Photocatalytic Degradation of Toluene and BTEX Compounds in Gas Reactor Modified by TiO_2/Ti Net Nanotubes

Ikha Rasti Juliasari

Center for Industrial Pollution Prevention Technology: Balai Besar Teknologi Pencegahan Pencemaran Industri

Januar Arif Fatkhurrahman

Center for Industrial Pollution Prevention Technology: Balai Besar Teknologi Pencegahan Pencemaran Industri

Yose Andriani

Center for Industrial Pollution Prevention Technology: Balai Besar Teknologi Pencegahan Pencemaran Industri

Cholid Syahroni

Center for Industrial Pollution Prevention Technology: Balai Besar Teknologi Pencegahan Pencemaran Industri

Ningsih Ika Pratiwi

Center for Industrial Pollution Prevention Technology: Balai Besar Teknologi Pencegahan Pencemaran Industri

Alex L. Suherman (✉ alexsuherman@telkomuniversity.ac.id)

Telkom University <https://orcid.org/0000-0003-4582-5236>

Research Article

Keywords: Photocatalytic, TiO_2/Ti Net Nanotube, Volatile Organic Compound, Toluene, BTEX

Posted Date: September 2nd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-699777/v1>

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Abstract

Exposure to volatile organic compounds (VOCs), such as toluene and BTEX gas, may cause severe impacts on the environment and long-term health problems for the workers. Industry must place this issue as a priority in supporting occupational health and efforts to minimize the environmental effects. However, many industries still have not paid more attention to degrading their industrial waste containing these compounds. Several studies on VOCs degradation in liquid and aerial media were developed in line with the rapid progress of nanomaterial technology. In this work, we have successfully synthesized TiO_2/Ti Net nanotubes thin film resulted from anodization of Ti plate at 25 V vs Ag pseudo-reference electrode for eight hours and physically characterized by SEM/EDX and XRD. The activity test of photocatalysis was performed to determine the TiO_2/Ti Net Nanotube's performance to degrade toluene steam and BTEX standard gas. Under the optimum experimental condition, the results showed that approximately 70% of toluene and 60% of BTEX standard gas were degraded in 120 min under the optimum experimental condition. The gas reactor generated approximately 400 ppm CO_2 as a byproduct.

1. Introduction

The workers in crumb rubber, painting, solvent, and automotive industries generally spend more than 80% of their time inside the workspace dealing with hazardous chemicals. They are possibly at high risk of exposure to hazardous volatile organic compounds (VOCs) within the workspace, either in the open air or in a closed workspace. They are experienced exposure risk of H_2S , NH_3 , and other VOCs groups from its drying process (Andriani et al., 2019).

The air quality inside the workspace currently attracting serious attention. Some of the effects of VOCs exposure to workers are headache, get tired quickly, sore throat up to mental fatigue symptoms (Obee and Brown, 1995). Therefore, it is essential to diminish or minimize these pollutants so that the ambient air quality is still safe for workers. The industry may use air pollution control integrated into its chimney. However, air pollution control integration still becomes an issue for some industries, considering their compliance to minimum prerequisites for chimney emission testing.

Several technologies were developed to eliminate benzene, toluene, ethylbenzene, and xylene (BTEX) contamination, through biological treatment, chemical absorption, and advanced oxidation process (AOPs) (Chakrabarti and Dutta, 2004). AOPs can degrade a BTEX by producing a reactive $\cdot\text{OH}$ radical, which attacked BTEX and converted it into a less dangerous compound, such as CO_2 , H_2O , and acidic minerals [6,7]. AOPs had several advantages, such as cost-effective, safe, and able to simultaneously treating a significant number of organic compounds (Li et al., 2016) (Bervian et al., 2017). Photocatalysis technology can degrade NO , NO_2 , SO_2 , and VOCs up to 80% (Ayal, 2019)(Regonini and Clemens, 2015). One of the applications of AOPs technology was the use of semiconductor materials under UV-ray exposure or visible light, which would mineralize organic compound (Chakrabarti and Dutta, 2004). The zinc oxide (ZnO), titanium dioxide (TiO_2), and tin dioxide (SnO_2) semiconductors are having a relatively

wide bandgap for photocatalysis (Rana et al., 2017)(Mo et al., 2009). However, the progress of BTEX degradation in solution and the effectiveness of photocatalysis performance still required many studies.

Many research uses metallic oxide plate in a photocatalytic reactor to degrade both wastewater or air pollutants. The synthesis of TiO_2/Ti in the form of a thin layer net has shown that the particular anodization time and voltage applied significantly influence the resulting nanotubes morphological properties and its catalytic performance (Sugawati et al., 2019). In this paper, we use a Ti net plate to synthesize TiO_2/Ti Net Nanotube. This material was grown by electrolysis on the Ti net surface as a supporting material. The anodizing process occurred at 25 V vs Ag pseudo-reference electrode for eight hours consecutively and generated a bandgap of 3.2 eV (Djarwanti and Syahroni, 2014).

The application of photocatalysis for degradation of the VOCs needs a significant width of the contact plane so that the air or steam pollutants had a sufficient contact time with TiO_2/Ti Net Nanotube. The photocatalytic performance of the TiO_2/Ti Net Nanotube was evaluated by assessing the degradation of toluene steam and BTEX gas standard in the homemade gas reactor. The intermediate compound or bypass product formation, such as CO_2 , was detected and analyzed using an electrochemical sensor (Sari et al., 2019). The results of this study are beneficial in providing new options for material choices for photocatalytic degradation that can be applied in industry, specifically industries dealing with VOCs such as toluene and BTEX.

2. Materials And Methods

2.1. Synthesis of TiO_2/Ti Net Nanotube

The preparation of anodizing comprised cleaning the Cu and Ti net plates and preparation of the electrolyte solution. Cu and Ti net plates (0.3 mm thickness of 100 mesh size, 10 x 14 cm) are thoroughly washed by detergent and then rinsed with nanopure water. Subsequently, both plates were thoroughly cleaned with 600 cc and 1000 cc sandpapers and rinsed again with nanopure water. Cu and Ti net were soaked in a mixture of 48% v/v of hydrogen fluoride (HF) solution, 65% v/v of nitric acid (both pro-analysis grades, sourced from Merck, Indonesia) and nanopure water, with the ratio of 1:3:6, respectively. The soaking process was done for 1 minute, then rinse again with nanopure water and dried up under ambient temperature.

The electrolyte solution used was 9.72% v/v NH_4F in one litre of glycerol. It can be made by dissolve 9.72 gr NH_4F with nanopure water and gradually adding glycerol, then making it homogenous by magnetic stirrer SIBATA Magnestir MG-5E for approximately three hours at medium speed. The anodizing process was conducted by connecting Cu and Ti net plates to the power supply of GW Instek SPS-3610, as shown in Fig. S1. Cu plate at the negative pole and Ti plate at the positive pole. Following this, put the two slabs into the electrolyte solution, then anodize them at the 25 V vs Ag pseudo reference electrode. The anodization times were distinguished into four and eight hours, separately. When the designated time

was complete, the Ti net was rinsed with nanopure water and dried up under ambient temperature. Finally, it was calcined by furnace Lindberg/Blue M BF51828C at 550° C for three hours.

2.2. The characterization of TiO₂/Ti Net Nanotube

The Ti net anodized for four and eight hours were then characterized by SEM-EDS or Scanning Electron Microscopy (FEI, Quanta 650)-Energy Dispersive Spectroscopy (Oxford Instruments) and X-Ray Diffraction (XRD) from PANalytical. Type-X'Pert PRO Source of Cu with K- α of 1.54 Å. The photocatalytic activity performance of this synthesized material was tested using *Digi-ivy DY2100* potentiostat; the flow diagram of the activity test can be seen in Fig. S2.

2.3. BTEX Degradation using TiO₂/Ti Net Nanotube Photocatalytic

BTEX degradation resulted from a chamber that contained toluene steam and BTEX standard gas 20 ppm of Mesa Gas brand. TiO₂/Ti Net Nanotube was taken from the best morphology results of SEM/EDS and XRD readings. The photocatalytic degradation analytical time was set up to 120 minutes. The sample steam was circulated at the flow rate of 0.2 litres per minute. The experimental setup using toluene steam and BTEX standard gas can be seen in Fig. S3 and Fig. S4, respectively.

3. Results And Discussion

3.1. Characterization of TiO₂/Ti Net Nanotube

The formation of TiO₂ nanotube optimized by the increased anodizing time (Li et al., 2016). The result was TiO₂/Ti Net Nanotubes (thin film) after eight hours of anodization. The SEM-EDS shown in Fig. 1 shows a significant difference in depicting between the four and eight hours anodization time. The TiO₂/Ti Net thin film still did not form tubes in four hours anodizing, and it was only seen in the form of the nanotube after eight hours of anodization. Eight hours of anodization time produce a nano-size varied between 60–80 nm. The EDS result showed the composition of Ti and O as the main composing component. This result presumed that formation of TiO₂ higher in eight hours than four hours, indicated by lower Ti composition in eight hours, which higher in O composition.

SEM results were then made more apparent again by cross-section view to see the vertical tube cross-section built for TiO₂/Ti Net Nanotubes thin film from eight hours anodizing. It was found parallel evidence with the building of its peak and relative intensity (Bervian et al., 2017). A thicker layer of nanotubular is seen within a more extended period, as shown in Fig. S5.

The X-ray diffraction pattern from TiO₂/Ti Net Nanotubes thin film prepared on an anodization basis is presented in Figs. 2 and 3. It is seen in the diffraction pattern of TiO₂/Ti Net Nanotubes that additional peaks emerged at the diffraction pattern of blank Ti plate, i.e., at the angles of 2 θ , which are 25.7, 48.41

53.32, and 55.35, respectively. This result referred to (101), (200), (105), and (211) planes in anatase TiO₂ structure (PCPDF No. 841286). Compared with blank Ti plate as shown in Fig. 2, TiO₂ peak pattern of four hours anodizing time sign no additional peak (as shown in Fig. 3.a), while eight hours anodizing time shows different peak patterns of 25.7, 48.41, 53.32, and 55.35 (as shown in Fig. 3.b). It is important to note that the anodization time significantly increases the formation of nanotubes (Ayal, 2019), (Regonini and Clemens, 2015). The calcination process (thermal heating) affected the type of crystal built at TiO₂/Ti Net Nanotubes (Yu and Wang, 2010). Literatures indicates that anatase type constituted a crystallization phase with excellent photocatalytic activity and a tabular structure (Yu and Wang, 2010).

TiO₂ photocatalytic activity depended highly on the preparation and post-making conditions since they had a decisive influence on the film and physical and chemical characteristics (Yu and Wang, 2010). The presence of UV-ray triggered a TiO₂ net photocatalytic activity, as seen in Fig. S6. The eight hours anodization showed a more considerable photocatalytic activity compared to that of four hours anodization. As well as photocatalytic activity, the characterization result of SEM-EDS and XRD, as seen in Fig. 1, showed that the eight hours of anodizing time gave the best depiction of performance than four hours anodizing time. It was expected to degrade VOC pollutants optimally.

3.2. Degradation of Toluene and BTEX

UV-Light Photocatalytic (UVLP) activity of TiO₂ nanotube in Ti net was then studied for toluene steam removal in a circulated gas reactor (homemade). Sample extracted using charcoal tube then analyzed by GC/MS. Due to the limited supply of gas calibration standards, toluene was used as a sample. Toluene steam is generated by vaporizing 25 ml of liquid toluene in the circulating gas chamber reactor. Figure 4 shows the degradation profile of toluene steam as individual monoaromatic hydrocarbon (initial concentration was approximately 256 ppm) in the presence and absence of TiO₂ nanotubes in the Ti net plates under UVLP condition.

As seen in Fig. 4, more than 70% of toluene degraded within 120 minutes of observation periods. A 50% degradation of toluene was observed in about 77 minutes. Degradation of toluene steam can be calculated using another observation using the 20 ppm gas calibration standard of BTEX (Fig. 5).

Similar profile with toluene as single species of BTEX, concentration reduction of BTEX standard gas under UV light has a potential reduction of BTEX until 60% in 120 minutes. Even 40% degradation of BTEX occurs in the initial 30 minutes of the experiment. Compared with the toluene steam degradation experiment, degradation of BTEX occurred more rapidly than toluene steam as a single species; this phenomenon occurs as toluene supposedly greater degradation performance over benzene, ethylbenzene, and xylene as BTEX component with 90% than 65% in benzene (Al-Sabahi et al., 2017). This degradation of BTEX will produce byproducts, such as carbon dioxide (Rana et al., 2017).

The complete mineralization of the toluene may produce CO₂ and H₂O (Mo et al., 2009), follow the Eq. 1.

Toluene degradation was investigated using 256 ppm of toluene in the gas chamber reactor. Investigation of toluene degradation analyzes by measure CO₂ as an intermediate byproduct measured in parallel with observation periods of toluene degradation using commercial CO₂ gas sensor of Winsen MH-Z19. Monitoring of the CO₂ formation can be seen in Fig. 6.

Production of CO₂ resulted from successive photo-oxidation of toluene as BTEX species, and the intermediate byproduct was produced soon after the UVLP process occurs. The process was found optimum at 70 minutes when more than 500 ppm of CO₂ produced, then gradually decline within an average of 300–400 ppm CO₂ during the whole process. As shown in Fig. 6, the result has a good agreement with the degradation process of toluene, as seen in Fig. 4, where the degradation process of BTEX standard gas may produce CO₂.

4. Conclusion

TiO₂/Ti Net Nanotube was successfully grown by the electrolysis method on the Ti net surface as supporting material. The preferable material for photocatalytic degradation of toluene steam and BTEX gas standard was TiO₂/Ti Net Nanotube obtained from anodizing 25 V vs Ag pseudo reference electrode for eight hours. The photocatalytic degradation results showed that toluene steam could be degraded by 50% for 77 minutes and 70% for 120 minutes. Meanwhile, the optimum degradation of BTEX standard gas can be achieved by 40% in 30 minutes and 60% in 120 minutes. The formation of CO₂ gas as a byproduct during the degradation was detected at approximately 400 ppm. The result indicates the possible application of TiO₂/Ti Net Nanotubes for photocatalytic degradation of VOCs; remarkably useful as a reliable toxic air elimination technology for the particular industry dealing with toluene and BTEX.

5. Declarations

5.1. Ethics Approval and Consent to Participate

Not applicable

5.2. Consent for Publication

Not applicable

5.3. Availability of Data and Materials

Not applicable

5.4. Competing Interests

Not applicable

5.5. Funding

The authors declare no competing financial interest.

5.6. Authors' Contributions

The authors confirm contribution to the paper as follows: study conception and design: IRS and JAF; data collection: JAF, YA and CS; analysis and interpretation of results: JAF, NIP, and ALS; draft manuscript preparation: IRS, JAF, and ALS. All authors reviewed the results and approved the final version of the manuscript.

5.7. Acknowledgements

The authors thank to Ministry of Industry of the Republic of Indonesia for the technical support.

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Figures

(A)

(B)

(C)

(D)

Figure 1

SEM-EDS of TiO₂/Ti Net thin film at four (A, B) and eight (C, D) hours of anodization.

Figure 2

Diffraction pattern of X-ray on blank Ti plate.

(a)

(b)

Figure 3

TiO₂/Ti Net Nanotubes diffraction pattern at four hours (a) and eight hours (b) of anodization.

Figure 4

Reduction in the concentration of toluene under simulated UV light in the presence and absence of TiO₂ nanotubes in Ti net plates. The initial concentration of the toluene was 256 ppm.

Figure 5

Reduction in BTEX gas standard under simulated UV light in the presence and absence of UV light on TiO₂ Net Nanotubes. The initial concentration of the BTEX standard gas was 20 ppm.

Figure 6

Formation of CO₂ over time during toluene photocatalytic degradation. Measurement using commercial CO₂ gas sensor from an initial concentration of 256 ppm of toluene under UVLP condition.

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