



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 (TiO₂), to cleanse gaseous volatile organic compounds (VOCs) at indoor levels. The surface chemistry investigation of N-doped TiO₂ suggested that there was no significant residual of sulfate ions or urea species on the surface of the N-doped TiO₂. Under visible-light irradiation, the photocatalytic technique using N-doped TiO₂ was much superior to that for unmodified TiO₂ for the degradation of VOCs. Moreover, the degradation efficiency by a reactor coated with N-doped TiO₂ 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.

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1. Introduction

Photocatalysis using titanium dioxide (TiO₂) 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 TiO₂ that exhibits photocatalytic activity only in the near ultraviolet (UV) region, certain researchers have modified TiO₂ 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 TiO₂. 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 TiO₂ 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 TiO₂, 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 acetaldehyde [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 TiO₂ 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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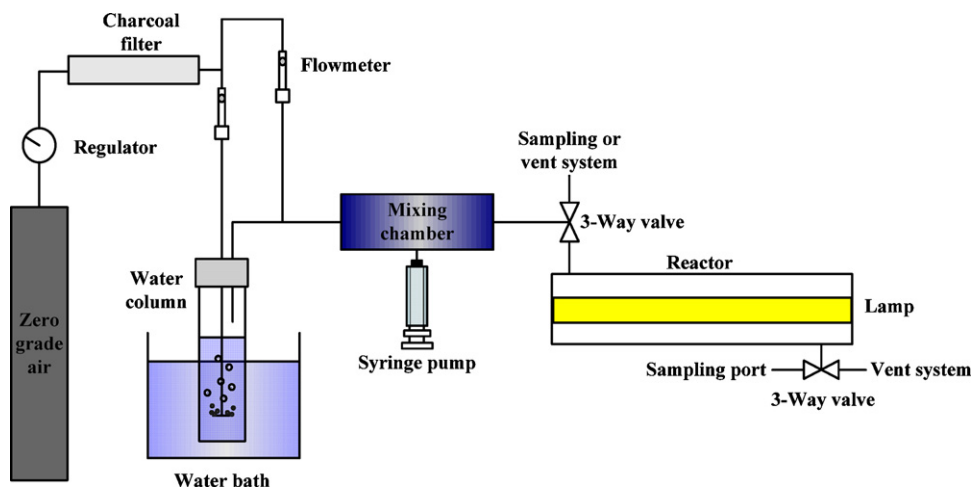


Fig. 1. Schematic diagram of experimental set-up.

pounds. For comparison, unmodified TiO₂ 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 TiO₂ 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 L min⁻¹. Measurements of SFR were carried out using identical rotameters (0–5 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 mW cm⁻². The weight of the unmodified TiO₂ film coated inside the reactor was 2.6 mg cm⁻².

Second, N-doped TiO₂ 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 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 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 TiO₂ film coated inside the reactor was 2.8 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

quantitative response differed more than 20% from that predicted by the specified calibration equation, a new calibration equation was determined. The method detection limits ranged from 1.2 to $5.3 \mu\text{g m}^{-3}$, depending upon the target compounds.

2.3. Preparation and coating of N-doped TiO₂

The method employed by Nosaka et al. [12] was applied for the preparation of N-doped TiO₂ powders. Urea was employed as a N source for mechanical N-doping, 8 g of commercially available TiO₂ powder (Degussa P-25) was added to 20 mL of aqueous solution of the organic nitrogen compounds and stirred at room temperature for 1 h. The mixture was kept in the dark for 1 day and then dried under reduced pressure. N-doped TiO₂ powder was calcined at 500 °C for 3 h under aerated conditions to obtain yellow powder. The calcined powder was washed with diluted sulfuric acid and then with pure water, and vacuum-dried. The PH of the final solution was 7. The prepared N-doped TiO₂ powders, along with the unmodified TiO₂ powders (Degussa P-25), were characterized using an FTIR spectrophotometer (Spectrum GX, PerkinElmer Limited, USA), a thermogravimetric analyzer with differential thermal analysis (TG-DTA, SDT Q600, TA Instrument, USA), and a diffuse reflectance UV-VIS-NIR spectrophotometer (Model CARY 5G, Varian, Australia).

The N-doped TiO₂ powders were coated on the inner surface of the reactors using the method employed by Xagas et al. [27]. Grinding 0.5 g TiO₂ powder (Degussa, P25) with 2 mL of a 0.1 M aqueous ethylenediaminetetraacetic acid (EDTA) solution was ground to produce a viscous paste. The paste was diluted by the slow addition of 1 mL of water. Then, 0.1 mL of Triton X-100 was added and the paste was smeared on a glass substrate immobilized by an adhesive tape strip. After drying at 100 °C for 15 min, the film was calcined in an oven at 500 °C for 30 min.

2.4. Experiment controls

Experiment controls included the use of new bulbs, catalyst pretreatment, and control test. New bulbs were used for every 6-h experiment to minimize any confounding factors that might influence the test results due to different bulb ages. The catalyst was pretreated for several hours by making zero-grade airflow through the illuminated reactor. The catalyst pretreatment was performed after the humidity level at the reactor outlet reached equilibrium. When no contamination with the target compounds was measured in the reactor, the target compounds were introduced. A control test using an uncoated Pyrex reactor, which was conducted while a visible-light lamp was turned on, had no effect on VOC degradation. In another control test using a coated Pyrex reactor, the CO levels measured after turning on the lamp were somewhat elevated compared to those measured prior to turning on the lamp. This indicates that some CO was generated as a result of the oxidation reaction of the surface-bound reactants and adsorbed intermediates. However, the CO generated during photocatalytic oxidation (≤ 0.4 ppm) was a negligible addition to indoor CO levels.

3. Results

3.1. Unmodified TiO₂ vs. N-doped TiO₂

Fig. 2 presents the UV-vis absorbance spectra of N-doped TiO₂ and unmodified TiO₂ powders (Degussa P-25). The unmodified TiO₂ exhibited the absorption edge at $\lambda \approx 430$ nm, which is similar to that reported by Wang et al. [28]. For the N-doped TiO₂ powders, a shift of the absorbance spectrum towards the visible-light region was observed. The absorption edge for the N-doped TiO₂ was shifted to

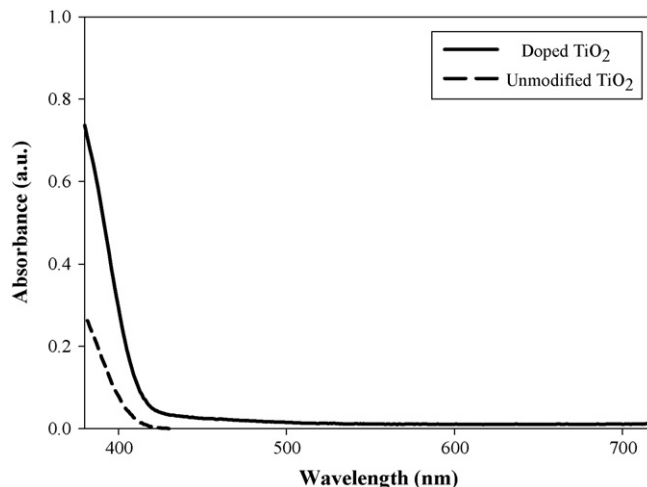


Fig. 2. UV-vis diffuse reflectance spectra of N-doped TiO₂ and unmodified TiO₂ powders (Degussa P-25).

$\lambda > 720$ nm, being in good agreement with that reported by Wang et al. [28]. This shift would be caused by N-doping as has been reported in the literature [11].

FTIR spectra of N-doped TiO₂ and Degussa P-25 TiO₂ powders are presented in Fig. 3. The absorption peaks were located at 3430–3410, 1640–1631, 1401, and 675–667 cm^{-1} . The band at 3430–3410 cm^{-1} corresponds to the O–H stretching vibration, while the band at 1640–1631 cm^{-1} results from O–H bending of adsorbed water molecules [29–31]. The frequency movements to a slightly lower wavelength for the N-doped TiO₂ as compared with the unmodified TiO₂ could be due to the interaction between the doped N and H [32]. A weak peak at 1401 cm^{-1} for the N-doped TiO₂ could be attributed to the ammonium ions [29,33] possibly produced by the dissociation of urea. The band below 1000 cm^{-1} corresponds to the titania crystal lattice vibration [29–31]. Meanwhile, no peaks appeared at 1135–1050 cm^{-1} , which are the typical IR bands of SO_4^{2-} [29], thereby suggesting that there was no significant residual of sulfate ions on the surface of the N-doped TiO₂. Similarly, the FTIR spectra did not present any of the characteristic bands of the urea, which are typically presented at 3210 cm^{-1} [34], thereby suggesting that urea species were significantly washed with diluted sulfuric acid and then with pure water.

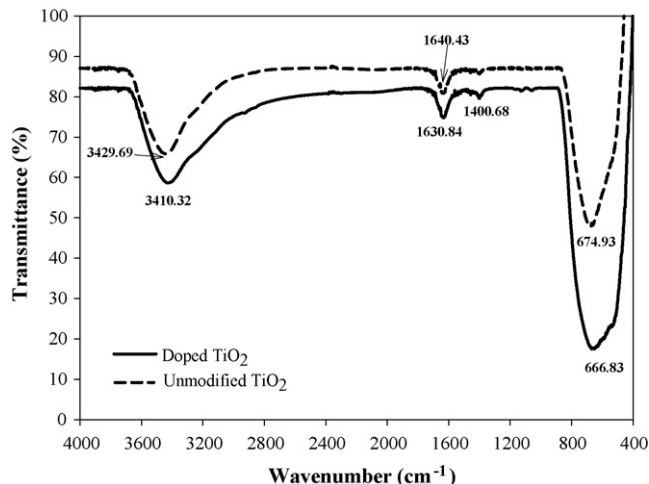


Fig. 3. FTIR spectra of N-doped TiO₂ and unmodified TiO₂ powders (Degussa P-25).

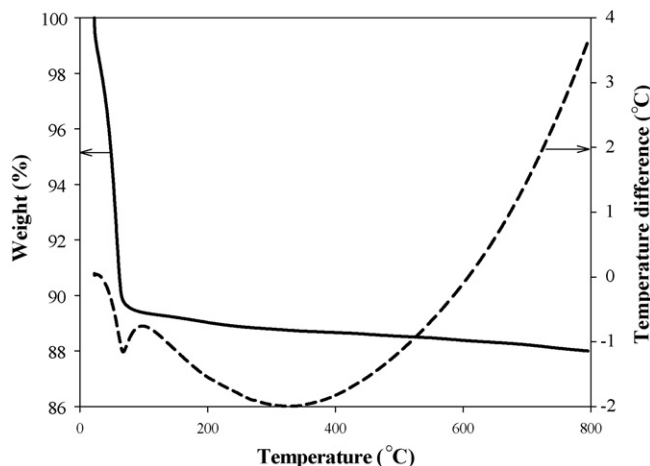


Fig. 4. TG-DTA curve of N-doped TiO₂.

The TG-DTA curve of N-doped TiO₂ powders presents a pattern of two-step weight loss observed in the temperature between 20 and 800 °C (Fig. 4). Between 20 and 85 °C, a rapid weight loss of the catalyst (ca. 10% loss) with endothermic process was observed. This weight loss is ascribable to the release of adsorbed water [35,36]. Minor weight loss (<2% loss) was also observed between 85 and 800 °C. This loss may be attributed to the partial dehydroxylation of the titania surface [35,36].

Fig. 5 presents the degradation efficiency of six VOCs (benzene, toluene, ethyl benzene, and *o,m,p*-xylenes) obtained by using two types of photocatalysts (unmodified TiO₂ and N-doped TiO₂) under the same experimental conditions. Under visible-light irradiation, the degradation efficiency of all target VOCs was much higher for the N-doped TiO₂ than for the unmodified TiO₂. The degradation efficiency for the N-doped TiO₂ was between 23 and 96%, while that for the unmodified TiO₂ was between 13 and 17%, depending upon compounds. Furthermore, the degradation efficiency by the N-doped TiO₂ was well above 90% for four compounds (ethyl benzene, *o,m,p*-xylenes). Among the target compounds, benzene exhibited the lowest degradation efficiency for the N-doped TiO₂. The degradation efficiency of toluene was nearly three times greater than that of benzene.

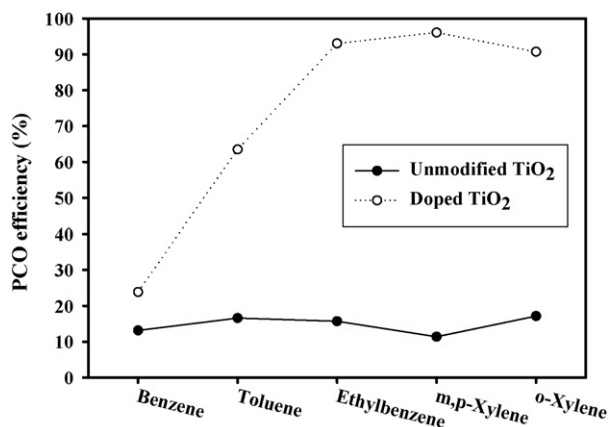


Fig. 5. Degradation efficiency of target VOCs obtained by using N-doped TiO₂ and unmodified TiO₂ which were tested under same experimental conditions: RH, 50–60%; input concentration, 100 ppb; HD, 20 mm; SFR, 0.5 L min⁻¹; and lamp type, 8-W fluorescent daylight lamp. One exception was that the weight of photocatalyst film coated inside the reactor was slightly different (2.6 mg cm⁻² of unmodified TiO₂ and 2.8 mg cm⁻² of N-doped TiO₂).

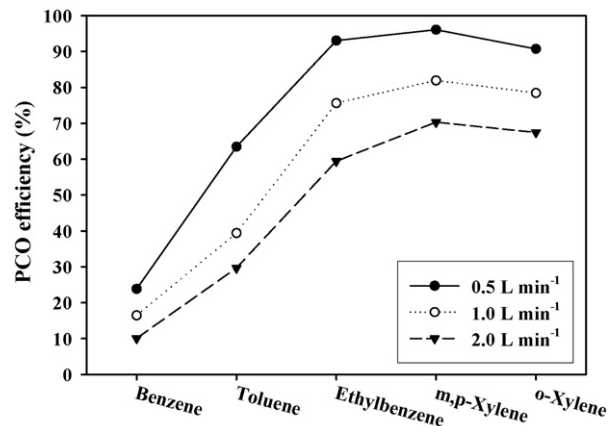


Fig. 6. Degradation efficiency of target VOCs determined via photocatalytic reactor with N-doped TiO₂ according to stream flow rate (SFR).

3.2. Degradation efficiency according to SFR

Three SFRs (0.5, 1.0, and 2.0 L min⁻¹) were tested for degradation efficiency of the target compounds, using a 20.0 mm-HD reactor coated with N-doped TiO₂. The residence times, which were calculated by dividing the reactor volume by SFR, were 22.0, 11.0, and 5.5 s for the SFRs of 0.5, 1.0, and 2.0 L min⁻¹, respectively. In addition, the respective face velocities were 1.1, 2.2, and 4.4 cm s⁻¹. The degradation efficiency of target compounds determined via photocatalytic reactor with N-doped TiO₂ according to SFR is shown in Fig. 6. For all three SFRs, the degradation efficiency for ethyl benzene and *o,m,p*-xylenes was higher than that of benzene or toluene. Benzene exhibited the lowest degradation efficiency with a range of 10–24%, depending upon SFRs. The degradation efficiency of all target compounds increased as the SFR decreased. At the lowest SFR (0.5 L min⁻¹), the degradation efficiency for four compounds (ethyl benzene and *o,m,p*-xylenes) was above 90%, while it was between 58 and 70% at the highest SFR (2.0 L min⁻¹). The degradation of toluene at the SFR of 0.5 L min⁻¹ (63%) was greater than twice that of the SFR of 2.0 L min⁻¹ (30%).

3.3. Degradation efficiency according to HD

Fig. 7 displays the degradation efficiency of target compounds determined via photocatalytic reactor coated with N-doped TiO₂, according to HDs. To avoid any effect from the reactor residence

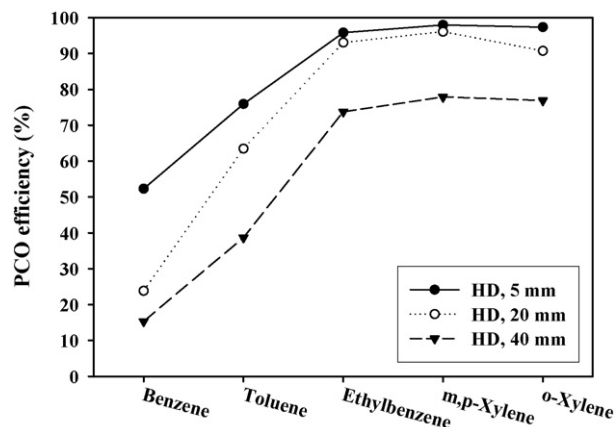


Fig. 7. Degradation efficiency of target VOCs determined via photocatalytic reactor with N-doped TiO₂ according to hydraulic diameter (HD).

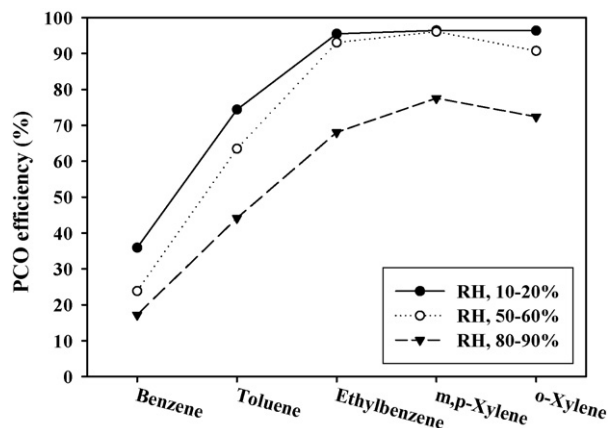


Fig. 8. Degradation efficiency of target VOCs determined via photocatalytic reactor with N-doped TiO₂ according to relative humidity (RH).

time on the destruction efficiency, the tests were conducted using the same reactor residence time (5 s) based on adjusting the SFRs. The degradation efficiency of most target compounds exhibited an increasing trend with an HD decrease. The degradation efficiency for the four target compounds was all above 90% for the reactors with the HDs of both 5.0 and 20.0 mm, while they were between 74 and 78% for the reactor with the HD of 40.0 mm, depending upon compounds. Benzene exhibited the lowest degradation efficiency with a range of 15–52%, depending upon HDs.

3.4. Degradation efficiency according to humidity

Three RH ranges (10–20, 50–60, and 80–90%), covering dry and humid environments, were tested for the degradation efficiency of target VOCs. Fig. 8 exhibits the degradation efficiency of target compounds determined via photocatalytic reactor with N-doped TiO₂ according to the relative humidity. For most compounds, the degradation efficiency increased as RH decreased. The degradation efficiency varied from 17 to 36% for benzene and from 44 to 74% for toluene. However, the degradation efficiency of four compounds (ethyl benzene, *o,m,p*-xylenes) was above 90% for two RH ranges of between 10 and 20% and between 50 and 60%.

4. Discussion

The surface chemistry investigations of N-doped TiO₂ suggested that there was no significant residual of sulfate ions or urea species on the surface of the N-doped TiO₂. Subsequently, the photocatalytic activity of the N-doped TiO₂ and unmodified TiO₂ was evaluated by the photodegradation of selected VOCs. The comparison of VOC degradation efficiency between unmodified TiO₂ and N-doped TiO₂ suggests that under visible-light irradiation, the photocatalytic technique using N-doped TiO₂ is superior to that of unmodified TiO₂ for the degradation of VOCs. This is likely due to the enhanced light absorption and photocatalytic activity of the N-doped TiO₂ under visible-light irradiation [7,12,14,15]. This assertion is further supported by the surface chemistry investigations performed in the present study (Figs. 2 and 3). The comparison was undertaken under identical conditions for all experimental parameters except for the weight of coating materials. The weight of N-doped TiO₂ film coated inside the reactor was 2.8 mg cm⁻², while that of unmodified TiO₂ film was 2.6 mg cm⁻². As such, this insignificant weight difference would not cause the difference in degradation efficiency. The current study also found that with the reactor coated with N-doped TiO₂, degradation efficiency for four

compounds (ethyl benzene, *o,m,p*-xylenes) was higher than that for toluene, which in turn was much higher than that for benzene. This result is supported by d'Hennezel and Ollis [37], who reported that the photocatalytic oxidation rate was, in increasing order: benzene, toluene, ethyl benzene, and *m*-xylene. Moreover, the degradation efficiency of the four compounds established via the reactor coated with N-doped TiO₂ was well above 90%. Accordingly, it was suggested that visible-light-induced N-doped TiO₂ could be effectively employed to cleanse these compounds at indoor levels.

Meanwhile, the degradation efficiency obtained from the visible-light-induced unmodified TiO₂ was substantially lower than those from the UV-induced unmodified TiO₂, which were reported by previous studies [24,26]. These previous studies found that under UV irradiation the destruction efficiency of indoor levels of VOCs and carbonyl compounds by unmodified TiO₂ was close to 100%. As such, it was suggested that the unmodified TiO₂ would not be so effective for light absorption and photocatalytic activity under visible-light irradiation as unmodified TiO₂ did under UV irradiation.

Three parameters (SFR, HD, and humidity) were tested for the degradation efficiency of target compounds with a visible-light-induced N-doped TiO₂ photocatalyst. Under specified conditions, a lower SFR exhibited a higher degradation efficiency of target compounds, thereby suggesting that SFR is an important parameter for the application of TiO₂ photocatalytic technology for cleansing indoor air VOCs. The lower destruction efficiency for the high SFR could be caused by an insufficient residence time inside the reactor. In addition, bulk mass transport of the target compounds from the gas-phase to the surface of the catalyst particle due to convection and diffusion, an important heterogeneous catalytic reaction process [38,39], would be insufficient for a high SFR (high face velocity for the same HD reactor). This assertion is further supported by Obee and Brown's study [25], which reported that the face velocity influenced the mass transfer of formaldehyde, toluene and 1,3-butadiene.

Three reactors with different HDs (5.0, 20.0 and 45.0 mm) were tested as regards the photocatalytic destruction efficiency for the target compounds under visible-light irradiation. For most target compounds, a reactor with a lower HD exhibited elevated degradation efficiency. To be activated, the photocatalyst should absorb enough light to provide the energy to overcome the band gap between valance band and conduction bands. The energy is provided by photons, and more photons are produced as light intensity increases. As such, since the distance of the catalyst from the light source increases when increasing the HD, the decrease in the light intensity in the reactor with a higher HD would seem to be the most obvious reason for the drop in the degradation of the target compounds. The effect of the light intensity is also supported by previous studies [40,41], which found that the oxidation rate of BTEX or trichloroethylene increased with an increase in the UV intensity. However, it is noteworthy that the quantum yield can decrease as the light intensity increases [40], and light intensity is one of the major parameters associated with the operation cost of photocatalytic systems [42]. Accordingly, it is suggested that selection of the HD can influence the operational cost of PCO systems as well as the degradation efficiency of pollutants.

The effect of humidity on the photocatalytic destruction efficiency of the target compounds was tested under visible-light irradiation. For most target compounds, the degradation efficiency increased as RH decreased. A possible explanation for this result is based on the theory that has been applied to understand unmodified TiO₂ photocatalytic systems. In the absence of water vapor, the degradation efficiency is substantially retarded because of lack of hydroxyl groups on photocatalyst surface. On the other hand, excessive water vapor will compete with pollutants for the active

reaction sites on the surface. As such, the current result appears to be due to the competitive adsorption between water and the contaminant on the catalyst surface [43]. Under high humidity conditions, excessive water molecules occupy the active sites of the reactants on the photocatalyst surface. This humidity dependence was also reported for toluene by Luo and Ollis [44]. However, it is noteworthy that the degradation efficiency of four compounds (ethyl benzene, *o,m,p*-xylenes) was still above 90% for two RH ranges (between 10 and 20% and between 50 and 60%). Thus, it is suggested that an N-doped visible-light induced photocatalyst could still be employed effectively to remove certain VOCs under relatively less humidified conditions, including the comfort range of the American Society of Heating, Refrigerating and Air-Conditioning Engineers.

It is noteworthy to consider potential byproduct formation and any deactivation effects associated with the PCO processes. The present study found that the CO generated during photocatalytic degradation (≤ 0.4 ppm) was a negligible addition to indoor CO levels. In addition, several previous studies [25,45,46] have reported that the TiO₂ PCO of many VOCs did not produce any significant by-products in the reactor effluent. Nevertheless, a further study is suggested to confirm the formation of various byproducts associated with the use of PCO systems with the N-doped TiO₂ photocatalyst. Meanwhile, the PCO reactors were tested for about 6 months, and then there were no deactivation effects of the N-doped TiO₂ photocatalyst during this entire period. Similarly, evaluations for longer-term performance of the photocatalyst are recommended for a future study.

5. Conclusions

The current study evaluated the feasibility of applying visible-light-induced TiO₂ doped with N element to cleanse air VOCs at a low ppb concentration commonly associated with IAQ issues. The surface chemistry investigation of N-doped TiO₂ suggested that there were no significant residual of sulfate ions or urea species on the surface of the N-doped TiO₂. It was found that under visible-light irradiation, the photocatalytic technique using N-doped TiO₂ was much superior to that for unmodified TiO₂ for the degradation of VOCs, and that the photocatalytic destruction efficiency by the N-doped TiO₂ was dependent on the SFR, HD, and humidity. Furthermore, within the conditions of the present study, the results clearly demonstrated that the use of visible-light-driven photocatalytic system coated with N-doped TiO₂ can effectively cleanse gaseous aromatic hydrocarbons.

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