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Photocatalytic performance of cylindrical reactor inserted with UV light-emitting-diodes for purification of low-level toxic volatile organic compounds

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ABSTRACT

The present study investigated the photocatalytic performance of a cylindrical reactor inserted with UV light-emitting-diodes for the decomposition of low-level (0.1 ppm) gas-phase organic compounds (benzene, toluene, ethyl benzene and xylene (BTEX)). The morphological and optical properties of photocatalysts (Degussa P-25 TiO_2) baked at different temperatures were determined using a range of spectral instruments. The photocatalyst baked at 350 °C exhibited the highest conversion efficiencies for both benzene and toluene (81 and ∼100%, respectively). The conventional lamp showed a higher conversion efficiency for benzene compared to the 380-nm UV-LED and a higher conversion efficiency for benzene and toluene than the 365-nm UV-LED. However, the ratios of conversion efficiency to electric power consumption were 2.5–3.0 times higher for the latter light source than the former source. Moreover, as the residence time increased from 0.2 to 1.2 min, the average conversion efficiencies for BTEX of the 3-h photocatalytic process increased from nearly zero to 81%, 7 to nearly 100%, 20 to nearly 100%, and 29–30 to nearly 100%, respectively. The cylindrical photocatalytic reactor inserted with UV-LEDs could be energy-efficiently applied for the decomposition of low-level toxic compounds after optimization of the operating conditions.

1. Introduction

Photocatalysis using semiconductors is one of most attractive advanced oxidation processes and has been shown to be an efficient tool for degrading various environmental pollutants [1,2]. This technology provides a number of advantages over traditional technologies such as activated carbon adsorption and thermal oxidation. While the conventional adsorption method only transfers gaseous pollutants to another phase [3,4], photocatalysis has the potential to degrade a broad range of volatile organic compounds (VOCs) to carbon dioxide and water [5,6]. Of all semiconductors, titanium dioxide (TiO_2) has been the most popular photocatalyst utilized for the oxidation of environmental organics due to its high photo-activity, excellent stability, and low cost [5]. Photocatalysis using TiO_2 requires a UV-light source, which emits light with quanta energy exceeding the band-gap energy of TiO_2, and the choice of the light source depends on economics as well as availability. Many studies [7–9] using TiO_2 powders for environmental applications have utilized conventional lamps, such as black lights and mercury lamps with major emissions near 254 or 365 nm. However, it should be noted that the use of light-emitting diodes (LEDs) as semiconductor light sources has several advantages over the use of conventional light sources. Specifically, LEDs are more efficient at converting electricity into light because they have high quantum yields that are typically close to unity, which leads to lower electricity consumption [10]. In addition, they have a longer lifetime. As such, LEDs have been suggested as promising alternatives to conventional lamps for photocatalytic processes of environmental pollutants. A few researchers [11–13] have suggested the feasibility of employing UV-LEDs used in photocatalytic applications for the efficient removal of certain environmental pollutants. These studies applied TiO_2/UV-LED units for the photocatalytic conversion of a water pollutant (o-cresol) [11,13] or a high-level (500 ppm) gaseous formaldehyde [12]. However, the gaseous formaldehyde level investigated by Shie et al. [12] was substantially higher than typical indoor air quality (IAQ) levels [14,15]. Even though typical IAQ levels of formaldehyde and other VOCs were higher than typical ambient air levels, they were still less than 1 ppm [15,16].

TiO_2/UV-LED applications for low-level gaseous pollutants are rarely found in literature, even though extrapolation of photocatalysis performance data collected at concentrations much higher than those in the intended application are likely not valid [17]. Moreover, photocatalytic reactors with high rates of gas-feeding

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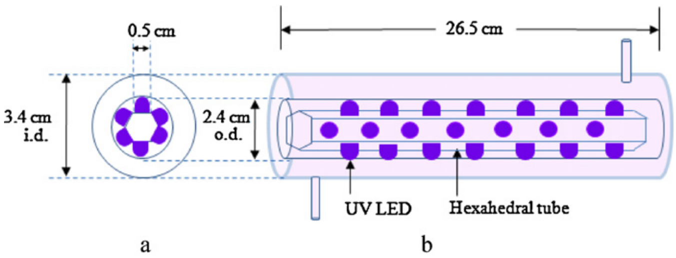

Fig. 1. Cylindrical reactor inserted with LED lamps: a and b represent the top- and side-view of the reactor, respectively.

are preferred for indoor air applications, since more air can be purified [18]. As such, a continuous-flow cylindrical photocatalytic reactor is preferred to the recirculating batch reactor used by Shie et al. [12] for those applications. The present study was conducted to evaluate the photocatalytic performance of a cylindrical reactor inserted with UV light-emitting-diodes for purification of toxic volatile organic compounds at low concentrations ($\leq$1 ppm) that are associated with IAQ issues. For practical purposes, this study used commercially available lamps as UV-light sources. This type of reactor geometry requires that a photocatalyst coating procedure be used on the inner wall of the reactor. In turn, this coating procedure involves a baking process. Therefore, this study also investigated the effects of baking temperatures of the photocatalyst during coating on the photocatalytic activity. The target compounds, benzene, toluene, ethyl benzene and xylene (BTEX) comprise an aromatic VOC group that is detected at high concentration levels in both indoor and outdoor environments [19] and is toxic or potentially toxic to humans [20].

2. Methodology

2.1. Experimental protocol

The continuous-flow cylindrical reactor consisted of two Pyrex tubes with different diameters but the same length. A conventional lamp or a hexahedral tube installed with LED lamps was inserted inside the smaller-diameter Pyrex tube (Fig. 1). The inner wall of the outer Pyrex tube was coated with a thin film made from commercially available Degussa P-25 TiO_2 powders (Japan Aerosil Inc.). The coated reactor was then dried for an hour at room temperature and baked at 350, 450, 550, or 650 °C for 30 min. The reactor was designed to direct the flow of the incoming air toward the UV light to increase the air turbulence inside the reactor, thereby enhancing distribution of the target compounds onto the TiO_2 surface. A standard gas (0.1 ppm), which was prepared by injecting standard compounds into a mixing chamber via a syringe pump (Model 210, KD Scientific Inc.), flowed through the annular region between the two Pyrex tubes. The humidity level was adjusted by passing zero-grade air through a charcoal filter, followed by a humidification device in a water bath (HAAKE W26, Cole-Parmer Inc.). The relative humidity (RH) was fixed at 50–55% and measured immediately in front of the photocatalytic reactor inlet using a humidity meter (Thermo Recorder TR-72S, T & D Co.). The residence time (RT) was adjusted to 0.2, 0.3, 0.4, 0.6, or 1.2 min by varying the flow rates. The UV radiation was supplied by two types of 3.1-W UV-LEDs (MS-L510UV365 & MS-L510UV380, Moksan Electric Co.), with maximum spectral intensities at 365 and 380 nm, respectively, or an 8-W fluorescent black light lamp (F8T5/BLB, Sankyo Denki Co.) with maximum spectral intensity at 352 nm. The light intensity was 3.4, 1.7, and 3.7 mW cm^{-2} for the conventional lamps, 365-nm UV-LEDs, and 380-nm UV-LEDs, respectively. The UV light intensity was measured at a distance from the UV lamp equal to half the hydraulic diameter of the reactor using a Black-Ray radiometer (Model J-221). For each parameter test, the other parameters were all fixed at representative values. The representative baking temperature was 550 °C, and the representative RT, which was calculated by dividing the reactor volume by the flow rate, was 0.4 min. The UV-LED with the maximum intensity at 380 nm (MS-L510UV380) was used as the representative light source. The coated TiO_2 powders were characterized using an X-ray diffraction (XRD) meter (D/max-2500 diffractometer, Rigaku Inc.), a diffuse reflectance ultraviolet–visible–near infrared (UV–vis–NIR) spectrophotometer (Model CARY 5G, Varian Inc.), and a Fourier transforms infrared (FTIR) spectrophotometer (Spectrum GX, PerkinElmer Inc.).

The survey protocol included a procedure control program. After the reactor outlet humidity level reached equilibrium, the cylindrical reactor was pretreated for several hours by flowing humidified zero-grade air through the illuminated reactor. When no contamination with the target compounds was measured in the reactor, the BTEX mixture was introduced. After the adsorption process between the titania catalyst and the target compounds reached equilibrium, as indicated by an equality between the inlet and outlet concentrations, the light source was turned on.

2.2. Sampling and analysis

Air samples were collected over time at the inlet and outlet of the photocatalytic unit prior to and after lamp activation. Prior to lamp activation, three 10-min samples were collected for 3 h, at an interval of 1 h. The adsorption equilibrium for the photocatalytic unit was observed over this time period. The lamp was then turned on, and air samples were collected for another 3 h at an interval of 1 h. All samples were collected at ambient room temperatures (19–25 °C). The gaseous compounds in the air stream were collected using a 0.64 cm outside diameter and 10 cm long stainless steel sorbent trap containing 0.3 g of Tenax TA connected to a constant flow sampling pump (Aircheck Sampler Model 224-PCXR8, SKC Inc.). The sampling times varied from 5 to 10 min depending on the flow rate.

The gaseous compounds collected on the Tenax TA trap were analyzed by coupling a thermal desorption system (TDS, ATD 400, PerkinElmer Inc.) to a gas chromatograph (GC, 7890A, Agilent Inc.) with a flame ionization detector using a 60-m long fused silica column (DB-1, Alltech Inc.). The adsorbent trap was thermally desorbed at 250 °C for 10 min, and the target compounds were then cryofocussed at −120 °C on a cryo trap (15.2-cm-long, 0.32-cm-o.d. tube packed with glass beads). The cold trap was rapidly heated to 250 °C, after which the contents were flushed into the Cryofocusing Module (CM) of the TDS and cooled to −120 °C to refocus the target compounds. The CM was then heated to 225 °C and flushed to transfer the target compounds to the GC. The initial oven temperature was set at 35 °C for 5 min and then ramped to 200 °C at 4 °C min^{-1}, where it was held for 5 min.

The quality control program included laboratory blank traps and spiked samples. At the beginning of the day, a laboratory blank trap was analyzed to check for any trap contamination; however, none was identified. An external standard was also analyzed daily to check the quantitative response. The method detection limits for the target compounds ranged from 0.1 to 0.3 ppb.

3. Results and discussion

3.1. Morphological and optical properties of photocatalysts

The morphological and optical properties of TiO_2 powders baked at different temperatures were obtained from XRD, UV–vis–NIR, and FTIR analyses. Fig. 2 shows the XRD patterns of TiO_2