PHOTOCATALYTIC REMOVAL OF TOLUENE VAPOR USING TIO_2-BASED MATERIALS IN A LAB-SCALE REACTOR

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Abstract: *In this study, we applied photocatalytic process for degradation of toluene vapor using two types of catalysts: TiO_2 nanoparticle (P25) and titania nanotubes (TNTs). TNTs nanomaterial was prepared using P25 as precursor via alkali hydrothermal method. The morphology, particle and tube sizes were determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The specific surface area, pore size and pore volume were analyzed by Brunauer-Emmett-Teller (BET) method. A lab-scale photocatalytic reactor was developed to investigate the removal of toluene vapor with different photocatalysts and operational conditions. Results showed that P25 and TNTs showed similar removal efficiency at low toluene concentration of ca. 80 ppm (e.g., 97% for both TNTs and P25). However, TNTs had better photocatalytic activity than P25 at high toluene concentration of ca. 375 ppm (e.g., 91% and 84% for TNTs and P25, respectively). This study also investigated the effects inlet concentration and retention time on the toluene removal efficiency.*

Keywords: Toluene, Environmental photocatalysis, TiO_2, TNTs.

1. INTRODUCTION

Toluene, having the formula $C_6H_5CH_3$, is an aromatic hydrocarbon used as a solvent in the paint, resin, gum, zinc, and zinc industries. This is also the raw material for organic compound synthesis. Toluene adversely affects human health as both acute and chronic poisoning. Therefore, WHO (2000) defines Guideline Values for Average ambient air concentration of toluene 5 - 150 $\mu g/m^3$. In Vietnam, the maximum allowable concentration of toluene in ambient air is regulated at 190 $\mu g/m^3$ (annual average concentration, QCVN 06:2009/BTNMT). In fact, there are many gaseous VOCs (including toluene) control technologies, including adsorption by activated carbon, condensation, thermal oxidation, catalytic oxidation, and biological filtration. Currently, photocatalysis is a preferable choice due to several advantages such as capability of decomposing organic air pollutants under room temperature, even for the pollutants that cannot be removed by traditional methods [1-3].

Nowadays, there are many studies focused on using TiO_2 materials due to its suitable physico-chemical characteristics, durable material, and environmentally friendly photocatalyst. Some popular applications of TiO_2 nanoparticles are environmental photocatalysis, air cleaning and deodorizing, and bactericidal effect. There are some studies to remove toluene vapor using TiO_2 P25 material. It was reported that the removal efficiency reached about 68% using P25 at toluene concentration of 26 ppm but declined to about 20% at toluene concentration of 170 ppm [4]. In another study, result from the effect of input toluene concentration showed that removal efficiency decreased from 100% to 23% when toluene concentration increased from 5 to 37 ppm [5]. Since these results showed very low removal efficiency at high toluene concentration, a study on looking for new photocatalytic materials with high removal efficiency at high concentration of toluene is attractive.

The objective of this study is to investigate the removal efficiency of toluene vapor using TiO_2 and TNTs. The effects of UV light, inlet concentration, and retention time on the removal efficiency was investigated.

2. MATERIALS AND METHODS

In the study (from Feb. to Jun. 2016), TiO_2 P25 nanoparticles and TiO_2 nanotubes (TNTs) were applied for photocatalytic removal of toluene vapors. TiO_2 P25 is a high purity fine white powder made by Merck (Germany) with an average particle diameter of 21 nm and specific surface area of 50 m^2/g. As seen in Figure 1, TNTs was synthesized by hydrothermal method using nanoparticles TiO_2 P25 [6]. The SEM and TEM images of P25 and TNTs are displayed in Figure 2. Both the materials were then directly used without any pretreatment.

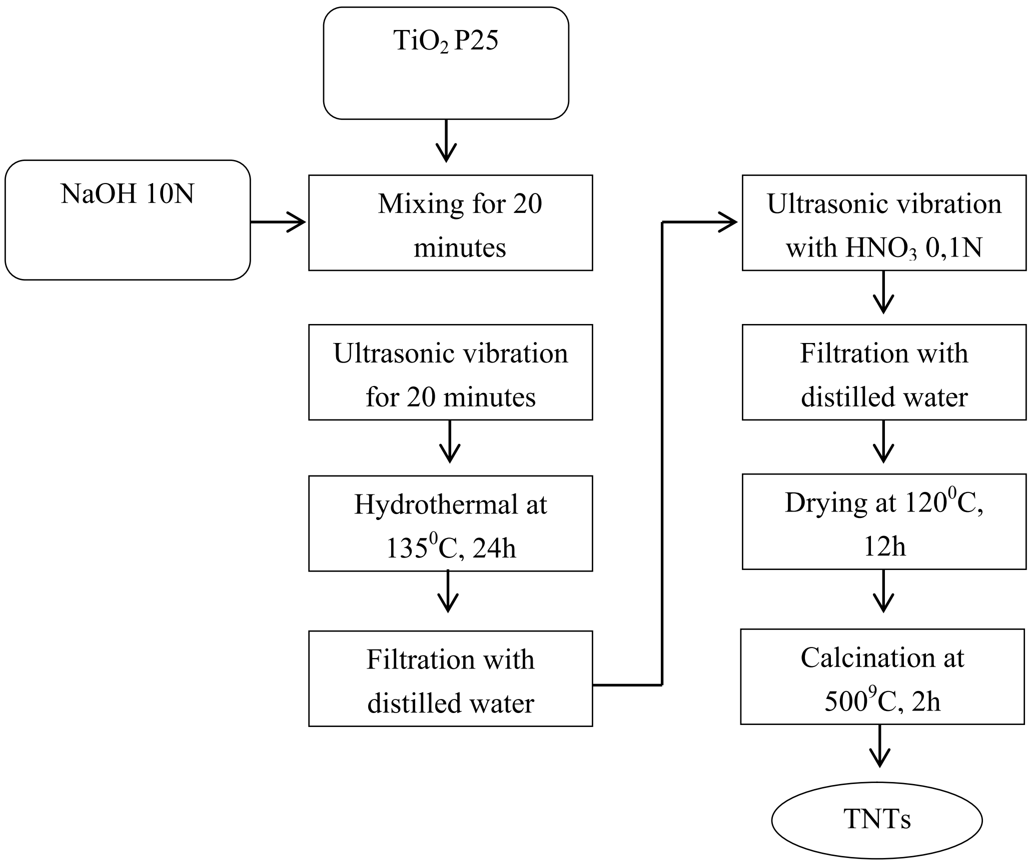

Figure 1. *Synthesis of TNTs by hydrothermal method.*

In order to study the photocatalytic removal of toluene vapors, a laboratory scale model was employed. Details of the research model are shown in Figure 3. The air flow from the compressed air tank was divided into two lines. The primary air went through the gas flow adjustment valve (3). The other line passed through the toluene flow adjustment valve (5) to the impinger (7) containing the toluene solution (8). The gas flow containing evaporated toluene in the impinger was then mixed with the primary air and passed through the photocatalytic reactor.

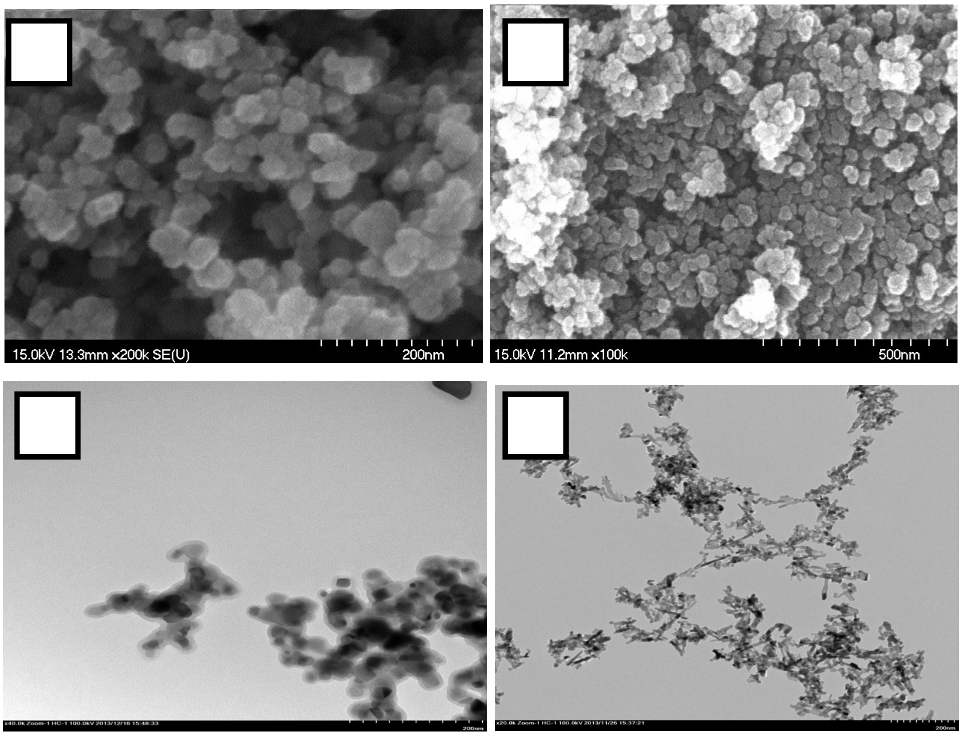

Figure 2. *SEM images of (a) P25 and (b) TNTs and TEM images of (c) P25 and (d) TNTs.*

In the reactor, three glass supports coated with photocatalyst were placed under three UV-A lights (intensity of 1.25 mW/cm^2, highest intensity at wavelength of 365 nm). The distance from the lamp to the surface of the catalyst material was 35 cm. Toluene concentrations in inlet and outlet were sampled and measured by using a KITAGAWA Gas Detector Tube System (Komyo Rikagaku Kogyo K.K., Japan)

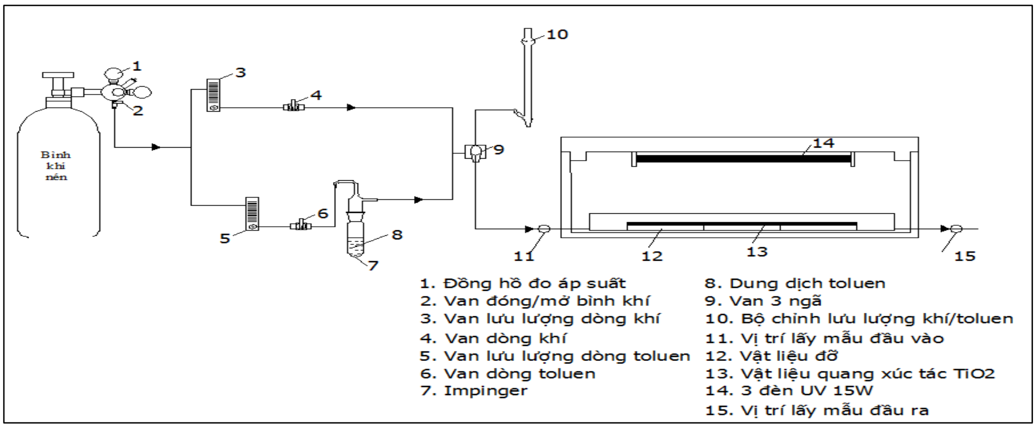

Figure 3. *Diagram of experimental model.*

3. RESULTS AND DISCUSSION

3.1. Effect of photocatalyst material

Results from photocatalytic experiments using P25 and TNTs are shown in Figure 4. It can be observed that the removal efficiency of P25 material was 97.5% at a low inlet concentration of about 80 ppm. Removal efficiency by P25 and TNTs was comparable at about 97.5%. Hence, it was unable to compare the efficiency between the two materials. In addition, the results showed that the time for both materials to reach a steady-state condition was 60 min. Therefore, additional experiments were carried out under the same operating conditions but with higher toluene concentrations of about 375 ppm.

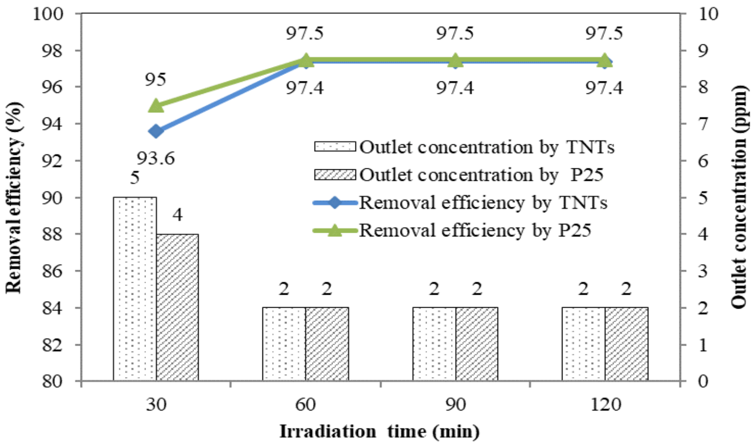

Figure 4. *Toluene removal efficiency over time using P25 and TNTs (Experimental condition: gas flow rate 0.7 l/min, retention time 20 s, toluene concentration 75 ppm).*

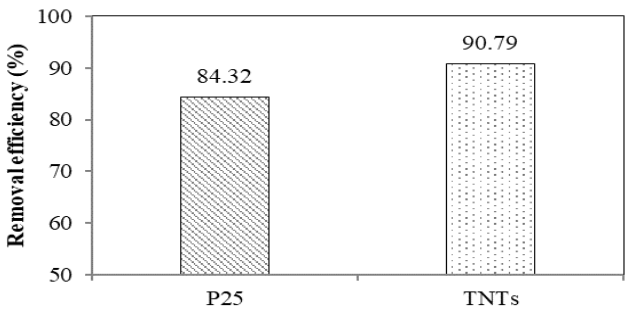

Figure 5. *Toluene removal efficiency after 60 minutes using P25 and TNTs (Experimental condition: gas flow rate 0.7 l/min, retention time 20 s, toluene concentration 375 ppm).*

The removal efficiency after 60 min is presented in Figure 5, where declined to 84 and 91% when using P25 and TNTs, respectively. As compared to literature, the removal efficiency of toluene at 26 ppm using P25 was about 68%, but that at concentrations higher than 170 ppm was only about 20% [4]. It can be concluded that the P25 material is only highly effective at low concentrations of toluene. On the other hand, TNTs showed lower efficiency decline when inlet concentration increased in this study (i.e. from 97 to 91%). This may be due to its more anatase crystalline structure, larger surface area, and higher density as compared to P25. TNTs had specific surface area of 106.3 m^2/g, which was two times higher than P25 (50 m^2/g) and 100% anatase crystalline phase structure while P25 had a mixed anatase and rutile phase with ratio of 89/11. The crystal size of TNTs (12.4 nm) was smaller than that of P25 (anatase is 23 nm and rutile is 21.1 nm). Therefore, with the same amount of catalytic material, the density of TNTs is higher than that of P25.

3.2. Effect of toluene concentration

Inlet concentration is one of the important technical parameters affecting the removal efficiency of photocatalysis. Figure 6 demonstrates the effect of initial toluene concentration on the removal efficiency using TNTs. When inlet toluene concentration increased from 75 ppm to 375 ppm, the removal efficiency slightly decreased from 97% to 89%. Some other studies on photocatalysis of TiO_2 materials [4,5] also showed similar decline trends such as from 68% to 20% when concentration increased from 26 to 170 ppm [4] and 100% to 23% when concentration increased from 5 to 37 ppm [5]. These similar results may be explained by the fact that the intermediates generated during the reaction would increase as the inlet concentration increases. Consequently, adsorption competition occurs on the catalyst surface, which decreases the contact of toluene vapor and the surface of the photocatalytic material. On the other hand, the amount of products produced increases with the increase of inlet concentration. Therefore, the products cannot be completely removed from the catalyst surface, which then causes a decline in the reaction rate. In addition, the greater the amount of toluene vapor in the incoming air stream could also competitively absorb UV radiation with the photocatalytic material, which also causes a reduction in the removal efficiency.

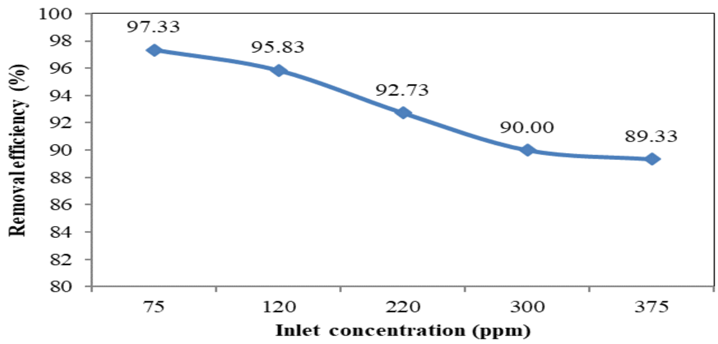

***Figure 6**. Effect of inlet concentration on toluene removal efficiency (Experimental condition: gas flow rate 0.7 l/min, retention time 20 s).*

3.3. Effect of retention time

In addition to the inlet concentration, retention time (i.e. air velocity) is also an important technical parameter that determines the efficiency of the photocatalytic process. Figure 7 illustrates the effect of retention time on the removal efficiency. When retention time increased from 14 s to 20 s, the efficiency increased from 88 %

to 93%. Theoretically, when the retention time increases, the time for the toluene to remain in the reactor and the contact between toluene and photocatalyst will increase, which is beneficial for the photocatalytic reaction. However, as the retention time increased from 20 s to 26 s, the efficiency began to decrease from 93% to 85%. This may be because the increase of retention time lead to the accumulation of by-products on the surface of photocatalyst. This is also consistent with those reported by Liang *et al.* [7] where the removal efficiencies using TiO_2 were 20%, 60%, 50%, and 30% with flowrate of 1, 3, 5, and 7 liter per minute, respectively. In other work, Zhang and Liao [5] also found that the removal efficiency of toluene were 40%, 55%, 67%, 92%, 60%, and 52% at gas velocity of 1, 2, 3, 4, 5, and 6 cm/s, respectively. These revealed that the retention time affects the removal efficiency in both intrinsic photocatalytic reaction rate and mass transfer of reactants, products, and by-products on the surface of the photocatalytic material.

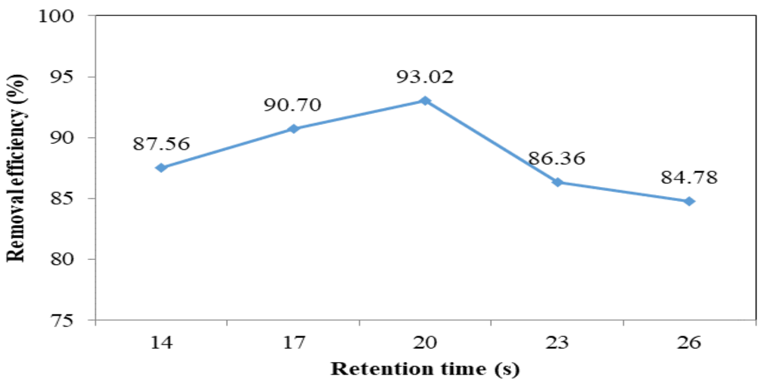

***Figure** 7. Effect of retention time on toluene removal efficiency (Experimental condition: TNTs, toluene concentration 225 ppm).*

4. CONCLUSIONS

This study has successfully applied TNTs for toluene vapors removal by photocatalysis. The type of photocatalyst as well as the optimum conditions for the reaction including inlet concentration and retention time were assessed. Both P25 nanoparticles and TNTs nanotubes were effectively applied for toluene removal at low concentrations, which could be applied in ambient condition. However, at high toluene concentration, TNTs showed superior activity due to its higher surface area and anatase crystallinity as compared to P25, which could be applied in industrial VOCs control. Future research should also focus on application and modification of some other TiO_2 materials to obtain high removal efficiencies with low costs and investigation for other VOCs such as benzene, xylene, and ethylbenzene.

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TÓM TẮT

NGHIÊN CỨU XỬ LÝ HƠI TOLUEN BẰNG CÔNG NGHỆ QUANG XÚC TÁC TRÊN VẬT LIỆU TIO_2 TRÊN QUY MÔ PHÒNG THÍ NGHIỆM

Bài nghiên cứu này cho thấy lần đầu tiên ứng dụng quá trình quang xúc tác để xử lý hơi toluen của hai vật liệu xúc tác là TiO_2 dạng hạt (P25) và TiO_2 dạng ống (TNTs). TNTs được điều chế từ P25 ban đầu bằng phương pháp thủy nhiệt ở nhiệt độ 500^0C. Hình dạng, kích thước hạt và ống được xác định bằng kính hiển vi điện tử quét (SEM) và kính hiển vi điện tử truyền qua (TEM). Diện tích bề mặt riêng, kích thước lỗ và thể tích lỗ rỗng được phân tích bằng phương pháp Brunauer-Emmett-Teller (BET). Đề tài đã xây dựng một mô hình thử nghiệm để khảo sát hiệu quả xử lý hơi toluen của P25 và TNTs ở các nồng độ khác nhau. Kết quả cho thấy P25 và TNTs cho hiệu quả xử lý tương đương nhau ở nồng độ thấp (>95%) và TNTs xử lý hơi toluen tốt hơn P25 ở nồng độ cao (>90%). Đồng thời, đề tài cũng khảo sát sự thay đổi của ba thông số vận hành mô hình: đèn UV; nồng độ đầu vào; thời gian lưu.

Từ khóa: Toluene, TNTs, Xúc tác quang, TiO_2.

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