

PHOTOCATALYTIC DEGRADATION OF TOLUENE IN WASTEWATER BY SUSPENDED AND DIPPING COATED TITANIUM DIOXIDE INCORPORATING WITH SURFACTANT

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Abstract

The toluene degradation in synthetic wastewater was performed by liquid-solid photocatalytic process using titanium dioxide (anatase phase) as the catalyst under UV irradiation and flowing oxygen gas. Two different systems of titania catalyst; suspension and dipping coated titanium dioxide catalysts containing 0.1-1.0 mM of sodium dodecylsulfate (SDS) surfactant, were carried out. The mixture was irradiated with UV lamp at $27 \pm 1^\circ\text{C}$ and toluene concentration was analyzed by HPLC. The toluene degradation on coefficients (C/C_0) of 250 mL, 100 mg.L⁻¹ toluene solution catalyzed by suspension titania and that containing dipping coated titania catalyst were compared. The toluene degradation catalyzed by 0.5 mg.L⁻¹ suspension titania catalyst containing 0.6 mM surfactant was complete within 60 min, whereas the optimum of the toluene degradation coefficient for the dipping coated titania system containing 1.0 mM surfactant was 0.20 at 60 min. However, the maximum toluene degradation based on specific activity of the dipping coated titania with 1.0 mM SDS was 1,000 mg.g⁻¹ titania, higher than that of the suspended titania which was 200 mg.g⁻¹. Furthermore, the toluene degradation by the dipping coated titania is cost saving and convenient to be reused.

Keywords: Photocatalytic, TiO₂, toluene, wastewater, surfactant

Introduction

Water pollutions have been occurred from releasing of non-treatment toxic effluents, especially the organic solvents such as benzene derivatives, aliphatic compounds, phenol compounds, chlorohydrocarbon etc to the environment. Toluene is a benzene derivative, widely used as industrial chemical to synthesize many chemical compounds, i.e. benzoic acid, benzaldehyde, benzyl alcohol etc. Toluene is still used as a solvent for a variety of industries as well as paint, chemical reactants, rubber, printing ink, adhesives, fuel mixer, plastic etc

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(Marci *et al.*, 2003). In addition, toluene has been used in various fields of academic research such as organic solvent in chemical, rubber and polymer laboratory, therefore it can contaminate wastewater from many industries and laboratories. The concentration of toluene in the wastewater collected from chemical laboratory at Prince of Songkla University (PSU), Pattani, Thailand was about 100 mg.L^{-1} . It has been reported that the threshold Limit Value-Time Weighted Average (TLV-TWA) of ACGIH limit is 50 mg.L^{-1} , NIOSH limit is 100 mg.L^{-1} and OSHA limit is 200 mg.L^{-1} (MSDS, 2006). Toluene is the most toxic of BTEX group, it is chronic and toxic chemical for human and environment. The oral rat LD_{50} of toluene is 636 mg.kg^{-1} (MSDS, 2006). Many methods have been reported to reduce releasing waste toluene to the environment (Marci *et al.*, 2003; Duarte, *et al.*, 2004; Hamdi *et al.*, 2004; Hamed *et al.*, 2004; Pernyeszi and Dékány, 2004; Ying *et al.*, 2005; Zhang, 2005; García *et al.*, 2006; Negishi *et al.*, 2006; Saïen and Nejati, 2007).

Many strategies have been studied to treat organic waste that contaminates water. Some methods give low efficiency compared to the reaction rate, such as biodegradation by the microorganism (Hamed *et al.*, 2004; Ying *et al.*, 2005). The cost of many methods such as electron beam irradiation method (Duarte, *et al.*, 2004) or adsorption method (Hamdi *et al.*, 2004) is high and difficult to control.

Photocatalytic oxidation (PCO) is a method that offers various advantages compared to other methods. PCO can be done at room temperature and atmospheric pressure and under UV irradiation. Titanium dioxide (TiO_2) or titania has been used as photocatalyst with high efficiency for organic waste degradation and it can be regenerated. Three phases of titania are anatase, rutile and brookite. Anatase is the most effective phase for degrading organic compounds in photocatalytic process (Zhang, 2005). The photocatalytic oxidation method has been used in two systems, liquid-solid and gas-solid systems. For the liquid-solid photocatalytic system, suspended titania system (Pernyeszi and Dekany, 2004; García

et al., 2006; Saïen and Nejati, 2007) and dipping coated titania on the supports (Marci *et al.*, 2003; Zhang, 2005; Negishi *et al.*, 2006) have been studied for toluene degradation with high efficiency.

Recently, using surfactant to enhance the photocatalytic reaction rate for low soluble compound degradation has been reported. The mixture of 164 ppm toluene and asphatene could be degraded in 1 h by using suspended P25 TiO_2 containing 1% H_2O_2 and sodium dodecylsulfate (SDS) (Pernyeszi and Dekany, 2004). In addition, dibenzo-thiophene (DBT) was highly degraded by TiO_2/UV light with adding Triton X-100 in aqueous solution (Vargas and Núñez, 2008).

The aim of this work was to investigate of toluene degradation in synthetic wastewater by liquid-solid photocatalytic process using suspended and dipping coated titania. In order to enhance the toluene degradation rate, sodium dodecylsulfate (SDS) surfactant was added to the mixture. The photocatalytic processes were monitored as toluene degradation coefficient (C/C_0). The concentration of toluene in synthetic wastewater was prepared nearly to toluene concentration in real wastewater collected from chemical laboratory at Prince of Songkla University (PSU), Pattani, Thailand.

Materials and Methods

Reagents and Materials

The chemicals have been used in this work: Titanium dioxide (AR grade, Merck, Germany), sodium dodecylsulfate (AR grade, Riedel-de Haen, USA), toluene (99.99%, AR grade, Fisher Scientific, UK), sulfuric acid (AR grade, Merck, Germany), oxygen gas (99.9%, Pattani Oxygen production, Thailand), deionized water, and acetonitrile (HPLC grade, LabScan, Poland).

The equipments such as mercury UV lamp (20 W, Philips, Holland), 500 mL reaction kettle (Quickfit, England), $0.45 \mu\text{m}$ nylon membrane filter (47 mm diameter, Sartorius, Germany), and stainless steel S304 screen (Thai Prasit Textile, Thailand) were

used in this work.

Analysis of Toluene in Wastewater

Wastewater was collected from laboratory wastewater reservoir of Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani, Thailand. Wastewater sample was filtered through 0.45 μm nylon membrane filter and analyzed for toluene quantity by High Performance Liquid Chromatography (HPLC, HP1100, Agilent, USA) equipped with PinnacleII-C₈ column, 150 x 4.6 mm (Restek, USA), 12.5 x 4.6 mm Zorbax SB-C18 guard column, diode array detector (Agilent, USA) at 254 nm, 60% acetonitrile mobile phase with 1 mL.min⁻¹ flowing and 20 μL of injection volume.

Synthetic Wastewater and Catalyst Preparation

Synthetic wastewater with similar toluene concentration in laboratory wastewater was prepared. Aqueous toluene solution (100 mg.L⁻¹, 250 mL) was added with 0.1, 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0 mM SDS solution. The controlled sample was prepared without SDS, titania and UV irradiation.

Titanium dioxide powder was suspended in synthetic wastewater to contain 0.5 mg.L⁻¹ titania. The solution was stirred by magnetic stirrer at 60 rpm to guarantee a satisfactory suspension of the photocatalyst and the

uniformity of the reacting mixture for suspension titania system.

For dipping coated titania, 4 stainless steel S304 screens (3.8 x 2.8 cm) were pretreated with 30% sulfuric acid for 2 h in order to increase the roughness of surface (Giornelli *et al.*, 2006). After that, they were sonicated by ultrasonic bath (950D, Crest, Malaysia) for 30 min in deionized water to eliminate acidic trace before coated with 0.3:10 (w/v) of titania in isopropanol. Coated screens were dried at 80°C and calcined at 600°C for 2 h. The coated screens were attached to a propeller connecting with 60 rpm mechanical stirrer. The propeller of photoreactor consists of four vertical rectangle blades (3.5 x 2.5 cm inner; 3.8 x 2.8 cm outer; 0.3 cm thickness). Titania quantities on the four coated screens determined by weighing before and after coating were about 0.02 g in 250 mL of synthetic wastewater.

Photocatalytic Process

The 250 mL of synthetic wastewater was stirred in darkness for 30 min before starting the reaction. Pyrex photoreactor was set up as shown in Figure 1. Toluene in synthetic wastewater was irradiated by Hg UV lamp which produced UV light at wavelength 290-400 nm, the distance between UV lamp and reactor was 10 cm. The radiation energy imprinting gave an average value of 420 $\mu\text{W.cm}^2$ measured by a UV radiation meter (Digicon D20, Taiwan). Percentage transmittance of

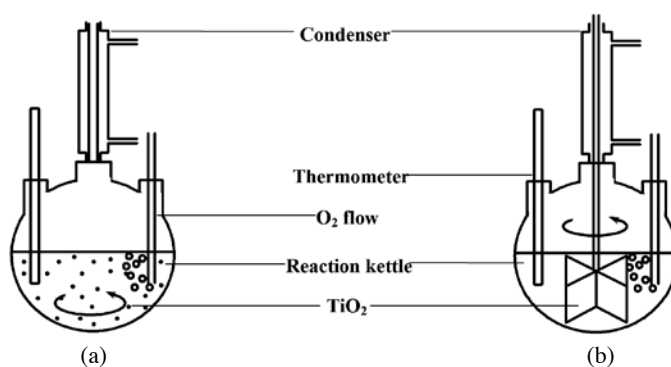


Figure 1. Toluene degradation reactor using (a) suspended and (b) dipping coated titania

pyrex glass at 388 nm is about 92% (Corning Incorporated, 2009). Pure oxygen gas was added into the solution with flow rate 30 mL.min⁻¹ at room temperature (27± 1°C). The synthetic wastewater was collected from the reactor every 15 min, then filtered through millipore membrane and toluene concentration was determined by HPLC. The HPLC analysis condition was the same as the analysis of toluene in wastewater. Percentage of titania remained on the screens after treatment was determined by weighing before and after reaction.

Characterization of Phase and Morphology of Titania

The calcined titania at 600°C and commercial titania powder for suspended titania and dipping coated titania were analyzed by X-ray diffractometer (D5005, BRUKER) using Cu K_α radiation and scanning electron microscope (JSM6400, JEOL) to characterize phase and morphology.

Results and Discussion

Toluene Content in Wastewater

Toluene concentration in laboratory wastewater analyzed by HPLC was found to be 104.4 mg.L⁻¹, higher than Threshold Limit Value-Time Weighted Average (TLV-TWA) of ACGIH limit (50 mg.L⁻¹) and NIOSH limit (100 mg.L⁻¹), but lower than OSHA limit (200 mg.L⁻¹) (MSDS, 2006). Toluene is chronic and toxic chemical for human and environment since the oral rat LD50 of toluene is 636 mg.kg⁻¹ (MSDS, 2006). The toluene contaminated wastewater must be treated before release to the environment.

Degradation of Toluene in Wastewater by Photocatalytic Process

The monitoring of toluene degradation was determined by toluene degradation coefficient (C/C₀), calculated from the ratio between concentration of toluene at anytime during photodegradation and initial toluene concentration;

$$C/C_0 = \frac{\text{Concentration of toluene at anytime}}{\text{Initial concentration of toluene}}$$

In the absence of the UV radiation, the photocatalytic degradation of toluene in the first 30 min by both suspended and dipping coated titania was low. The toluene degradation coefficient (C/C₀) were about 0.86-0.94 (Figures 2-3) resulting from the adsorption of toluene on the titania surface. It was supported that the degradation of toluene required UV radiation. In Figures 2 and 3, during the first 30 min of photocatalytic reaction, C/C₀ in titania suspension and dipping coat types added with 0.4 mM SDS decreased rapidly from 0.93 to 0.61 and 0.77, respectively. After that, the degradation rates slowed down. The toluene degradation coefficients (C/C₀) at 60 min for suspension titania mixed with 0.1, 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0 mM of SDS were 0.27, 0.22, 0.18, 0.03, 0.0, 0.0 and 0.0, respectively (Figure 2). The system containing dipping coated titania gave 0.52, 0.46, 0.41, 0.35, 0.29, 0.29 and 0.28 C/C₀ at the same SDS concentration, respectively (Figure 3). Complete toluene degradation was only observed in suspended titania photocatalytic type incorporating with 0.6-1.0 mM SDS which could degrade toluene completely at 60 min. On the other hand, dipping coated titania photocatalytic system showed nearly complete toluene degradation (C/C₀ ≈ 0.02) at 150 min reaction time for solution containing 0.6-1.0 mM SDS (Figure 3).

SDS addition can improve toluene solubility in aqueous phase, thus increasing SDS concentration in solution may result in increasing rate of toluene degradation as shown in Figures 2 and 3. The toluene solutions without SDS addition slightly degraded and reached steady state at 135 min. The increase of degradation rate could be explained by a higher solubility of toluene in aqueous media containing surfactant which led to more adsorption on the titania surface. Thus, toluene molecules in this system can be adsorbed on the titania surface higher than the system without surfactant. The results agreed with

literatures that the photocatalytic reaction was more favorable in the presence of surfactant. (Marci *et al.*, 2003; Pernyeszi and D  kny, 2004).

At the initial reaction time (0-30 min), toluene concentration decreased rapidly because many toluene molecules in the solution were adsorbed on active sites of titania surface. In addition, toluene molecule was converted to intermediates and then these intermediates were adsorbed on the titania surface, resulting in a decrease of titania active sites (Negishi *et al.*, 2006). However, an increase of SDS concentration which was less than 8 mM could decrease the adsorption of intermediates on the titania surface (Pernyeszi and D  kny, 2004). This was supported by an increase of toluene degradation rates when increasing the amount of SDS. Moreover, a release of the intermediates during photocatalytic reaction of toluene such as benzaldehyde, benzoic acid and benzyl alcohols from titania surface into media phase could be increased for the system containing SDS.

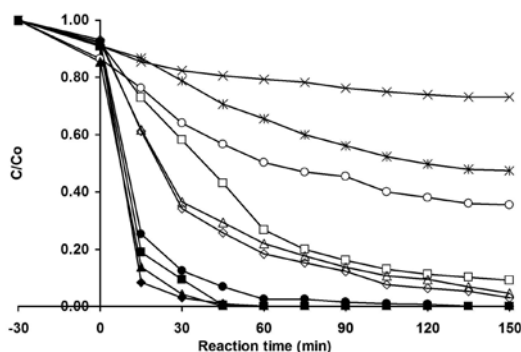


Figure 2. Toluene degradation coefficient of toluene degradation by suspended titania photocatalytic process from 30 min before starting reaction to 150 min of reaction containing SDS; control (x), 0.0 mM (*), 0.1 mM (○), 0.2 mM (□), 0.3 mM (△), 0.4 mM (◇), 0.5 mM (●), 0.6 mM (■), 0.8 mM (▲), and 1.0 mM (◆)

The toluene degradation efficiencies catalyzed by dispersed and dipping coated titania at 60 min in Figure 2 and 3 were compared. The degradation of toluene catalyzed by suspension titania was better than that by dipping coated titania. However, the amount of titania in both systems were different. The titania amount in suspension system was about 0.125 g in 250 mL solution which was higher than that in dipping coated system, 0.020 g in the same volume of solution. Thus, the specific activities of titania were calculated to compare these systems as shown in figure 4. The specific activity at 60 min reaction time of suspended titania to degrade toluene were 68-200 mg.g⁻¹ (mg toluene per gram titania) incorporating with 0.0-1.0 mM of SDS concentration. Whereas the specific activity of dipping coated titania were 575-1,000 mg.g⁻¹ at the same SDS concentration. The toluene degradation activity of dipping coated titania at 1,000 mg.g⁻¹ titania containing 1.0 mM SDS could degrade 100 mg.L⁻¹ toluene solution in 1 h and toluene remained about 20 mg.L⁻¹.

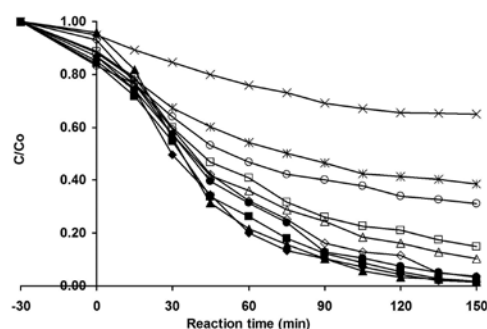


Figure 3. Toluene degradation coefficient of toluene degradation by dipping coated titania photocatalytic process from 30 min before starting reaction to 150 min of reaction containing SDS; control (x), 0.0 mM (*), 0.1 mM (○), 0.2 mM (□), 0.3 mM (△), 0.4 mM (◇), 0.5 mM (●), 0.6 mM (■), 0.8 mM (▲), and 1.0 mM (◆)

The degradation of toluene by dipping coated titania was better than that of suspension titania because of light scattering and screening effects of titania particles. These effects reduced the specific activity of the catalysts (Wei *et al.*, 2009; Nam *et al.*, 2009). The excess titania particles in the solution cause turbidity of aqueous media which could be observed during the experiments. Beside light scattering and screening effects, particle aggregation of titania might also reduce the catalytic activity as well (Jiang *et al.*, 2008). Therefore, the specific activity of titania for toluene degradation catalyzed by suspended titania was lower than that by dipping coated titania.

At appropriate SDS concentration of 0.6 mM, the suspended titania could completely degrade toluene within 60 min whereas the percentage of toluene degradation using dipping coated titania was about 80% and the toluene was degraded for 95% at 120 min. The toluene concentration remained at 20 mg.L⁻¹ (80% toluene degradation) was lower than the threshold limit of ACGIH, NIOSH and OSHA limit. The degradation time using dipping coated titania is about twice compared to suspended titania system.

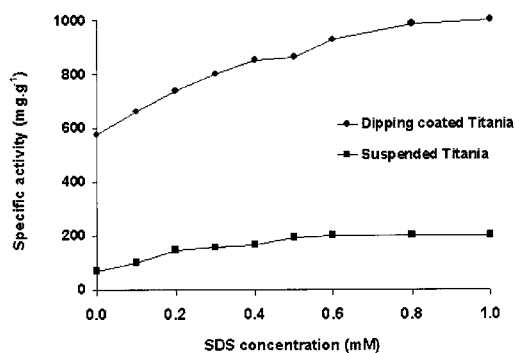
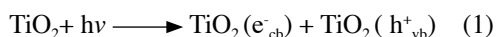


Figure 4. Specific activities of titania for toluene photodegradation at 60 min reaction time catalyzed by suspended and dipping coated titania containing various SDS concentration

However, the specific activities of dipping coated titania were higher than those of suspended titania system. Thus, it could be acceptable to develop and use dipping coated titania catalyst in the future. Moreover, dipping coated titania is convenient to be reused because the titania particles remained on screens after reaction. The percentage of the titania amount remaining on screens after 150 minutes reaction was 87%.

Photocatalytic Degradation of Toluene on Titania Surface

The first step of photocatalytic process is absorption of photon on the titania surface, then the electrons and holes of the catalyst are activated by the appropriate energy from photon and the redox reaction occurs. The wavelength 388 nm gave energy around 3.2 eV which is corresponding to band gap energy of titania. The surface reaction has been proposed (Saien and Nejati, 2007).



cb = conduction band, vb = valence band

Valence band electron was excited and elevated from valence band to conduction band by photon ($h\nu$) from UV radiation, produced electron (e_{cb}^-) and hole (h_{vb}^+). Water, oxygen and adsorbed molecules on titania surface were oxidized and gave hydroxyl radical

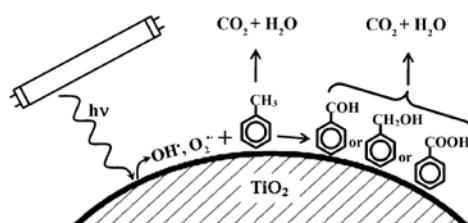


Figure 5. Proposed photocatalytic reaction of toluene degradation on titania surface during UV radiation

and reacted further to form products (Maira *et al.*, 2001).

The liquid-solid photocatalytic system with bubbling of oxygen gas produced hydroxyl radical (HO^\bullet) and superoxide radical (O_2^\bullet). Adsorbed toluene on the titania surface was oxidized by $\text{HO}^\bullet/\text{O}_2^\bullet$, then decomposed into intermediates, e.g. benzoic acid, benzyl alcohol, and benzaldehyde. The final products of the reaction will be carbon dioxide and water. Toluene could be degraded directly to carbon dioxide and water (Marci *et al.*, 2003).

Some of the intermediates could be adsorbed on the active sites of titania and degraded via oxidation reaction to carbon dioxide and water as shown in Figure 5.

Phase and Morphology of Titania

The phases of both titania types used in this work were characterized by X-ray diffraction (XRD). Figure 6 shows XRD patterns of calcined titania at 600°C and commercial titania powder. Both XRD patterns of titania powder contained anatase (1 0 1), (0 0 4), and (2 0 0) with 2θ at 25.3° , 38° , and 48° , respectively (Zhang, 2005). The phase of titania catalysts did not transform from anatase to rutile phase after calcinations at 600°C . The anatase phase gives high catalytic efficiency compared to rutile phase (Zang, 2005). The SEM images of commercial titania powder and titania particles after dispersion in

isopropanol and calcination at 600°C (Figure 7a and 7b) show the spherical particles about $0.2\ \mu\text{m}$ diameter, porous and homogeneous of titania particles.

Conclusions

The specific activities of dipping coated titania for photocatalytic toluene degradation in synthetic wastewater mixed with SDS surfactant were better than that of suspended titania. The specific activity of dipping coated titania with $1.0\ \text{mM}$ SDS concentration was $1,000\ \text{mg}\cdot\text{g}^{-1}$ titania at 1 h of reaction and toluene remained about $20\ \text{mg}\cdot\text{L}^{-1}$. For the suspended titania system, the degradation of $100\ \text{mg}\cdot\text{L}^{-1}$ toluene solution, $250\ \text{mL}$ incorporating with $0.6\ \text{mM}$ SDS was complete within 60 min of reaction. It is interesting to develop the dipping coated titania system since the amount of dipping coated titania in the system was less than 6 times of suspended titania and it is convenient to be reused.

Acknowledgement

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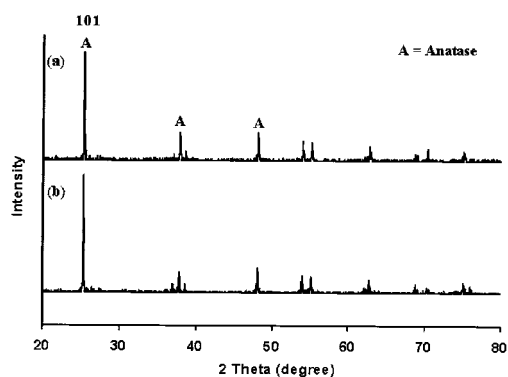


Figure 6. X-ray diffraction patterns of (a) calcined titania (at 600°C) and (b) commercial titania powder for photocatalytic process

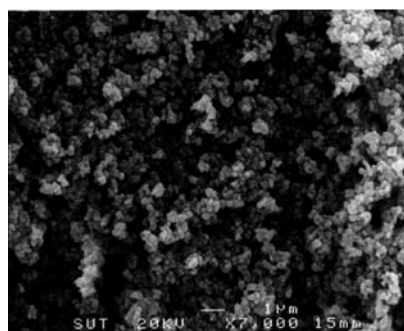


Figure 7. SEM images of (a) commercial titania and (b) calcined titania powder (at 600°C) ($\times 7,000$)

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