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Application of visible-light photocatalysis with nitrogen-doped or unmodified titanium dioxide for control of indoor-level volatile organic compounds

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ABSTRACT

The present study evaluated visible-light photocatalysis, applying an annular reactor coated with unmodified or nitrogen (N)-doped titanium dioxide (TiO_2), to cleanse gaseous volatile organic compounds (VOCs) at indoor levels. The surface chemistry investigation of N-doped TiO_2 suggested that there was no significant residual of sulfate ions or urea species on the surface of the N-doped TiO_2. Under visible-light irradiation, the photocatalytic technique using N-doped TiO_2 was much superior to that for unmodified TiO_2 for the degradation of VOCs. Moreover, the degradation efficiency by a reactor coated with N-doped TiO_2 was well above 90% for four target compounds (ethyl benzene, *o*,*m*,*p*-xylenes), suggesting that this photocatalytic system can be effectively employed to cleanse these pollutants at indoor air quality (IAQ) levels. The degradation efficiency of all target compounds increased as the stream flow rate (SFR) decreased. For most target compounds, a reactor with a lower hydraulic diameter (HD) exhibited elevated degradation efficiency. The result on humidity effect suggested that the N-doped photocatalyst could be employed effectively to remove four target compounds (ethyl benzene, *o*,*m*,*p*-xylenes) under conditions of less humidified environments, including a typical indoor comfort range (50–60%). Consequently, it is suggested that with appropriate photocatalytic conditions, a visible-light-assisted N-doped photocatalytic system is clearly an important tool for improving IAQ.

1. Introduction

Photocatalysis using titanium dioxide (TiO_2) has become a highly promising technology for environmental pollutant remediation, due to a number of advantages over conventional processes [1–3]. In recent studies, in order to overcome the main drawback of TiO_2 that exhibits photocatalytic activity only in the near ultraviolet (UV) region, certain researchers have modified TiO_2 to enhance light absorption and photocatalytic activity under visible-light irradiation. Several methods such as reductive hydrogen plasma treatment [4], dye sensitization [5], transition metals doping [6], and non-metal doping [7,8] have been proposed to modify the electronic properties of bulk TiO_2. In case of dye sensitization, sensitizer depletion due to continuous electron injection can limit its long-term stability [9]. Transition metal doping also has two possible limitations: photo-corrosion and promoted charge recombination at metal sites [10]. Consequently, a non-metallic N-doped TiO_2 technique has been investigated as an alternative approach for the degradation of various environmental pollutants [7,11]. For the N-doped technique, N atoms could be incorporated into two different sites of the bulk phase of TiO_2, and these interstitial nitrogen atoms could be responsible for visible-light response [12,13].

The environmental pollutants which were tested using the N-doped catalyst included acetaldhyde [7,14,15], acetone [16], benzene [14], 4-chlorophenol [14], methylene blue [7], 2-propanol [17], toluene [18], and trichloroethylene [15]. However, most of these studies were focused on water applications [11]. Moreover, less-documented air studies have primarily dealt with high parts per million (ppm) concentrations, which is more typical for chemical process stream concentrations than indoor air quality concentrations (IAQ). Extrapolation of oxidation performance data collected at concentrations much higher than those in the intended application may not be valid. Consequently, the current study evaluated the feasibility of applying visible-light-induced TiO_2 doped with the N element to cleanse air VOCs at a low ppb concentration commonly associated with IAQ issues. This investigation was conducted under a wide range of humidity that covers dried and humidified environments. Another characteristic is that the present study employed a continuous flow reactor, since most previous studies employed batch reactors. Because of the prevalence of aromatic VOCs in various indoor environments [19–21] and because of their adverse health effects [22,23], they were selected as target com-

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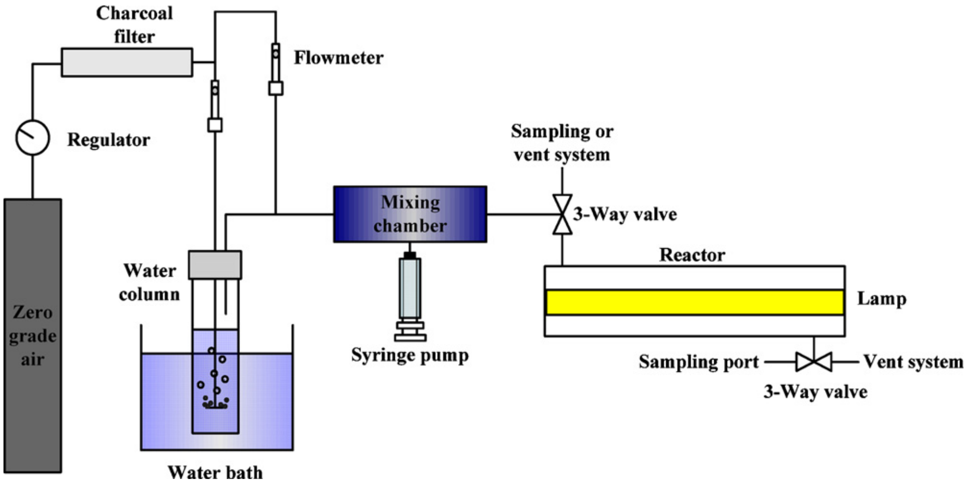

Fig. 1. Schematic diagram of experimental set-up.

pounds. For comparison, unmodified TiO_2 was also evaluated for the photocatalytic degradation under visible-light irradiation.

2. Methods

2.1. Survey protocol

Two experiments were conducted to evaluate photocatalysis applying unmodified or N-doped TiO_2 catalyst for the control of indoor levels of VOCs under visible-light irradiation. A schematic diagram of the experimental set-up is presented in Fig. 1. For the first experiment, the inner surface of a *Pyrex* reactor was coated using a 20% Degussa P-25 slurry by following the coating procedure described in a previous publication [24]. Main parameters for this system were fixed to their representative values. Relative humidity (RH) was fixed to between 50 and 60%, which was adjusted by passing zero-grade air through a humidification device in a water bath (Cole-Parmer HAAKE W26). The RHs were measured just prior to the photocatalytic reactor inlet using a humidity meter (Thermo Recorder TR-72S, T & D Co.). The concentration surveyed was 100 ppb to represent an indoor air quality level. The desired concentration was achieved through the use of a syringe pump (KdScientific Model 210). The representative hydraulic diameter (HD, defined as the inside diameter of the annular reactor tube minus the outside diameter of the lamp) of the reactor was 20 mm. The fixed stream flow rate (SFR) was $0.5\,\mathrm{L\,min^{-1}}$. Measurements of SFR were carried out using identical rotameters ($0–5\,\mathrm{L\,min^{-1}}$) calibrated against a dry test meter (URG 3000-020C). Visible radiation was supplied by an 8-W fluorescent daylight lamp (F8T5DL, Youngwha Lamp Co.). The spectrum of this lamp ranged from 400 to 720 nm. The visible radiation intensity measured at a distance from the visible-light lamp equal to half the HD of the reactor using a Digital Lux Meter (INS Model DX-100) was $1.9\,\mathrm{mW\,cm^{-2}}$. The weight of the unmodified TiO_2 film coated inside the reactor was $2.6\,\mathrm{mg\,cm^{-2}}$.

Second, N-doped TiO_2 photocatalyst was evaluated for BTEX degradation efficiency under different conditions. Three parameters were tested: SFR, HD, and humidity. The range of SFR investigated was $0.5–2.0\,\mathrm{L\,min^{-1}}$, which is comparable to previous reports by other researchers [25,26]. Three different HDs (5.0, 20.0, and 40.0 mm HD) were also tested using the same residence time (5 s), which was calculated by dividing the SFR by the volume of the reactor. The total volumes of the reactor were 83.2, 255, and 629 mL for the three HDs, respectively. The respective light intensities for the three HDs were 3.4, 1.9, and $1.3\,\mathrm{mW\,cm^{-2}}$. The relative humidity (RH) range for these experiments was 10–90% (10–20, 50–60 and 80–90%). For each parameter test, the other parameters were all fixed at the representative values employed in the first experiment. One exception was that the weight of the N-doped TiO_2 film coated inside the reactor was $2.8\,\mathrm{mg\,cm^{-2}}$.

2.2. Measurements

A time-series of concentration measurements of the target compounds was performed at the inlet and outlet of the reactor prior to or after turning on the visible-light lamp. Prior to turning on the lamp, air samples were collected in Tedlar bags for 10 min every 30 min at both the inlet and outlet. A total of six air samples were collected for a three-hour process. Adsorption process between the titania catalyst and target compounds reached equilibrium, nominally 2 h after the introduction of the target compounds, as indicated by equality between the inlet and outlet concentrations. After 3 h after the introduction of the target compounds (adsorption equilibrium), the lamp was turned on. Then, another six 10-min samples were collected for 3 h with an interval of 30 min at both the inlet and outlet. Since the outlet concentrations of the reactor reached a steady state within 0.5 h after the lamp was turned on for all target compounds, the steady-state results were discussed as regards the destruction efficiency of the target compounds. Each experiment was repeated three times, and the repeated experiments showed very similar patterns. Thus, average values are presented for all experimental conditions. Target compounds in the air stream were collected by filling an evacuated 5 L Tedlar bag at a constant flow rate. Air from this bag was then drawn through a sorbent trap containing 0.3 g of Tenax TA using a constant flow-sampling pump (A.P. Buck Inc., Model I.H). All samples were taken at ambient room temperature (19–25 °C). The target compounds collected on the sorbent trap were analyzed by coupling a thermal desorption system (Tekmar Model Aerotrap 6000) to a gas chromatograph (Varian 3400CX) with a flame ionization detector using a 0.32-mm-i.d. by 60-m-length fused silica column (Supelco Co. SPB-5).

The quality assurance/quality control program for the measurements of target compounds 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, no trap contamination was identified. An external standard was analyzed daily to check the quantitative response. When the