Photocatalytic degradation of maleic anhydride using visible light-activated NF-codoped TiO₂

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1. Introduction

Many recalcitrant organic compounds are easily found in industrial wastewater. The presence in the environment and high toxicity of various contaminants, such as aromatic compounds (e.g., phenol, benzoic acid, aniline, chlorobenzene, and nitroaromatics), pose a serious threat to environmental and human health [1]. Moreover, lack in water supplies in many areas around the world, rapid industrial growth in many countries with a variety of consequences on water quality, and new toxicity information of many conventional and emerging environmental contaminants necessitate critical advances in the treatment and reuse of industrial wastewater.

In recent years, advanced oxidation processes (AOPs) have been used successfully as effective technologies for the degradation of most organic contaminants [1–4]. Among the different AOPs, one popular process is TiO₂ photocatalysis, which is an effective technology for the treatment of recalcitrant organic pollutants due to the high photocatalytic activity of TiO₂ in the presence of UV light [1–4]. Due to its green characteristics (i.e., chemical inertness, high photoactivity at room temperature, low toxicity and reusability) [5–8], TiO₂ has become the most widely used photocatalyst for the decomposition of organic pollutants. In recent years, the TiO₂ photocatalytic degradation of various organic pollutants, such as phenols, dyes, halogenated hydrocarbons, phthalates, and organochlorine pesticides, has been extensively studied [9–11].

However, conventional TiO₂ materials have a wide band gap (3.2 eV for anatase phase of TiO₂) and can be activated only by UV irradiation, which is only 4–5% of the whole solar spectrum [12–14]. To overcome these constraints, various catalyst synthesis methods have been investigated for the development of visible light-activated TiO₂. Many efforts have been made to alter the photocatalytic properties of TiO₂ under visible light by dye sensitization [15–17], doping of TiO₂ with transition metals such as Cr, Co, V, and Fe [18,19] and non-metals such as N, S, F and C [5,20–30]. In dye sensitization, continuous electron injection causes the sensitizer depletion and limits the long term stability. Metal doping is also limited due to several drawbacks, including thermal instability, increase of carrier recombination centers, risk of metal ion leaching, and expensive metal ion implantation techniques [31–34]. Therefore, non-metal doping of TiO₂ has gained considerable attention as an approach to overcome the drawbacks of dye sensitization and metal doping. Moreover, codoping of TiO₂...
exhibited significant improvement in photocatalytic activity as compared to single doping due to synergistic effects of two different non-metal elements [35]; examples include carbon and sulfur codoped TiO₂ [23], sulfur and nitrogen codoped TiO₂ [36], and NF-TiO₂ [7,37,38].

In this study, 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. Therefore, MAN and its intermediates can easily come into the environment through various streams during the manufacturing processes. MAN is listed by the United States Environmental Protection Agency (USEPA) as a “priority pollutant” due to its substantial effects and ubiquity in the environment. Under section 311(b) (2) (A) of the Federal Water Pollution Act, it is also designated as a hazardous substance. Therefore, TiO₂ photocatalysis was investigated in this study for decomposing MAN in water. The work compared the degradation of MAN using two different TiO₂ materials (NF-TiO₂ and Kronos; a commercial carbon-doped TiO₂) under UV–visible light illumination and examined the effect of catalyst loading, initial pH, and initial MAN concentration 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.

2. Experimental

2.1. Materials

NF-TiO₂ catalyst was prepared by following the method reported by Pelaez et al. [7]. 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.

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 2 h 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 [41]. 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.

2.3. Photocatalytic degradation of MAN under UV–visible light illumination

A quartz slurry reactor (4 cm I.D. × 16 cm height, cylinder) fitted with centrally mounted stirrer was used for all the experiments.
Fig. 3. TEM images for Kronos (A) and NF-TiO₂ (B), TEM fringes for Kronos (C) and NF-TiO₂ (D), and SAED patterns for Kronos (E) and NF-TiO₂ (F).

Fig. 4. UV–vis absorbance of Kronos and NF-TiO₂.

Fig. 5. Adsorption study of MAN with Kronos and NF-TiO₂.
It was ensured that the photocatalyst (Kronos or NF-TiO$_2$) remained in suspension because of continuous stirring of the solution and air sparging from the bottom during the experiments. Five hundred mL of MAN solution was added with known weight of photocatalysts in the reactor. The reaction temperature was maintained at 32–36 °C by circulating tap water through the coil to avoid any evaporation. External UV–visible light source (Philips, 125 W) was used for all experiments. 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$^{-2}$.

The Ocean Optics sensor was used to measure light emission spectrum of the light source and the wavelengths with 435 and 546 nm were mainly observed (see Fig. S2). The UV–visible light source was placed at the bottom of the reactor.

To study the effect of catalyst loading on photocatalytic degradation of MAN, the catalyst loading was varied from 0.1–0.4 g L$^{-1}$ for Kronos to 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. To investigate the effect of initial pH on MAN degradation, different pH values (2.3, 3.2, 5.8, 6.5, 7.0, and 10.5) were chosen. 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 min using a syringe and analyzed with a high-performance liquid chromatograph (HPLC, Dionex ULTIMATE 3000, US) equipped with C8 column (250 × 4.6 mm × 5 μm). 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 μL. 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.

2.4. Effect of H$_2$O$_2$ and K$_2$S$_2$O$_8$ oxidants on photocatalytic degradation of MAN

In order to enhance the efficiency of the process, the effect of external oxidants such as H$_2$O$_2$ and K$_2$S$_2$O$_8$ on photocatalytic degradation of MAN has been investigated.

To evaluate the effect of external oxidants, experiments were performed at 200 mg L$^{-1}$ MAN concentration with optimal catalyst loading and optimized quantity of H$_2$O$_2$ (3.6 mM) and K$_2$S$_2$O$_8$ (4.6 mM) as external oxidants in separate experiments.

2.5. Identification of reaction intermediates and unveiling degradation pathway

The intermediates formed during the photocatalytic degradation of MAN were identified by HPLC (High performance liquid chromatography) and LC–MS/MS (Liquid chromatography–Tandem mass Spectrometry) (Triple Quad, Agilent 6460, ESI source, Netherlands) analysis. The possible degradation pathways were proposed illustrating the various steps in the degradation of MAN.
3. Result and discussion

3.1. Structural characteristics of catalysts

XRD spectra of Kronos and NF-TiO₂ exhibited the major peak of anatase crystal phase manifested by its (101) peak at (2θ = 25.5°) as shown in Fig. S3. Using Scherrer formula the average crystalline size was determined to be 8.4 nm for Kronos and 8.7 nm for NF-TiO₂ which is in agreement with those reported by Kronos International Inc. and Pelaez et al. [7]. Table 1 summarizes the structural characteristics of Kronos and NF-TiO₂.

Fig. 1 illustrates N₂ adsorption–desorption isotherms for Kronos showing type IV H3 hysteresis loop of IUPAC classification indicating mesoporous structure of the catalyst [29]. Fig. 1 (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. [7] reported sharp monomodal distribution curve for NF-TiO₂. The morphology of the photocatalyst 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. Because of more active sites, a larger surface area results in better photocatalytic activity. Another factor that influences photocatalytic activity is crystal size. It is commonly accepted that a smaller crystal size corresponds to more powerful redox ability as it induces a larger band gap due to the quantum size effect [42]. 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 [43]. Fig. 2(A) and (B) illustrates SEM images of Kronos and NF-TiO₂, respectively, indicating the small agglomerates of different dimensions. Fig. 3(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. 3(B) shows TEM image of NF-TiO₂ exhibiting interconnected pore structure. Fig. 3(C) and (D) shows the uniform fringes with the interval of 0.35 nm corresponding to (101) lattice spacing of anatase phase for Kronos and NF-TiO₂, respectively. The TEM results are in agreement with X-ray diffraction patterns showing the presence of anatase phase. Fig. 3(E) and (F) illustrates the selected area electron diffraction (SAED) patterns showing Debye–Scherrer rings of (101), (004), (200) and (105) of anatase phase for Kronos and NF-TiO₂, respectively. Fig. 4 illustrates UV–vis absorbance spectra of Kronos and NF-TiO₂ exhibiting a significant shift of the absorption edge towards the visible region. The absorption maxima of Kronos and NF-TiO₂ 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 and Gratzel [44]):

\[
E_g (\text{eV}) = 1240/\lambda_g \quad (\text{where } \lambda_g = \text{absorption maxima})
\]

Using the above equation the effective band gap energy for Kronos and NF-TiO₂ 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. [45].

3.2. Photocatalytic degradation of MAN under UV–visible light illumination

The photocatalytic degradation experiments using Kronos and NF-TiO₂ were conducted under UV–visible light illumination. After 4 h of UV–visible light illumination, 98% and 83% of MAN were degraded for Kronos and NF-TiO₂, respectively. Fig. 5 illustrates adsorption studies for Kronos and NF-TiO₂ 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-TiO₂, 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-TiO₂. After 4 h, 89% and 95% of initial concentration of MAN remained in the solution for Kronos and NF-TiO₂, respectively. Then in a sequential experiment, pH increased to 10.5, and it was observed that 93% and 99% of MAN for Kronos and NF-TiO₂, respectively, remained in the solution after 60 min. From the adsorption studies, it was observed that the amount of MAN adsorbed decreased at higher pH, as at higher pH the repulsion forces restricts the interaction between the photocatalyst and substrate, resulting in decrease in photocatalytic degradation.

The effect of catalyst loading on photocatalytic degradation of MAN using Kronos and NF-TiO₂ was investigated and the results are reported in Fig. 6(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 [46,47]. Once it reaches the optimal loading (0.2 g L⁻¹ Kronos and 0.6 g L⁻¹ NF-TiO₂), 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 [10,48,49]. In addition, 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 [50].

Fig. 7(A) and (B) illustrates 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 ± 0.102 × 10\(^{-5}\) mM min\(^{-1}\) m\(^{2}\)) for NF-TiO\(_2\) compared to Kronos (7.38 ± 0.088 × 10\(^{-5}\) mM min\(^{-1}\) m\(^{2}\)).

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. 8 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. 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. 9.

3.3. Degradation mechanism

Adsorption of maleic anhydride is depicted in Fig. 10(A) showing olefin van-der wall attraction with TiO\(_2\) surface. The formation of e\(^-\) and h\(^+\) was reported by Tseng and Haung [51] and Herrmann

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**Fig. 10.** Degradation mechanism.
Based on the same, as shown in Fig. 10(B) reaction pathway is proposed assuming MAN can be remained in anhydride or acid form in water. C2 symmetric MAN has two reactive centers, 1-carbonyl and 2-α-β-unsaturated olefin.

Attack at C1 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 tarteric 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⁺ will render anionic radical which further quenched with water leading to succinic acid. α-H of succinic acid further reacts with OH radical to give α-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 tarteric acid were confirmed by observation of m/z ratios equals to 115, 117, 90 and 150, respectively.

3.4 Effect of H2O2 and K2S2O8 on the photocatalytic degradation of MAN

Fig. 11 displays the results of degradation of MAN by NF-TiO2 in presence of H2O2 and K2S2O8 added as external oxidants. The applied wavelength in the experiment was in the UV-visible spectra (360–546 nm) region and was not enough to activate H2O2. At this wavelength H2O2 has low absorption resulting in less degradation of MAN. In case of photochemical degradation better results would have been obtained using UV source with shorter wavelength, i.e. 180–200 nm [3].

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 sulfate radical anion (SO4⁻) which is a strong oxidant and also promotes the charge separation by scavenging the conduction band electron.

\[
\text{SO}_4^{2-} + e^- (CB) \rightarrow \text{SO}_4^- + \text{SO}_4^{2-}
\]

The effect of addition of persulfate on photocatalytic degradation has a significant effect on degradation and showed 99.6% degradation of MAN.

The study exhibited pseudo first order reaction with rate constants 0.0078 min⁻¹, 0.0094 min⁻¹ and 0.033 min⁻¹ for NF-TiO2, NF-TiO2 + H2O2 and NF-TiO2 + K2S2O8, respectively.

4. Conclusions

In the present study, 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-TiO2 (8.5 ± 0.012 × 10⁻⁵ mM min⁻¹ m⁻²) than with Kronos (7.38 ± 0.088 × 10⁻⁵ mM min⁻¹ m⁻²) in 120 min. The effect of external oxidants on the photocatalytic degradation of MAN using H2O2 and K2S2O8 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 H2O2 (3.6 mM) while significant increase (up to 99%) was noticed by adding K2S2O8 (4.6 mM).

This study confirms that Kronos and NF-TiO2 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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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2015.07.021.

References


