PHOTOCATALYTIC OZONATION FOR THE DEGRADATION OF TETRADIFON PESTICIDE ON Mn/TiO$_2$ UNDER VISIBLE LIGHT

MADDILA S.
NDABANKULU V.O.
JONNALAGADDA S.B.

School of Chemistry, University of KwaZulu-Natal
Westville campus, Chiltern Hills, Durban-4000, South Africa

Received: 16/12/2015
Accepted: 29/02/2016
Available online: 13/04/2016

*to whom all correspondence should be addressed:
e-mail: sureshmskt@gmail.com

ABSTRACT
The photocatalytic activity of Mn doped TiO$_2$ for the ozonation of tetradifon pesticide in aqueous solution was studied. Various loadings of catalysts Mn/TiO$_2$ (1%, 2.5% and 5%) was prepared and characterized by standard analytical techniques. Photocatalyzed ozonation with 2.5% Mn/TiO$_2$ yielded 100% degradation and mineralization of tetradifon in 2.0 h under basic pH conditions. The extent of degradation of tetradifon pesticide and its mineralization were confirmed by GC-MS. For 10 mg l$^{-1}$ of tetradifon, 0.1 g l$^{-1}$ of catalyst was found to be the optimum for effective mineralisation. The reused experiment confirmed that Mn/TiO$_2$ kept a good photocatalytic activity and stability, and it was a promising heterogeneous catalyst. The catalyst is fully recoverable and reusable multiple times with no loss of activity.

Keywords: Tetradifon; Advanced Oxidation; Photocatalyst; Mn/TiO$_2$; Degradation

1. Introduction
A wide diversity of organic contaminants is introduced into the water system from different sources, such as industrial sewages, agricultural run-off, pharmaceutical and chemical spills (Marc et al., 2003). Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to the societies and regulation authorities around the world (Aragay et al., 2012). During the past several years, pesticides (Tetradifon) have been one of the most commonly applied insecticides in agriculture, industrial and medicinal products (Rissato et al., 2007). Because of their high toxicity and long persistence in environment, chlorine contains sulfonated aromatic compounds, as well as by-products of their production, have become major environmental problems (Field and Sierra-Alvarez, 2008). Consequently, they can be present together with their degradation products in natural water resources. Contamination of waters and soil can also occur from pesticide discharges from manufacturing plants, from storage sites and run-offs from vegetation and soil. However, the pesticide residues on agricultural products cause detrimental effects on human health such as carcinogenesis, neurotoxicity, irregular reproduction and cell development. Therefore, the control of organic pollutants in water is an important measure in environmental protection. Among many processes proposed and/or being developed for the destruction of the organic contaminants, biodegradation has received the greatest attention (Angelidaki et al., 2000). However, many organic pesticide chemicals, especially those that are toxic or refractory, are not amendable to microbial degradation (Maddila et al., 2015a). Recently considerable much attention has been developed on the use of photodegradation with ozone as a means to oxidize toxic organic pesticides (Maddila et al., 2015b).
In recent years, heterogeneous photocatalysis with semiconductors is commonly considered as a beneficial method, not only for the degradation of pollutants in waste water and air (Chong et al., 2010). Photocatalysis is proven to be as an excellent method over than others due to the use of oxygen as an oxidant, for photooxidation of the organic compounds at its chemical stability, nontoxicity, low concentrations and at low temperatures, relatively low cost, and to achieve comprehensive degradation and mineralization (Kabra et al., 2004). Photocatalytic degradation involves the use of certain semiconductors as catalysts for the production of the highly reactive radicals under light irradiation (Chen et al., 2010). The proficiency of this system is based on the production of reactive species, such as hydroxyl radicals, holes, superoxide anions. However, use of titania is diminished by its wide bandgap (3.2 eV), which requires ultraviolet irradiation (λ < 387 nm) for photocatalytic activation to inject electrons into the conduction band and leave holes in the valence band (Dahl et al., 2014). To progress the reaction of titania by enhancing the separation of electron–hole pairs, there are different strategies to reduce electron–hole recombination rates and increase the photocatalyst efficiency, including doping titania with transition metal (Chen et al., 2010; Dahl et al., 2014). The photocatalyst for the photo-oxidation of organic compounds has conventional much significance as it is plentiful, economical, powerful, eco-friendly, and pollutants can be degraded effectively and ultimately mineralized to CO$_2$, H$_2$O and inorganic anions under visible light irradiation.

Ozonation is one of the best methods that give better results in the degradation of organic species at low concentrations in water and wastewater (Maddila et al., 2014a; 2014b). However, it is commonly chosen to removal of the pollutants present in water effluents due to its higher oxidation potential. In addition, heterogeneous photocatalytic ozonation has received great attention due to its high oxidation potential that originates from the formation of hydroxyl radicals as well as a lack of secondary pollutants generation compared with the homogeneous catalytic process (Fathinia et al., 2015). In this process, the presence of the heterogeneous catalyst surfaces induces the decomposition of ozone, and subsequently generates the hydroxyl radicals. As significant functional materials in solid catalysts, manganese loaded titania have been commonly employed because of their stability and abundance in nature, as well as their higher catalytic efficiency during the photocatalytic ozonation process. Our group has proved that photocatalytic ozonation with Mn doped TiO$_2$ improves the degradation and mineralization of pesticide.

2. Materials and method

2.1 Photocatalytic Ozonaanalysis Experiment

For photoozone generation, the light source was a 500-W xenon lamp (CHFXQ500 W) with a UV filter that can cut off UV light with wavelengths shorter than 420 nm and a fischer ozone 500 generator was used. Ozone enriched oxygen stream was passed through a sintered glass (porosity 2) into the 50 cm$^3$ reactor at a flow rate of 10 mL per min. The reactor temperature was maintained at 19 ± 1 °C by circulating water through double walled jacket. For each run, 20 mL 10 % w/v of tetradifon and fixed ozone concentration (0.05 M) and flow rate of 10 mL/min. A magnetic stirrer was used to ensure continuous mixing. Ozone concentration in oxygen stream was determined using KI method (Maddila et al., 2014a; 2014b). Before and after each of the experiment the flow rate and photoozone content were monitored in duplicate runs.

2.2. Catalyst preparation

The photocatalysts were prepared by deposition-precipitation method by impregnating Mn over titania. 1.6 g of TiO$_2$ was suspended in 60 mL of deionized water under vigorous stirring for 30 min. Then, 1.8 ml of 0.2 M manganese nitrate aqueous solution (Mn(NO$_3$)$_2$, Aldrich, 99.98 % trace metals basis) was added. This solution was preserved unstirred for 1.0 h. Then the manganese aqueous solution was added slowly into the TiO$_2$ suspension under stirring. For the completion of addition, the pH was adjusted to 11 using 0.1 M NaOH solution. The suspension was vigorously stirred for another 2 h. The precipitate was aged at 60-70 °C for 2 h in the mother solution. Then the precipitate was filtered and washed with deionized water
for three times. The samples were dried at 110-120 °C for overnight and then calcined in the presence of air, at 450 °C for 4 h to obtain the 1.0%, 2.5%, and 5.0% w/w of Mn/TiO₂ catalysts.

2.3. Instrumentation

All the catalyst characterization and product identification was achieved adopting the following techniques: PXRD, SEM-EDX, TEM, N₂ sorption, ICP, PL, FTIR, GC-MS, ¹H NMR spectral analysis (Maddila et al., 2013a; 2013b; 2014c).

3. Results and discussion

3.1. BET Surface and elemental analysis

The N₂ sorption study was carried out over bare TiO₂ and Mn doped TiO₂ catalysts (Figure 1). N₂ sorption resulted in typical type IV isotherm, with a H₂ hysteresis loop. The BET surface areas of bare TiO₂ and Mn/TiO₂ catalysts were found to be 38.45 and 79.82 m² g⁻¹, respectively. It is evident from these results that there was a significant change in the surface area from the TiO₂ to Mn doped TiO₂ catalyst. Table 1 summarizes the obtained BET surface area, pore diameter and pore volume.

Table 1: BET surface area, elemental analysis and band-gap of Mn loaded supports

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mn Wt% (From ICP)</th>
<th>Surface Area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Mn wt % (From EDX)</th>
<th>Band-gap Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare TiO₂</td>
<td>-</td>
<td>38.45</td>
<td>0.24</td>
<td>-</td>
<td>3.20</td>
</tr>
<tr>
<td>1.0 % Mn-TiO₂</td>
<td>0.98</td>
<td>51.66</td>
<td>0.16</td>
<td>0.98</td>
<td>3.10</td>
</tr>
<tr>
<td>2.5 % Mn-TiO₂</td>
<td>2.46</td>
<td>64.48</td>
<td>0.14</td>
<td>2.48</td>
<td>2.84</td>
</tr>
<tr>
<td>5.0 % Mn-TiO₂</td>
<td>4.98</td>
<td>79.82</td>
<td>0.10</td>
<td>4.97</td>
<td>2.76</td>
</tr>
</tbody>
</table>

Figure 1. N₂ sorption of 0%, 1%, 2.5% and 5% Mn/TiO₂ catalysts

3.2. SEM and TEM

The morphology of bare and Mn doped titania (1%, 2.5% & 5.0%) catalysts were examined by scanning electron microscopy; the images obtained are presented in Supporting Information Figure. 2a-d respectively. The SEM images of bare titania and Mn doped titania at various amplifications display the partial crystalline nature. The surface morphology of titania appears to be changed after Mn loading. The EDX analysis evidently specifies the presence of Mn species on the surface of titania. The TEM images of the undoped and doped titania calcined catalysts and used are shown in Figure.3a-d. In these catalysts, the concentration of Mn increases average particle size decreases and the agglomeration between the particles also reduces.
3.3. XRD analysis

Figure 4 shows the XRD diffraction patterns of bare titania and Mn doped titania (1%, 2.5% and 5%) powder samples calcined at 450 °C. The diffractograms indicates peaks which corresponds to 2θ values of 25.3° for (1 0 1), 37.8° for (0 0 4) and 47.9° (2 0 0) (JCPDS file no. 21-1272) and are typical for anatase phase.

3.4. UV-DRS

UV-diffuse reflectance spectra of titania and various (% w/w) Mn loaded titania catalysts are acquired in Figure 5. TiO₂ has a strong absorption band at approximately 384 nm corresponding to band-gap energy of 3.2 eV calculated from the formula \( \kappa = \frac{1239.8}{E_{bg}} \) (Table 1S). On doping with Mn, a red-shift was observed which could foster the photocatalytic activities of the catalyst under visible light.
PHOTOCATALYTIC OZONATION FOR THE DEGRADATION OF TETRADIFON PESTICIDE

3.5. Photoluminescence Spectra

Figure 5. UV-DRS images of Bare TiO$_2$ and Mn doped TiO$_2$ catalysts

Figure 6. PL spectra of Bare TiO$_2$ and Mn doped TiO$_2$ catalysts

Figure 6 shows the PL spectra of samples in the range of 350–500 nm with the excitation wavelength of 360 nm. The PL spectra might be closely related to the recombination of photo-induced electrons and holes, and free and self-trapped excitons, which possibly generate from surface defects in the TiO$_2$ crystals, such as lattice distortions and surface oxygen deficiencies (Venier et al., 2014). The spectra show that the intensity of the Mn doped titania was decreased as compared to the bare titania, which indicates the reduction of the recombination centers for the electrons and holes in the samples. This describes that the Mn doped titania may have low electron-holes recombination rate under light irradiation and may show better photocatalytic activity than bare TiO$_2$.

3.6. Effect of pH

The influence of pH on the effectiveness of tetradifon degradation by ozonation is shown in Figure 7. The degradation experiments were carried out at pH values of 3, 7 and 11. The degradation rate increased as the pH increased from 3 to 11. Under acidic pH, O$_3$ molecule is main reactive species and its reactivity is very low relative to hydroxyl radical, so the degradation of tetradifon very low. As the solution becomes more basic, the rate of photocatalyzed decomposition of ozone to secondary oxidants, such as hydroxyl radicals increases. While the increase in pH facilitates the hydroxyl radical concentration, the effect of pH
on the substrate reactivity is also equally vital for efficient conversion. The obtained results indicate that the process effectiveness increases significantly and highest conversion was recorded at pH 11.

![Graph](image1)

**Figure 7.** Effect of the different photooxidations at pH 3, 7 and 11

### 3.7. Effect of catalyst concentration

The effects of catalyst concentration on the tetradifon photodegradation, it is observed from Figure. 8. The photocatalytic efficiency of the tetradifon samples increases up to the catalyst concentration of 0.05 to 0.250 g L\(^{-1}\), for the tetradifon photooxidation. The optimum weight of catalyst loading was found to be 0.1 g L\(^{-1}\). Further increase in catalyst weight resulted in the decrease of the reaction rate. This can be explained in terms of availability of active sites on the catalyst surface and the penetration of visible light into the suspension (Oseghe *et al.*, 2015). The total active surface area increases with increasing catalyst weight but at the catalyst weight above optimum loading decrease in visible light penetration may be due to screening effect of excess catalyst particle in the solution. Hence, the initial rate decreases at the higher catalyst loading.

![Graph](image2)

**Figure 8.** Effect of Mn/TiO\(_2\) catalyst concentration at pH 11

### 3.8. Effect of Mn doping concentrations

Photo induced oxidation of tetradifon in the presence of the bare TiO\(_2\) and Mn on titania was carried out in order to study the photocatalytic activity under visible light. The photocatalytic activity of Mn/TiO\(_2\) photocatalyst was significantly enhanced on the addition of Mn loading. Additionally, the photocatalytic activity of Mn doped titania increased with the increasing doping concentration of Mn (1 to 5.0%). An increase in the amount of Mn dopant resulted in the increasing visible light absorption and hence
enhanced photocatalytic activity. The optimal tetradifon degradation was found to be at 5 wt.% Mn concentration with the removal efficiency.

3.9. Catalyst testing and product identification

![Figure 9](image)

**Figure 9. GC-MS chromatogram of product mixture**

All the photocatalyzed ozonation experiments were accompanied by exposing the reaction mixtures with visible light and with a flow of ozone enriched oxygen. After ozone aeration, the organic portion of the reaction mixture was extracted and analyzed after every reaction with 20 min intervals. The six products identified by GC-MS (Figure 9).

![Figure 10](image)

**Figure 10. GC-MS mass spectra’s products of (a) OA, (b) TCB, (c) FA, (d) DHDDA, (e) CBSA and (f) HDDA**

The peaks from 8.00-17.00 retention times refer to the intermediates and various carboxylic acid compounds formed due to the further oxidation of the products of the reaction. The peaks at retention time 8.507, 9.709, 11.401, 13.558, 15.807 and 16.658 minutes refer to the compounds of (a) oxalic acid (OA), (b) trichlorobenzene (TCB), (c) fumaric acid (FA), (d) dihydroxyhexa-2,4-dienedioic acid (DHDDA), (e) 4-chlorobenzenesulfonic acid (CBSA), and (f) 3-hydroxyhexa-2,4-dienedioic acid (HDDA) respectively.
Furthermore, the formation of these products was confirmed by GC-MS with their respective (M⁺) m/z values (Figure 10a-f). The peaks observed in 1H-NMR and FT-IR spectra of the products were in good agreement with spectra of the functional groups present in the products. Additionally, the qualitative lime water test confirmed the release of CO₂ during the reactions and suggested some mineralization of pesticides. Photo catalytic ozonation of pesticides in water is known to produce more biodegradable oxygenated organic products and low molecular weight acids.

3.10. Reaction mechanism

Based on the observed experimental results, the probable mechanism for the photocatalysed degradation of tetradifon on Mn/TiO₂ in presence of ozone is proposed. In photocatalysed ozonation using heterogeneous catalyst, the photoinduced holes and electrons in semiconductor particles reportedly produce highly oxidizing species, which play a key role in degradation of organic pollutants (Zhang et al., 2009). The heterogeneous photocatalysed ozonation in the presence of metal oxides or metals/metal oxides on supports, the effectiveness of the catalytic process depends to an abundant scope on the properties of catalyst surface, which influence the properties of the surface active sites and photocatalysed ozone decomposition reactions in aqueous solutions. The most important chemical properties for the sustainable activity of catalyst are chemical stability and the presence of active surface sites, which are responsible for catalysed reactions (Kasprzyk-Hordern et al., 2003).

Proposed Mechanism: Mechanism of the Scheme
It is well well-known that the electrophilic reactions of photolytic ozone take place on sites with strong electronic density. In particular, aromatics substituted with electron-withdrawing groups are highly reactive with photoinduced ozone electrons on carbons located in the ortho and para positions due to high electronic densities on these aromatic carbons whereas aromatics substituted with electron withdrawing groups (−SO2, −Cl) are weakly photolytically reactive. The molecular structure of tetradifon pesticide contains electron-withdrawing groups (−SO3 and −Cl), hence photolytically ozone reactions should occur initially on certain preferential sites. In order to illustrate this, sites with strong electronic density were identified, and the analysis showed that it is likely that photocatalyzed ozone attack would take place at the sulfonyl group. Besides the electrophilic attack, ozone undergoes cycloaddition reaction with unsaturated bonds leads to the formation of compounds having the carbonyl group (−C=O) or the acid group (−COOH). With this in mind and in order to illustrate a possible reaction mechanism, further analysis was made with spectral analysis to identify the intermediate products. Based on, the sulfone compound, 4-chlorobenzenesulfonic acid (CBSA) and trichlorobenzene (TCB). According to this postulate that the bonds C–S and C–Cl in A and B are cleaved leading to the formation of another intermediates 4-chlorophenol and 2-chlorobenzene-1,4-diol. Further attacks of photoozone radicals leads to the conversion of 4-chlorophenol to 3-hydroxyhexa-2,4-dienedioic acid (HDDA), then to oxalic acid (OA) and also fumaric acid (FA), and eventually conversion to mineralization (CO2 and H2O).

On the other hand, through cleavage of the C–Cl bond in compound trichlorobenzene (TCB) and with further photolytic ozone attack, dihydroxyhexa-2,4-dienedioic acid (DHDDA) is formed. Through further photolytic ozone attack, OA and FA are converted. Additionally, extended photolytic oxidation of the intermediates leads to complete mineralization to produce carbon dioxide and water (Scheme).

4. Conclusions

Our study showed that the deposition-precipitation method permits the synthesis of Mn doped titania catalysts with good metal dispersion. The results of this study clearly indicate that Mn/TiO2 can efficiently catalyze the degradation and mineralization of the tetradifon pesticide in the presence of light and ozone. The size of catalyst particles, and reaction parameters play a significant role in ozonolysis, so catalytic properties are strongly affected by the preparation method of the catalyst. Titania is a suitable support for loading of Mn catalysts. The tetradifon photooxidation was quantitative with 100% degradation. CBSA, TCB, HDDA and DHDDA were main products of which OA and FA were the secondary product, with partial mineralization. Photocatalysed ozonation is proved to be an effective method to remove chloro, sulfonyl and hydroxy groups from substituted organic pesticide.

Acknowledgements

The authors are thankful to the National Research Foundation of South Africa, University of KwaZulu-Natal, Durban, South Africa and Department of Chemistry, Annamacharya Institute of Technology & Sciences, Tirupati, India for providing facilities.

References


