Chapter 5

Photocatalytic Degradation of Maleic Anhydride Using Kronos 7000 and N-F Codoped TiO$_2$ Under UV-Visible Light
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5.1 Introduction
In this system, NF-TiO₂ was used to decompose MAN in water. MAN has been widely used in the production of unsaturated polymer resins and fiber-reinforced plastics for automobile and construction industries as well as in the production of pharmaceuticals and agricultural chemicals because of which MAN and its intermediates easily come into the environment through various streams during the manufacturing processes. It is listed by the United States Environmental Protection Agency (USEPA) as a "priority pollutant" due to its substantial effects and ubiquity in the environment. It is also designated as a hazardous substance under section 311(b) (2) (A) of the Federal Water Pollution Act, MAN has adverse effects on human health such as immunotoxicity and specific toxicity to organs, including digestive system and kidneys (Humiston et al., 1975 a & b). It also causes urticaria (Japan GHS MSDS clarification).

Table 5.1 shows the properties of phthalic anhydride.
Table 5.1 Properties of Maleic anhydride:

<table>
<thead>
<tr>
<th>Chemical name and formula</th>
<th>Maleic anhydride C₄H₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>98.06</td>
</tr>
<tr>
<td>Melting point</td>
<td>52.6 deg.cent.</td>
</tr>
<tr>
<td>Boiling point</td>
<td>202 deg cent.</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>0.2 mm Hg at 20 deg.cent.</td>
</tr>
</tbody>
</table>

Due to the resistance of MAN to biodegradation and its toxic effects on microbial processes (Iraja do Nascimento et al., 2003), conventional biological wastewater treatment processes are ineffective for MAN removal. Therefore, TiO₂ photocatalysis was investigated in this study for decomposing MAN in water. The work compared the degradation of MAN using two different photocatalysts (NF-TiO₂ and Kronos; a commercial carbon-doped TiO₂) under UV-visible light illumination and examined the effect of various parameters on degradation rates. The study also investigated the effect of addition of external oxidants, H₂O₂ and K₂S₂O₈, on MAN degradation rates and the formation of reaction intermediates and degradation pathways during MAN degradation.

5.2 Materials and Methods:

5.2.1 Materials:

NF-TiO₂ catalyst was prepared by following the method reported by Pelaez et al. (2009). Kronos material was provided by Kronos International Inc., Germany. Analytical grade MAN
was purchased from Modern Chemical Corporation, India. H₂O₂ (30%) was purchased from Loba Chemie (P) Ltd. India, and K₂S₂O₈ (99 %) was obtained from E Merck India Ltd.

5.2.2 Characterization of Catalysts:
The crystal phases of Kronos and NF-TiO₂ were determined by XRD analysis using Bruker AXS (D-8 advance model) with Cu Kα (λ=1.5406 Å) radiation. A Tristar 3000 (Micromeritics) porosimeter analyzer was used to determine Brunauer-Emmett-Teller (BET) surface area, pore volume, porosity, Barret-Joyner-Halenda (BJH) pore size and pore size distribution of both catalysts. During the analysis, the samples were purged with nitrogen for 2h at 150 °C using flow prep 060 (Micromeritics). SEM (JEOL JSM 840, Japan) was used to study the morphology of Kronos and NF-TiO₂. The HR-TEM (TECNAI G² 20 Ultra-Twin FEI-Netherlands) with field emission gun at 200 kV was used to obtain the crystal size and structure of the catalysts. For HR-TEM, the samples were prepared in methanol (Merck, India) using ultrasonicator (PCI analytics Pvt. Ltd, India) for 30 min and then fixed on a 200 mesh carbon coated copper grid (TED PELLA Inc.). The HR-TEM images were analyzed using image-J software. The UV-vis absorption spectra were obtained for Kronos and NF-TiO₂ using a UV-Vis spectrophotometer (Shimadzu 2501 PC) mounted with an integrating sphere accessory (ISR1200) using BaSO₄ as a reference standard.

5.2.3 Photocatalytic degradation of MAN under UV-visible light illumination
All experiments were carried out in a quartz slurry reactor as described in section 3.2.2. External UV-visible light source (Philips, 125 W) was used for all experiments which was placed at the bottom of the reactor. The intensity of the UV-visible light was measured by an intensity meter (Sun meter, Sun associates, India) and was found to be 80 W m⁻². Oceanoptics sensor was used to measure light emission spectrum of the light source and the wavelengths with 435 and 546 nm were mainly observed (see the Fig. 5.1).
The effect of catalyst loading on photocatalytic degradation of MAN was studied by varying catalyst loading from 0.1-0.4 g L \(^{-1}\) for Kronos and 0.1-0.8 g L \(^{-1}\) for NF-TiO\(_2\) while the concentration of MAN was fixed at 200 mg L \(^{-1}\) (2.03 mM) at pH 3.2. The effect of initial pH on MAN degradation was investigated at different pH values (2.3, 3.2, 5.8, 6.5, 7.0, and 10.5). The pH was adjusted using perchloric acid for acidic solutions and 0.1 NaOH for basic solutions. The concentration of MAN was kept at 200 mg L \(^{-1}\). The effect of initial MAN concentration on the photocatalytic degradation was studied using different initial concentration values (80, 120, 200, and 360 mg L \(^{-1}\)) at pH 3.2. All samples were withdrawn at regular time interval of 60 minutes using a syringe and analyzed with a high-performance liquid chromatograph (HPLC, Dionex ULTIMATE 3000, US) equipped with C8 column (250 X 4.6 mm X 5 \(\mu\)m). The mobile phase composition was 0.1 % formic acid in water and acetonitrile (50:50 % v/v) and the sample was analyzed with flow rate 1 mL min\(^{-1}\) and injection volume was 0.20 \(\mu\)L. The elution time for MAN was 5.60 min. Before HPLC
analysis, all samples were centrifuged and filtered with Whatman membrane filter (pore size: 0.45 µm) to remove photocatalysts from the samples.

5.2.4 **Effect of H\textsubscript{2}O\textsubscript{2} and K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} oxidants on photocatalytic degradation of MAN**

The effect of H\textsubscript{2}O\textsubscript{2} and K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} added as external oxidants on photocatalytic degradation of MAN has been investigated. To evaluate the effect of external oxidants, experiments were performed at 200 mg L\textsuperscript{-1} MAN concentration with optimal catalyst loading and optimized quantity of H\textsubscript{2}O\textsubscript{2} (3.6 mM) and K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (4.6 mM) as external oxidants in separate experiments.

5.2.5 **Identification of reaction intermediates and unveiling degradation pathway**

The intermediates formed during the photocatalytic degradation of MAN were identified by HPLC and LC-MS/MS (Triple Quad, Agilent 6460, ESI source, Netherlands) analysis. The possible degradation pathways were proposed illustrating the various steps in the degradation of MAN.

5.3 **Result and Discussion**

5.3.1 **Structural characteristics of catalysts:**

XRD spectra of Kronos and NF-TiO\textsubscript{2} exhibited the major peak of anatase crystal phase manifested by its (101) peak at (2\textdegree;=25.5\textdegree;) as shown in Fig.5.2. Using Scherrer formula the average crystalline size was determined to be 8.4 nm for Kronos and 8.7 nm for NF-TiO\textsubscript{2} which is in agreement with those reported by Kronos International Inc. and Pelaez et al. (2009) Table 5.2 summarizes the structural characteristics of Kronos and NF-TiO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Surface area (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>Pore Volume (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>Crystal Size (nm)</th>
<th>% Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kronos</td>
<td>275</td>
<td>0.39</td>
<td>6.24</td>
<td>60.3</td>
</tr>
<tr>
<td>NF-TiO\textsubscript{2}</td>
<td>141.6</td>
<td>0.24</td>
<td>10.9</td>
<td>49.1</td>
</tr>
</tbody>
</table>

Table 5.2. Structural characteristics of Kronos and NF-TiO\textsubscript{2}
Fig. 5.2 XRD pattern for [A] Kronos [B] NF-TiO₂

Fig. 5.3 illustrates N₂ adsorption-desorption isotherms for Kronos showing type IV H₃ hysteresis loop of IUPAC classification indicating mesoporous structure of the catalyst (Liuet al., 2012). Figure 5.3 (inset) shows a bimodal distribution with first peak between 3.7 nm and second curve at 18.5 nm representing small and medium mesoporosity. Pelaez et al. (2009) reported sharp mono modal distribution curve for NF-TiO₂. The morphology of the catalyst may play a major role in photocatalytic activity. Higher photocatalytic activity of mesoporous photocatalyst can be explained in terms of its large surface area and small crystal size. A larger surface area is likely to result in better photocatalytic activity because it provides more active sites. Another factor that influences photocatalytic activity is crystal size. It is commonly accepted that a smaller the crystal size corresponds to more powerful
redox ability as it induces a larger band gap due to the quantum size effect that arises due to destructive reduction in number of free electrons (Kim et al. 2009). Mesoporous structure harvests light scattered radiation via multiple reflections, thus increasing the utilization of incident photons, so the higher the surface area is, the higher are the photon absorption and pollutant adsorption (Pelaez et al., 2012).

Fig. 5.3 Pore size distribution for Kronos (The insert shows N₂ adsorption–desorption pattern for Kronos).

Fig. 5.4 (A) and (B) illustrate SEM images of Kronos and NF-TiO₂, respectively, indicating the small agglomerates of different dimensions. Fig. 5.5 (A) shows the agglomerated spherical particles of Kronos with average particle size of 6-8 nm, which is in agreement with the crystalline size calculated from XRD spectra.
Fig. 5.4 SEM images for Kronos (A) and NF-TiO$_2$ (B).

Fig. 5.5 (B) shows TEM image of NF-TiO$_2$ exhibiting interconnected pore structure. Fig. 5.5 (C) and (D) show the uniform fringes with the interval of 0.35 nm corresponding to (101) lattice spacing of anatase phase for Kronos and NF-TiO$_2$, respectively. The TEM results in agreement with X-ray diffraction patterns showing the presence of anatase phase. Fig. 5.5 (E) and (F) illustrate the selected area electron diffraction (SAED) patterns showing Debye-Scherrer rings of (101), (004), (200), (105) of anatase phase for Kronos and NF-TiO$_2$, respectively.
Fig. 5.5. TEM images for Kronos (A) and NF-TiO$_2$ (B), TEM fringes for Kronos (C) and NF-TiO$_2$ (D), and SAED patterns for Kronos (E) and NF-TiO$_2$ (F).

Fig. 5.6 illustrates UV-vis absorbance spectra of Kronos and NF-TiO$_2$ exhibiting a significant shift of the absorption edge towards the visible region. The absorption maxima of Kronos and NF-TiO$_2$ at 515 nm and 436 nm, corresponds to visible range of spectrum indicating that both the catalysts are active in the visible region. The “effective” band-gap was calculated from the absorption maxima by using the following equation
(O’ Regen & Gratzel, 1991):

\[ \text{Eg (eV)} = \frac{1240}{\lambda_g} \]  (where \( \lambda_g \) = absorption maxima);

Using above equation the effective band gap energy for Kronos and NF-TiO\(_2\) was obtained as 2.33 eV and 2.75 eV, respectively, and it was observed that the calculated value of bandgap energy of Kronos is the same as that provided by Kronos International Inc. (Carl, 2007).

![UV-vis absorbance of Kronos and NF-TiO\(_2\).](image)

**Fig. 5.6** UV-vis absorbance of Kronos and NF-TiO\(_2\).

### 5.3.2 Photocatalytic degradation of MAN under UV-visible light illumination

The photocatalytic degradation experiments using Kronos and NF-TiO\(_2\) were conducted under UV-visible light illumination. After 4 hr of UV-visible light illumination, 98% and 83% of MAN were degraded for Kronos and NF-TiO\(_2\), respectively. Fig. 5.7 illustrates adsorption studies for Kronos and NF-TiO\(_2\) in the dark condition. From the experiment, it
was observed that the adsorption reached a plateau after 60 min. The MAN adsorption for Kronos was slightly higher than that of NF-TiO$_2$, which can be attributed to higher BET surface area of Kronos. The adsorption of MAN under dark condition was performed at pH 3.2 using Kronos and NF-TiO$_2$. After 4 h, MAN remained in at about 89% and 95% of the initial concentration, respectively. Then in a sequential experiment, pH was increased to 10.5, and it was observed that 93% and 99% of MAN, respectively, remained in solution after 60 min. From the adsorption studies, it was observed that the amount of MAN adsorbed decreased at higher pH, resulting in decrease in photocatalytic degradation.

![Fig. 5.7 Adsorption study of MAN with Kronos and NF-TiO$_2$.](image)

The effect of catalyst loading on photocatalytic degradation of MAN using Kronos and NF-TiO$_2$ was investigated and the results are reported in Fig 5.8 (A) and (B). It was observed that
initially the photocatalytic degradation increases with increase in catalyst loading which is caused due to the increased number of active sites on photocatalyst surface which in turn increases the number of reactive oxygen species (ROS) involved in the degradation process (Chen et al., 2007, Sun et al., 2008). Once it reaches the optimal loading (0.2 g L$^{-1}$ Kronos and 0.6 g L$^{-1}$ NF-TiO$_2$), the degradation of MAN decreases with further increase in catalyst loading due to the shielding effect (i.e., the increased opacity of the solution hinders the light transmission through the solution) and consequently the rate of degradation is reduced (Bhatkhande et al., 2003 and 2004, Narayanan et al., 2006). In addition, as seen from Fig. 5.8 (A and B) agglomeration of catalyst particles at higher catalyst loading (above the optimal loading) may reduce the rate of degradation due to the reduction of the catalyst surface available for photon absorption (Haung et al., 2008).
Fig. 5.8  Effect of catalyst loading for Kronos (A) and NF-TiO\(_2\) (B) on the degradation of MAN

Fig. 5.9 (A) and (B) illustrate the effect of initial concentration of MAN on the photocatalytic degradation at different initial concentrations (80, 120, 200, and 360 mg L\(^{-1}\)) at pH 3.2 using Kronos and NF-TiO\(_2\), respectively. It was observed that the initial rate of degradation increases with increase in initial concentration of model compound. For 200 mg L\(^{-1}\) concentration of MAN, the initial rate of degradation per unit surface area was observed to be higher (8.5 x 10\(^{-5}\) mM min\(^{-1}\) m\(^{-2}\)) for NF-TiO\(_2\) compared to Kronos (7.38 x 10\(^{-5}\) mM min\(^{-1}\) m\(^{-2}\)).
Fig. 5.9 Effect of initial concentration for Kronos (A) and NF-TiO$_2$ (B) on the degradation of MAN.
The effect of initial pH of the solution on degradation was studied at different pH (2.3, 3.2, 5.8, 6.5, 7.0, and 10.5) with 0.2 g L\(^{-1}\) Kronos and 200 mg L\(^{-1}\) MAN. Fig. 5.10 shows the effect of pH on the degradation of MAN. It illustrated that in 4 h 69% degradation was obtained at pH 7.0 compared to 98% degradation at pH 3.2. The maximum degradation was found at pH 3.2. It was observed that if the pH is increased towards more basic condition, the amount of MAN adsorbed is decreased thereby decreasing the photocatalytic degradation.

[Graph showing the effect of pH on MAN degradation]

Fig. 5.10  Effect of initial pH on the degradation of MAN with Kronos.

Photocatalytic degradation of MAN (200 mg L\(^{-1}\)) using NF-TiO\(_2\) and Kronos exhibited pseudo first order reaction with rate constants 0.006 min\(^{-1}\) and 0.01 min\(^{-1}\) for NF-TiO\(_2\) and Kronos, respectively, as shown in Fig. 5.11.
5.3.3 Degradation Mechanism

Adsorption of maleic anhydride is depicted in Fig. 5.12 (A) showing olefin van-der wall attraction with TiO\textsubscript{2} surface. The formation of e\textsuperscript{-} and h\textsuperscript{+} was reported by Tseng et al. (1990) and Hermann et al. (1999). Based on the same, as shown in Fig. 5.12 (B) reaction pathway is proposed assuming MAN can be remained in anhydride or acid form in water. C\textsubscript{2} symmetric MAN has two reactive centers, 1-carbonyl and 2–α–β- unsaturated olefin.

Attack at C\textsubscript{1} position by *OH radical results in α- hydroxyl succinic acid which subsequently leads to decarboxylation and water elimination resulting in acrylic acid. Otherwise *OH radical reacts with α- hydroxy succinic acid radical giving tartaric acid which further leads to α- hydroxy acetic acid to oxalic acid which further results in formation of carbon dioxide and water.
Photoelectric reduction of MAN with generated $e^- / h_\nu$ will render anionic radical which further quenched with water leading to succinic acid. $\alpha$-H of succinic acid further reacts with $^\cdot\mathrm{OH}$ radical to give $\alpha$-hydroxy succinic acid and further mineralizing to carbon dioxide and water.

The proposed intermediates were identified by the peaks obtained in HPLC analysis using standards of the pure compounds viz. maleic acid, oxalic acid, succinic acid and also using LC/MS/MS technique. The relative m/z ratios were defined and selected for the identification of intermediates. The presence of maleic acid, succinic acid, oxalic acid and tartaric acid were confirmed by observation of m/z ratios equals to 115, 117, 90 and 150, respectively.
5.3.4 Effect of H$_2$O$_2$ and K$_2$S$_2$O$_8$ on the photocatalytic degradation of MAN

Fig. 5.13 displays the results of degradation of MAN by NF-TiO$_2$ in presence of H$_2$O$_2$ and K$_2$S$_2$O$_8$ added as external oxidants. The applied wavelength in the experiment was in UV-
Visible spectra (360-546 nm) at which H₂O₂ has low absorption resulting in no significant change in degradation of MAN.

Persulfate is one of the strongest oxidants and has a higher potential (E₀=2.01 V) than H₂O₂ (E₀=1.76 V). Persulfate ion generates the sulphate radical anion (SO₄•⁻) which is a strong oxidant and also promotes the charge separation by scavenging the conduction band electron.

\[ \text{S}_2\text{O}_8^{2⁻} + e^- (\text{CB}) \rightarrow \text{SO}_4^{⁻} + \text{SO}_4^{2⁻} \]

The effect of addition of persulfate on photocatalytic degradation has a significant effect on degradation and showed 99.0 % degradation of MAN.

![Fig. 5.13 Effect of external oxidant on photocatalytic degradation of MAN](image)

5.4 Conclusions

In the present study NF- doped TiO₂ was tested for its effectiveness in visible light and its performance is compared with Kronos (C-doped TiO₂). We have determined the photocatalytic activity of NF-TiO₂ for degradation of MAN under UV-visible light. It was observed the catalyst loading, initial pH, and initial concentration of MAN, have a significant influence on photocatalytic degradation rates. It was observed that the initial rate of
degradation increases with increase in MAN initial concentration. MAN has comparatively higher degradation rate with NF-TiO$_2$ ($8.5 \times 10^{-5}$ mM min$^{-1}$ m$^{-2}$) than with Kronos ($7.38 \times 10^{-5}$ mM min$^{-1}$ m$^{-2}$) in 120 minutes. The effect of external oxidants on the photocatalytic degradation of MAN using H$_2$O$_2$ and K$_2$S$_2$O$_8$ was evaluated. It was found that at the applied wavelength (360-546 nm) in the experiment, there was no significant change in degradation by adding H$_2$O$_2$ while significant increase (up to 99 %) was noticed adding K$_2$S$_2$O$_8$.

This study confirms that of Kronos and NF-TiO$_2$ are effective in the photocatalytic degradation of MAN using UV-visible light illumination and forms a basis for the development of full scale photocatalytic process for industries.

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