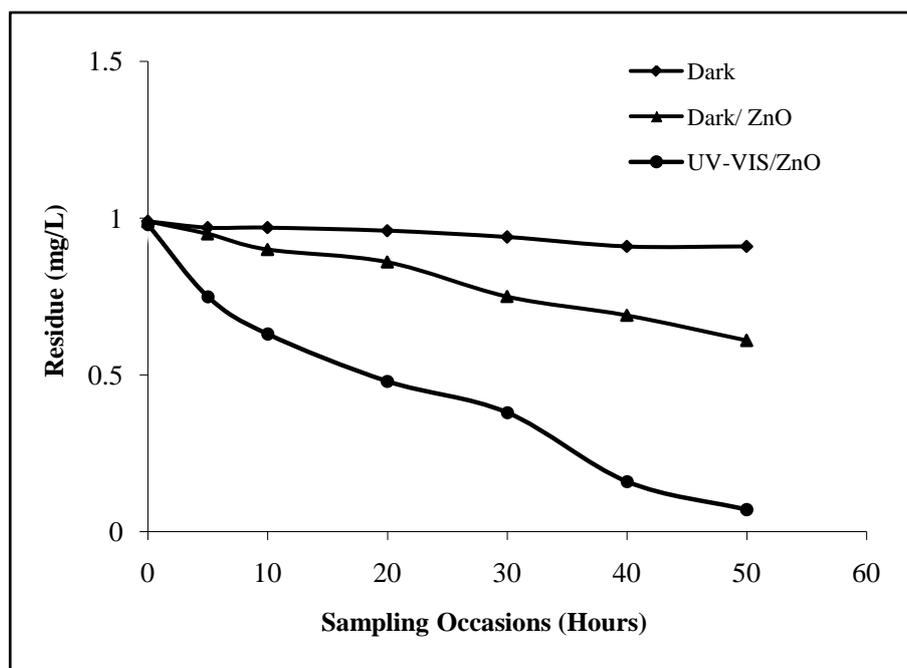


Figure 4. Effect of Light Source on the degradation of the Fomesafen

4.2. Effect of Amount of Catalyst on Degradation of Herbicide

The study was conducted to check the optimum amount of catalyst required to decontaminate the residues. The study was conducted with 10 mg L^{-1} of herbicide formulation and the concentration of the catalyst were varied from 10 to 150 mg L^{-1} . From the results it was established that the optimum concentration to decontaminate the residues as 100 mg L^{-1} . The gradual increase in the efficiency of the catalyst was observed when the concentration of the catalyst was ranged from 10, 20, 50, 100, and 150 mg L^{-1} . Up to 100 mg L^{-1} the decontamination efficiency was increased after that the efficiency was decreased. Increase in the load of the catalyst may show two opposite effects. One is on the surface of the particles it creates the high number of active sites available for the adsorption, and on the other hand, the catalyst particles may disperse the higher amount of light. Therefore these particles are unable to generate electron-hole pairs. By the other hand, through collision, the activated ZnO nano particles were deactivated. From the above observations, the amount of catalyst used was kept constant at 100 mg L^{-1} for all photocatalysis experiments. The results were represented graphically in the (Figure 5).

4.3. Effect of Aeration

To study the effect of aeration in the decontamination of the herbicide residues, the samples were continuously aerated and aliquots were collected and injected. From the results it was concluded that the rate of degradation was faster while the solution was aerated. The reason behind to increase the rate of the reaction is the enhancement of the dissolved oxygen content; it helps to formation of oxonium ions, and facilitate the faster decontamination process. The graphical representations of the results were presented in (Figure 6).

4.4. Effect of Addition of Oxidant in Photocatalysis

The addition of other powerful oxidizing agents, such as hydrogen peroxide (H_2O_2) and sodium persulphate ($\text{Na}_2\text{S}_2\text{O}_8$) to ZnO nano suspension is a very well-known and extensively studied procedure, and many cases lead to enhance the rate of the photo catalytic degradation because they trap the photogenerated electrons more efficiently than the molecular oxygen. A negative result was found [21] for the photo oxidation of the different pesticides; the addition of hydrogen peroxide does not improve the results. In fact, with an excess of peroxide, it can act as an OH^\cdot scavenger. On the contrary, the addition of $\text{Na}_2\text{S}_2\text{O}_8$ (100 mg L^{-1}) was beneficial because (1) the oxidant strongly enhances the reaction rate and increased the number of trapped electrons (2) to generate more radicals and other oxidizing species, (3) to increase the oxidation rate of intermediate compounds. No significant differences in the reaction rates were observed when there was an increase in the concentration of the oxidant. The peroxydisulfate enhancement effect is related to both scavenging's of electrons and production of additional oxidizing species. It traps the photo generated electrons and reduces the probability of recombination with the positive holes. The addition of this inorganic oxidant produces $\text{SO}_4^{\cdot-}$ radicals which are also a strong oxidizing species ($E_0 = 2.7\text{V}$) and produces more hydroxyl radicals. Due to these reasons the addition of oxidant to the reaction mixture is beneficial for the reduction in treatment time, and increases the reaction rate than ZnO alone.

The degradation rate of a compound in photo catalytic oxidation of ZnO occurs by photo generated holes it is well known that oxidation rate increases when the recombination process is suppressed. Peroxydisulfate has been shown to be a more reliable and cheaper electron acceptor [22]. The representative curve was presented in (Figure 7).

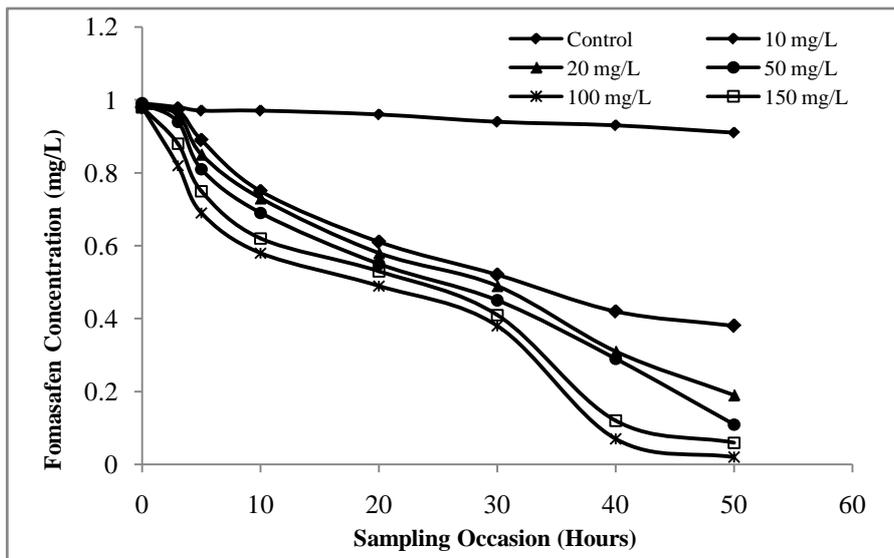


Figure 5. Effect of amount of catalyst used in the degradation of Fomesafen in the photo catalysis reaction; Catalyst Concentration: 10-150 mg L⁻¹

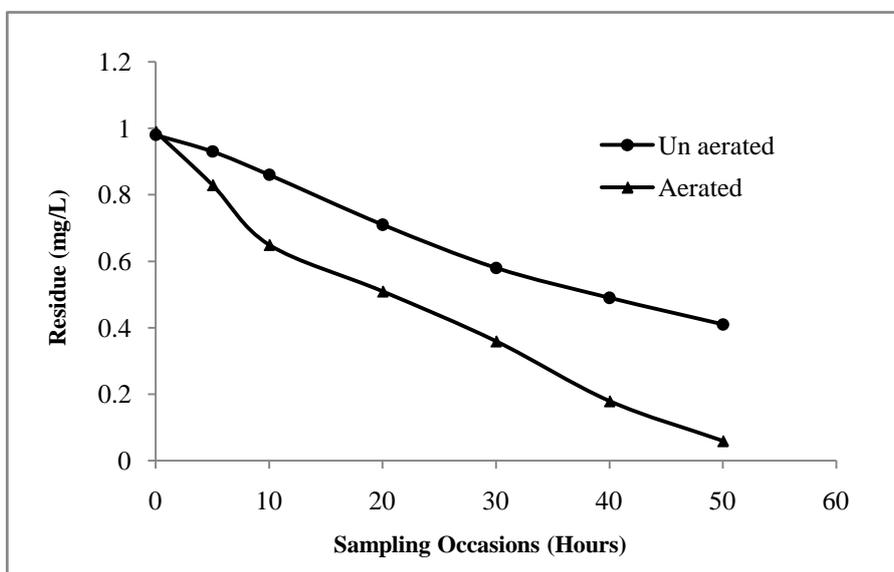


Figure 6. Influence of aeration on the degradation of Fomesafen, Catalyst Concentration: 100 mg L⁻¹

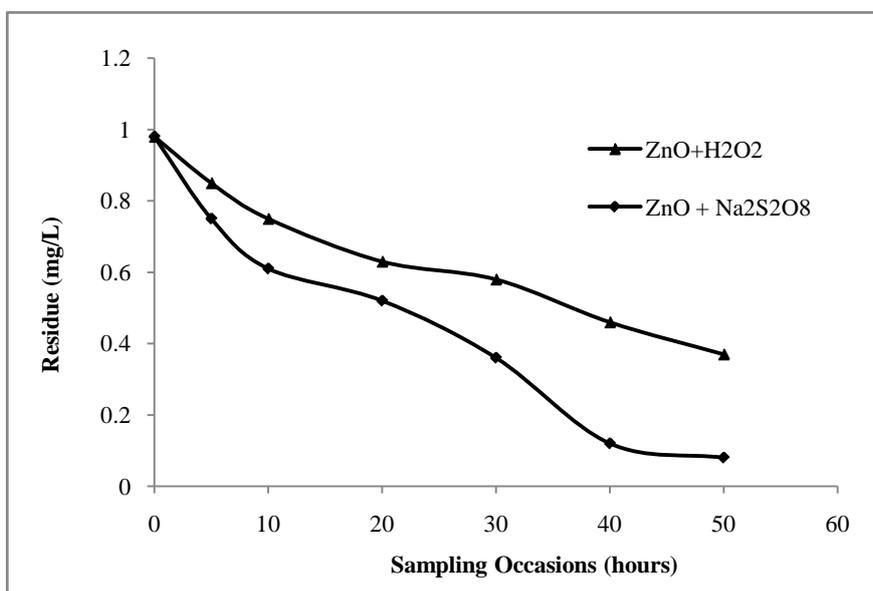


Figure 7. Effect of addition of Oxidant on the degradation of Fomesafen, Catalyst Concentration: 100 mg L⁻¹; Oxidant Concentration: 100 mg L⁻¹

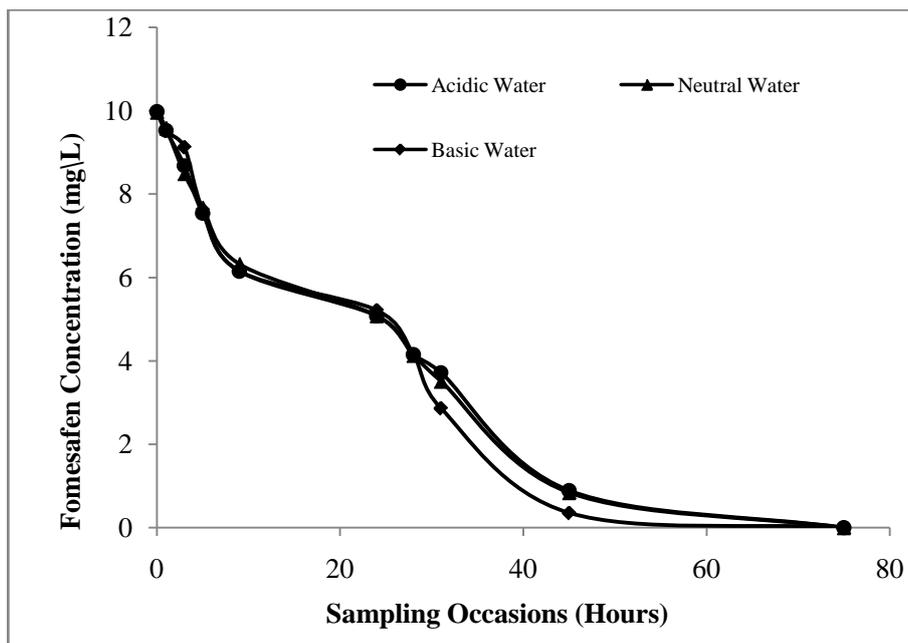


Figure 8. Degradation of Fomesafen under sunlight with 100 mg L⁻¹ catalyst and oxidant Na₂S₂O₈ (100 mg L⁻¹) in Acidic, Neutral and Basic buffers

Table 1. DT₅₀ values of Fomesafen in pH 4 buffer using ZnO/Na₂S₂O₈

Sampling occasion (Hours)	*Concentration (mg L ⁻¹)	Log of Concentration
0	9.98	0.999
1	9.53 (4.5)	0.979
3	8.68 (13.0)	0.939
5	7.54 (24.4)	0.877
9	6.15 (38.4)	0.789
24	5.08 (49.1)	0.706
28	4.15 (58.4)	0.618
31	3.72 (62.7)	0.571
45	0.89 (91.1)	-0.051
75	0.00	0.000
Slope		-0.019
DT₅₀		16.03 h
DT₉₀		53.24 h

*Mean of three replicates.

Table 2. DT₅₀ values of Fomesafen in pH 7 buffer using ZnO/Na₂S₂O₈

Sampling occasion (Hours)	*Concentration (mg L ⁻¹)	Log of Concentration
0	9.96	0.998
1	9.58 (4.0)	0.981
3	8.49 (14.9)	0.929
5	7.67 (23.1)	0.885
9	6.32 (36.7)	0.801
24	5.08 (49.1)	0.706
28	4.13 (58.6)	0.616
31	3.51 (64.8)	0.545
45	0.84 (91.6)	-0.076
75	0.00	0.000
Slope		-0.019
DT₅₀		15.56 h
DT₉₀		51.69 h

*Mean of three replicates.

Table 3. DT₅₀ values of Fomesafen in pH 9 buffer using ZnO/Na₂S₂O₈

Sampling occasion (Hours)	* Concentration (mg L ⁻¹)	Log of Concentration
0	9.96	0.994
1	9.51 (4.7)	0.978
3	9.12 (8.6)	0.960
5	9.76 (23.6)	0.882
9	6.15 (38.4)	0.789
24	5.21 (47.8)	0.717
28	4.15 (58.4)	0.618
31	2.86 (71.3)	0.456
45	0.35(96.5)	-0.456
75	0.00	0.000
Slope		-0.025
DT₅₀		11.91 h
DT₉₀		39.58 h

*Mean of three replicates

4.5. Photocatalysis Results

The degradation of fomesafen was studied in different pH buffer solutions with and without catalyst and oxidant (Na₂S₂O₈) under direct sunlight. The results were given in (Table 1 - Table 3), and the degradation curves were presented in Figure 8. The half-life values without the ZnO nano particles were observed 26.49, 26.28, and 18.52 days in pH 4, 7, and 9 buffers respectively. The Dt₅₀ values with the ZnO nano particles were 16.03, 15.56, and 11.91 hours, respectively. The fastest degradation observed in pH 9 buffer solutions. So it indicates that the fastest degradation was observed in the photocatalysis process (half-life is in hours) than the photolysis process (half-life is in days).

5. Conclusion

The results from the experiment clearly indicate that the persistent herbicide fomesafen was completely degraded in photocatalysis process. The degradation was rapid in UV light with ZnO nano particles. No degradation was observed in dark. The optimum amount of catalyst ZnO was 100 mg L⁻¹. The photocatalysis process was increased more than 15% while the addition of Na₂S₂O₈ than the addition of H₂O₂. The reaction follows pseudo-first-order kinetics. More than fifteen folds increase in the rate of the reaction was observed. The complete mineralization of the residues of fomesafen was observed at 75 hours of irradiation. In the process of photolysis the half-life values of the fomesafen was nearly a month.

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Conflict of Interest

No potential conflict of interest was reported by authors.

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