A Study on Photocatalytic Activity on the Degradation of Metsulfuron Methyl

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Abstract: This study examines the degradation of metsulfuron methyl sulfonylurea herbicide by photocatalytic oxidation (UV/semiconductor) using the catalysts TiO2 (Degussa P25), ZnO, and H2O2. Photo degradation kinetics of metsulfuron methyl was studied. The percentage degradation of irradiated samples was determined using UV Spectroscopy and HPLC analytical techniques. The dissipation was found to follow first order kinetics with rate constant, k = 1.02×10^{-2}, 8.63×10^{-3}, 5.87×10^{-3} in the presence of TiO2 (Degussa P25), ZnO and H2O2 respectively. The catalyst efficacy study confirmed the fast degradation of Metsulfuron methyl in aqueous solution using TiO2 (Degussa P25) photocatalyst when compared to two other catalysts studied under the same environmental conditions and time of exposure.

Key words: Metsulfuron methyl, photocatalyst, TiO2 (Degussa P25), solar irradiation, degradation.

I. INTRODUCTION

Modern agriculture depends on the wide variety of synthetically produced chemicals including pesticides. Pesticides are widely used in crop protection but with an increased pesticide use questions are rising on potential effect regarding public health and environment [1]. However, when applied to the field, pesticides do not only control targeted organism but it may also have potential residue impact on soil [2]. Heavy treatment of soils with pesticides can cause populations of beneficial soil microorganisms to decline [3]. Pesticides pollute air, soil, water resources and contaminate the entire food chain.

Metsulfuron methyl (chemical name: methyl 2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl carbomoyl sulfonyl) benzoate), C13H13N3O5S is a post emergence sulfonyl urea herbicide which controls most annual grass, broad leaf weeds in cereals and it has been used for a long time [2]. Sulfonyl urea herbicide is widely used at low application rate for post emergence broad leaf weed control in oil palm plantation. It has a good selectivity to oil palm and it is very effective against a wide range of broad leaf weeds at application rate of 15 to 30g ha\(^{-1}\) [4].

Metsulfuron methyl inhibits cell division in the roots and shoots of the plant [5]. It is biologically active at low application rate and rapidly taken up by plants through roots and foliage [6], [7] and [8]. It is relatively mobile in moist soil but it will be retained longer in soils with higher percentage of organic matter. It is more mobile in alkaline soil than in acidic soil. It degrades faster in acidic condition and in soil with higher moisture content and higher temperature. It is stable to photolysis, but it will break down in UV light. The widely used analytical tool for determination of the active ingredient of metsulfuron methyl is a reversed phase HPLC with UV detection [9]. The advanced oxidation process (AOP’s) using various nano photocatalyst has emerged as the best available technology (BAT) for the removal of organic pollutants [10]. Several semiconductors can act as photocatalyst for light induced chemical transformation because of their unique electronic structure e.g. TiO2, ZnO, Fe2O3, WO3 and CdS etc. [11].

The wide band-gap semiconductors can act as sensitizers for light-induced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. When a photon with energy of h\(\nu\) matches or exceeds the band gap energy of the semiconductor, an electron is excited from the valence band into the conduction band leaving a hole behind. The valence-band holes are powerful oxidants, while the conduction-band electrons are good reductants. In the absence of suitable electron and hole separation forces, the stored energy is dissipated within a few nanoseconds in the recombination process. If a surface defect state is available to trap the electron or hole, recombination is prevented /reduced and subsequent redox reactions may occur [12].

TiO\(_2\) (Degussa P-25) photocatalyst contains two different phases, anatase and rutile in the ratio of about 3:1. It is produced through high temperature (> 1200°C) flame hydrolysis of TiCl\(_4\) in the presence of H\(_2\) and O\(_2\). TiO\(_2\) so formed is treated with steam to remove HCl which is also produced as a part of the reaction. The product is 99.5% pure TiO\(_2\) (anatase : rutile, 70:30) which is non-porous with round edged cubic particles.
The Degussa P-25 TiO₂ powder has a surface area of 50 ± 15 m²g⁻¹ and an average particle diameter of 21 nm. Transmission electron microscopy distinguished anatase and rutile particles separately from their agglomerates. Theurich et al., found that the rutile phase does not exist as an overlay on the surface of the anatase particle but it exists separately from anatase particles [13]. The efficiency of three different catalysts TiO₂ (Degussa P-25), ZnO and H₂O₂ in influencing the dissipation rate of metsulfuron methyl in aqueous solution was analyzed and discussed in this article.

II. MATERIALS AND METHODS

2.1 CHEMICALS
Metsulfuron methyl, methyl 2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl carbomoyl) sulfomoyl benzoate, reference analytical standard of 99% purity and TiO₂ (Degussa P-25) were purchased from Sigma Aldrich Pvt. Ltd., Germany. ZnO and H₂O₂ were purchased from M/s, Ranbaxy Laboratories Ltd. All other chemicals used in the study were analytical grade reagents.

2.2. EQUIPMENTS
The residues of metsulfuron methyl at different time points were analysed using Shimadzu High Performance Liquid Chromatograph system equipped with LC-10 AT pump and SPD-10A UV-VIS detector and interfaced with CLASS-LC10 software system by Shimadzu Corporation Pvt. Ltd., Tokyo, Japan and Elico Double beam UV-Visible spectrophotometer with wavelength scanning range 190-1100 nm and Silicon photodiode detector supplied by Elico Pvt. Ltd., Hyderabad.

2.3. PREPARATION OF STANDARD
500 mg of Metsulfuron methyl reference analytical standard was weighed and transferred quantitatively into a 100 ml volumetric flask. To the flask 50 ml of acetonitrile was added and the contents were sonicated for 5 minutes. The solution was then made up to the mark volumetrically using acetonitrile.

2.4 PREPARATION OF WORKING SOLUTION
From the stock solution (500mg in 100 ml of Acetonitrile) of metsulfuron methyl (MSM), desired concentrations of working solutions were prepared by serial dilution with distilled water. Two control samples were maintained for this purpose, one metsulfuron methyl solution without the catalyst and the other catalyst in aqueous solution without metsulfuron methyl. The solution of optimal concentration 20 ppm (fixed after studying the influence of herbicide concentration on degradation rate) of Metsulfuron methyl was taken as working solution. 0.5g/L TiO₂ (fixed after studying the influence of catalyst loading on herbicide degradation) was added to the working solution. In the similar manner, the samples were prepared using other catalysts ZnO and H₂O₂ for the same 20 ppm of herbicide solution.

2.5 SAMPLE COLLECTION AND ANALYSIS
All the samples were exposed under the direct sunlight during the day time. Aliquots of sample solution were collected at regular time intervals (10, 20, 30, 40, 60, 80, 100 & 120 min). The samples were filtered through 0.4μm nylon (Millipore) filter paper to separate the tiny particles of the catalyst (TiO₂). The clear samples were then analyzed by validated HPLC and UV –Vis spectrophotometer at 220 nm wavelength.

2.6 CATALYST EFFICIENCY
The catalyst efficiency was calculated using the following formula:

\[
\text{Catalyst Efficiency} = \frac{[\text{Co} - \text{C}] \times 100}{\text{Co}}
\]

Where Co is the initial concentration and C is the concentration after photo irradiation.

2.4. HPLC PARAMETERS
Model : Shimadzu High Performance Liquid Chromatograph system
Column : C₁₈ column (5μm, 4.6x150mm)
Mobile phase : Acetonitrile and water (70:30)
Retention time : 2.6 minute
Flow rate : 1ml per minute
Wavelength : 220nm

III. RESULTS AND DISCUSSION
Rate of dissipation of metsulfuron methyl in aqueous solution using three different catalysts namely H₂O₂, ZnO, and TiO₂ (Degussa P25) were calculated and it was found to follow first order kinetics. The dissipation rate constant was calculated by linear regression from the transformed first order rate equation \( \ln C/C₀ = -kt \) where \( C \) is the metsulfuron methyl concentration as a function of time in minute \( t \), \( C₀ \) is the initial concentration of metsulfuron methyl and \( k \) is the rate constant (Fig. 1).

3.1. Dissipation of Metsulfuron methyl in the presence and absence of direct sunlight
The concentration of Metsulfuron methyl in aqueous solution was found at different time points and under different conditions. The concentration of metsulfuron methyl was declined to 16.5 ppm in the absence of sunlight and 8.6 ppm under the direct sunlight from its initial concentration 20 ppm at 120 minutes. This brings out the fact that the dissipation of metsulfuron methyl was greatly influenced by solar irradiation.

3.2 Dissipation of Metsulfuron methyl in the presence and absence of catalyst
Rate of dissipation of Metsulfuron methyl in aqueous solution under direct sunlight using three different catalysts (H₂O₂, TiO₂ (Degussa P-25) and ZnO) were studied. The concentration of Metsulfuron methyl was declined to 8.6 ppm from the initial concentration of 20 ppm at 120 minutes without using any catalyst. The same 20ppm (initial concentration) of Metsulfuron methyl solution degraded to 4.7 ppm using TiO₂...
3.3 Efficiency of the photocatalyst in the dissipation of Metsulfuron methyl

The efficiency of the photocatalyst was determined. It was found that TiO$_2$ (Degussa P-25) showed 76.5\% catalytic activity, ZnO 68\% and H$_2$O$_2$ 58\% towards the degradation of metsulfuron methyl in aqueous solution. It was also found from the results (depicted in Fig. 2) that the dissipation rate of metsulfuron methyl was faster in the presence of TiO$_2$(Degussa P-25) photocatalyst when compared to other two catalysts. The HPLC chromatogram of metsulfuron methyl (Fig. 3) without the catalyst showed approximately 25\% of herbicide removal at 120$^{th}$ minute whereas the dissipation found to be much greater in the presence of catalyst. The catalytic activity was in the order TiO$_2$ (Degussa P25) > ZnO > H$_2$O$_2$. This was evidenced from the HPLC chromatograms Fig 4,5 and 6. After 120 minutes of solar irradiation the concentration of metsulfuron methyl continued to decrease and reached the permissible limit(0.03mg/L) [14] after 130, 150, and 200 minutes using TiO$_2$(Degussa P25), ZnO and H$_2$O$_2$ respectively.

Table 1: Dissipation of MSM using TiO$_2$ (Degussa P25)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Std Control (ppm)</th>
<th>Sample (ppm)</th>
<th>% of degradation</th>
<th>Rate constant of sample dissipation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>19.1</td>
<td>17.8</td>
<td>11</td>
<td>1.17 $\times 10^{-2}$</td>
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<tr>
<td>20</td>
<td>18.2</td>
<td>15.7</td>
<td>21.5</td>
<td>1.21 $\times 10^{-2}$</td>
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<tr>
<td>30</td>
<td>16.9</td>
<td>14.4</td>
<td>28.0</td>
<td>1.10 $\times 10^{-2}$</td>
</tr>
<tr>
<td>40</td>
<td>15.8</td>
<td>12.6</td>
<td>37.0</td>
<td>1.16 $\times 10^{-2}$</td>
</tr>
<tr>
<td>60</td>
<td>14.0</td>
<td>10.9</td>
<td>45.5</td>
<td>1.01 $\times 10^{-2}$</td>
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<tr>
<td>80</td>
<td>12.3</td>
<td>7.8</td>
<td>61.0</td>
<td>1.18 $\times 10^{-2}$</td>
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<tr>
<td>100</td>
<td>10.4</td>
<td>6.5</td>
<td>67.5</td>
<td>1.12 $\times 10^{-2}$</td>
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<tr>
<td>120</td>
<td>8.6</td>
<td>4.7</td>
<td>76.5</td>
<td>1.21 $\times 10^{-2}$</td>
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</tbody>
</table>

* Std. control – MSM in aqueous solution without any catalyst

* Sample – MSM solution with the catalyst

Table 2: Dissipation of MSM using H$_2$O$_2$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Std Control (ppm)</th>
<th>Sample (ppm)</th>
<th>% of degradation</th>
<th>Rate constant of sample dissipation</th>
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<td>10</td>
<td>19.1</td>
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<td>18.2</td>
<td>17.6</td>
<td>12.0</td>
<td>6.39 $\times 10^{-3}$</td>
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<td>30</td>
<td>16.9</td>
<td>16.4</td>
<td>18.0</td>
<td>6.62 $\times 10^{-3}$</td>
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<td>22.5</td>
<td>6.37 $\times 10^{-3}$</td>
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<tr>
<td>60</td>
<td>14.0</td>
<td>13.8</td>
<td>31.0</td>
<td>6.18 $\times 10^{-3}$</td>
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<tr>
<td>80</td>
<td>12.3</td>
<td>12.0</td>
<td>40.0</td>
<td>6.39 $\times 10^{-3}$</td>
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<tr>
<td>100</td>
<td>10.4</td>
<td>10.1</td>
<td>49.5</td>
<td>6.83 $\times 10^{-3}$</td>
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</tbody>
</table>

* Std. control – MSM in aqueous solution without any catalyst

* Sample – MSM solution with the catalyst

Table 3: Dissipation of MSM using ZnO

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Std Control (ppm)</th>
<th>Sample (ppm)</th>
<th>% of degradation</th>
<th>Rate constant of sample dissipation</th>
</tr>
</thead>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>19.1</td>
<td>18.1</td>
<td>9.5</td>
<td>9.98 $\times 10^{-3}$</td>
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<tr>
<td>20</td>
<td>18.2</td>
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<td>19.0</td>
<td>10.5 $\times 10^{-3}$</td>
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<tr>
<td>30</td>
<td>16.9</td>
<td>14.8</td>
<td>26.0</td>
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<td>35.0</td>
<td>10.77 $\times 10^{-3}$</td>
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<tr>
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<td>14.0</td>
<td>11.5</td>
<td>42.5</td>
<td>9.22 $\times 10^{-3}$</td>
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<tr>
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<td>12.3</td>
<td>10.2</td>
<td>49.0</td>
<td>8.42 $\times 10^{-3}$</td>
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<tr>
<td>100</td>
<td>10.4</td>
<td>7.9</td>
<td>60.5</td>
<td>9.29 $\times 10^{-3}$</td>
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<tr>
<td>120</td>
<td>8.6</td>
<td>6.4</td>
<td>68.0</td>
<td>9.50 $\times 10^{-3}$</td>
</tr>
</tbody>
</table>

* Std. control – MSM in aqueous solution without any catalyst

* Sample – MSM solution with the catalyst

Figure 1: Dissipation of Metsulfuron methyl using three different catalysts.

Figure 2: Linear regression of Metsulfuron methyl dissipation confirming the first order kinetics.
IV. CONCLUSION

The photocatalytic degradation of Metsulfuron methyl in aqueous solution was studied using three different catalyst TiO\(_2\) (Degussa P25), ZnO and H\(_2\)O\(_2\). The data generated in the study highlights the effective destruction of the herbicide by solar irradiation. Under direct sunlight (at higher flux) the rate was greater, this means that the process works in a good photocatalytic regime, the incident photons were efficiently converted into active species that act in the degradation mechanism. The results further evidence that the catalyst TiO\(_2\) (Degussa P25) was efficient in degrading the metsulfuron methyl at a higher rate. The higher activity of TiO\(_2\) (Degussa P25) catalyst was due to its greater band gap, higher surface area which lower the electron–hole recombination. In Degussa P-25 the conduction band electron of the anatase phase jumps to the less positive rutile phase, reducing the rate of combination of electrons and holes in the anatase phase. The presence of electron and the hole results in the formation of active species like superoxide and hydroxide radicals which induce the oxidation of organic pollutant in the aqueous medium. The HPLC data indicated the formation of many persistent metabolites. Lot of work has to be done in the quantification of these intermediates. Quantification of these intermediates will help further in the mechanistic studies of the photocatalytic reactions. The better understanding of the photocatalytic mechanism could further give great opportunities for its application in the decontamination of environmental pollutants.

V. REFERENCES


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