



Decomposition of benzene in air streams by UV/TiO₂ process

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Abstract

Photocatalytic decomposition of gaseous benzene at room temperature was studied with a fixed-bed annular reactor using titania as the photocatalyst. The effects of humidity, UV light intensity and benzene concentration on the conversion and mineralization of benzene were presented. Experimental results can be adequately described by using the Langmuir–Hinshelwood (L–H) kinetic model. The concentration distribution of benzene in the annular reactors of various dimensions can be described by combining the reactor design equation with L–H kinetics. Deactivation of catalyst was observed and attributed to the adsorption of reaction intermediates on TiO₂ surface. The deactivated TiO₂ catalyst could be photochemically regenerated by ozone-purging in the presence of humidity. © 2003 Elsevier B.V. All rights reserved.

Keywords: Photocatalytic; Benzene; TiO₂; Humidity; Photoreactor; Langmuir–Hinshelwood kinetics; UV light intensity profile; Deactivation

1. Introduction

Volatile organic compounds (VOCs), especially aromatic hydrocarbons, are typical pollutants emitted from numerous urban and industrial sources. Among the technologies developed for the treatment of VOCs, the photocatalytic oxidation process is considered to be a promising technology to decompose VOCs to final products such as H₂O and CO₂ at ambient temperatures. The anatase form of titanium dioxide (TiO₂) is the most commonly applied photocatalyst because of its chemical stability and low toxicity. Electron–hole pairs with a band gap potential of about 3.0 V are formed on the surface of TiO₂ irradiated by UV light with wavelength shorter than 385 nm. The electron–hole pairs then interact with

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Nomenclature

C_A	concentration of gaseous benzene (ppmv)
D_{AB}	binary diffusivity of benzene in air ($\text{cm}^2 \text{s}^{-1}$)
k	reaction rate constant ($\text{ppmv}^{-1} \text{cm}^{-2} \text{s}^{-1}$)
K_T	adsorption equilibrium constant (ppmv^{-1})
I	UV light intensity (W m^{-2})
n	reaction order of UV light intensity
r_A	decomposition rate of benzene ($\text{mol s}^{-1} \text{l}$)
t	reaction time (s)
V_z	flow rate in axis direction (cm s^{-1})

adsorbed species to form highly reactive radical species [1–3]. The photocatalytic degradation of aromatic compounds, such as benzene and toluene, over a film of TiO_2 was found to be more effective than other treatment technologies for experiments conducted with low initial concentrations (2–70 ppmv) [4–6]. Several simplified L–H type models with respect to UV light intensity and species concentration were suggested to describe the kinetic behavior of the decomposition of VOCs in photoreactors [7,8]. The practical application of UV/ TiO_2 process for treatment of VOCs in the air streams is hinged upon the development of effective photoreactors. Photoreactors of various configurations have been developed; however, annular fixed-bed reactors with TiO_2 coated on the surface of reactor wall are the most commonly employed photoreactors for their ease of construction and operation [5,9–11]. However, gas flow pattern within the reactor is considered to be an important criterion for the designing of photoreactors, because the photocatalytic reaction is usually considered to be mass transfer-controlled [12,13]. The objective of this study is to examine the effect of process parameters on the temporal decomposition behaviors of benzene by UV/ TiO_2 process in an annular photoreactor covered with TiO_2 -immersed non-woven fiber textile. The decomposition behavior of benzene in air streams, in the annular photoreactor, was modeled with a L–H type rate equation.

2. Materials and methods

The schematic diagram of the photoreactor system employed in this research is shown in Fig. 1. The plug flow annular photoreactor is made entirely of Pyrex glass with an effective volume of 1.2 l. The photoreactor consisted of a 25 cm diameter quartz tube to house a GTE F15T8/BLB lamp, with approximately 15 W maximum output at about 365 nm. The output of the UV lamp was adjusted by a variable voltage transformer and was detected by a Spectroline model DRC-100X digital radiometer combined with a DIX-365 radiation sensor. Degussa P-25 TiO_2 was employed in this study as received without further treatment. The TiO_2 particles were approximately spherical and non-porous with greater than 99.5% purity; the composition was determined by a Philips MP 710 XRD to contain about 80% of anatase and 20% of rutile, similar to reports by previous studies [11,14]. The specific BET surface area of the TiO_2 particles was determined to be $50.7 \text{ m}^2/\text{g}$ with a Micromeritic

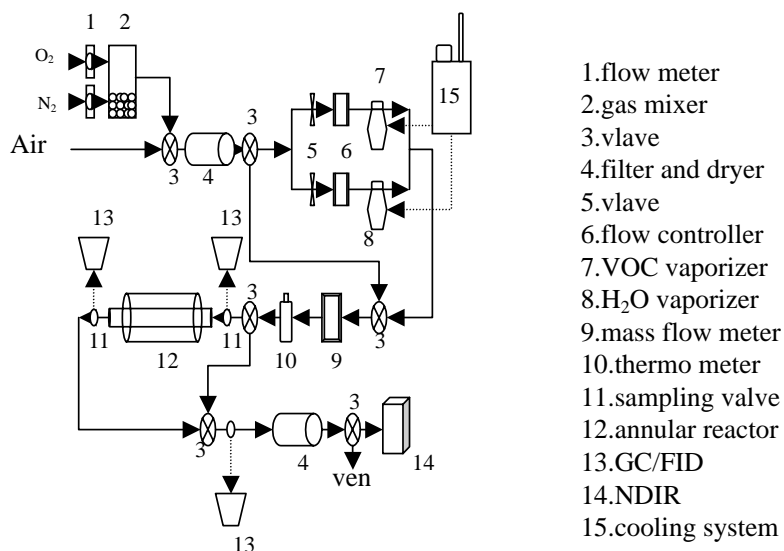


Fig. 1. Schematic diagram of the photoreactor system used in this study.

ASAP 2000 analyzer. The average particle size of the TiO₂ particles in aqueous solutions was reported to be 30 nm by our previous study [15].

A piece of pre-dried non-woven fiber textile of 20 cm × 41 cm was impregnated in a solution containing 25 g/l TiO₂ and 0.05 g/l dioctyl sulfosuccinate (used as dispersing agent) for 8 h before it was air dried in an oven (105 °C) for 2 h. The distribution of TiO₂ powder coated on the textile was visually observed and experimentally determined by a Cambridge S-360 SEM to be homogeneous. Fig. 2 shows the coating phenomena of TiO₂ on non-woven fiber textile. The TiO₂ particles attached tightly on fiber surface and dispersed uniformly. The amount of TiO₂ coated on the textile was calculated by the weight difference of this textile before and after impregnation. The impregnation process could be repeated several times to increase the amount of TiO₂ coated on the textile. This coated fiber textile was then wound on the inner wall of the tubular photoreactor.

Benzene and other chemicals used in this study were of analytical grade and were used without further purification. The benzene-laden air stream was prepared by extracting benzene vapor from the isothermal benzene solvent-containing bottle. The benzene-laden air stream was mixed with a humidity-containing air stream in a gas mixer to maintain the humidity. The mixed air stream was then directed into the pre-warmed photocatalytic reactor for the study of benzene decomposition. Gas samples were taken for further analyses after the temperature, flow rate, pressure, and humidity of the reactor system were steady. The operating time required for reaching the steady state was usually about 20 min. The temperature of the photoreactor system was maintained constant at 25 °C. A China Chromatography model 8700F GC, equipped with a flame ionization detector (FID), was used for analyzing the inlet and effluent benzene concentrations in the air streams. The concentrations of CO₂ in the effluent streams were determined with an O.I.C. model 700 TOC analyzer, equipped with a non-dispersed infrared (NDIR) detector.

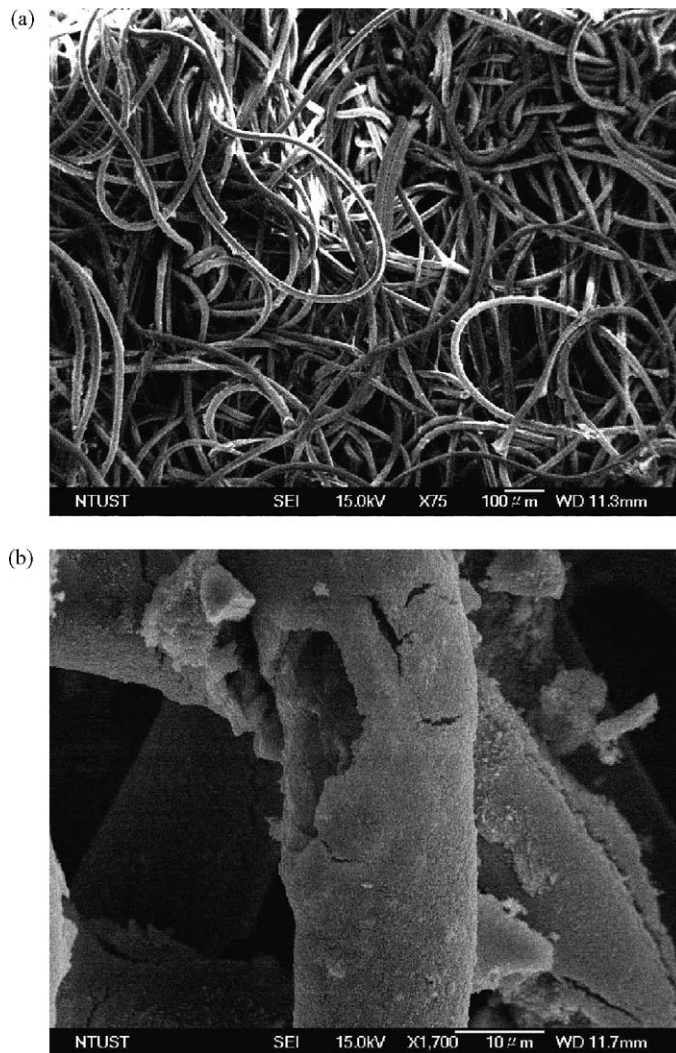


Fig. 2. SEM micrograph of TiO₂ coating phenomena on non-woven fiber textile: (a) non-woven fiber textile (b) TiO₂ coating on fiber surface.

3. Result and discussion

A schematic drawing of the employed annular UV photoreactor is shown in Fig. 3. Light is assumed to be emitted from a hypothetical line source located at the center of the reactor. The reflection or refraction of light at all interfaces is assumed to be negligible. The conservation equation for reacting species has been established in our previous studies for describing the decomposition behavior of benzene by UV/TiO₂ process under a series of

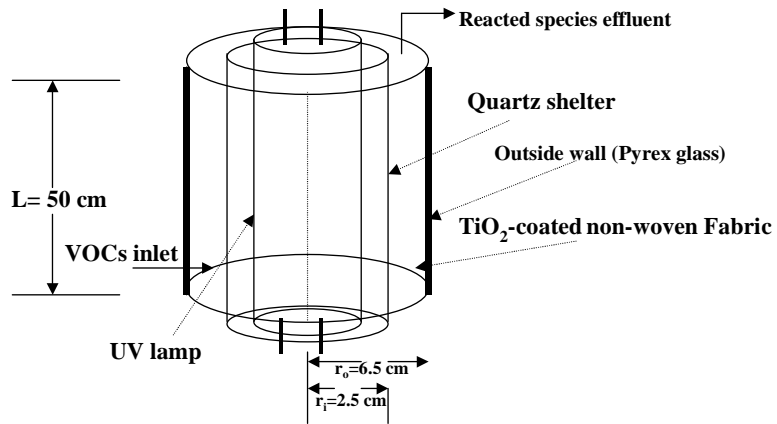


Fig. 3. Photocatalytic reactor geometry.

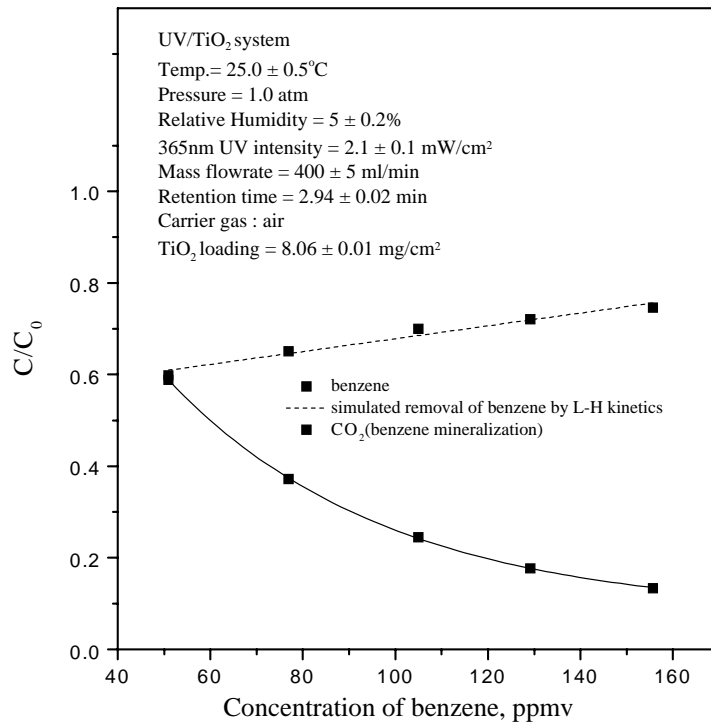


Fig. 4. The effect of initial benzene concentration on the decomposition of benzene by UV/TiO₂ process.

reasonable assumptions [16,17]

$$v_z \frac{\partial C_A}{\partial z} = \frac{\partial C_A}{\partial \tau} = D_{AB} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right) \right) \quad (1)$$

The solution for above equation provides the calculated concentration profile of reactants related to the flow characteristic in the photoreactor. Details of the numerical method for equation solving have been reported in our previous studies [16,17].

The photolysis of benzene in air stream by UV irradiation was studied and found to be minimal without the presence of TiO₂. Similarly, the removal of benzene contributing to the adsorption on TiO₂ during UV/TiO₂ process can also be neglected. Experimental results shown in Fig. 4 reveal that the extent of benzene decomposition decreased with increasing inlet benzene concentration, for experiments conducted with inlet benzene concentration in the range of 50–160 ppmv. Similar results were observed by other researchers [18,19] for the decomposition of toluene, 2-propanol, and formaldehyde by UV/TiO₂ process and attributed to the limited active sites on the surface of TiO₂. Nevertheless, the formation of intermediates was reported, by previous study [4], to be the major factor to inhibit the photocatalytic decomposition of TCE conducted with higher initial TCE concentrations.

The experimental results and simulation of benzene residual shown in Fig. 4 indicate that the decomposition of benzene increased with increasing inlet concentration of benzene, and

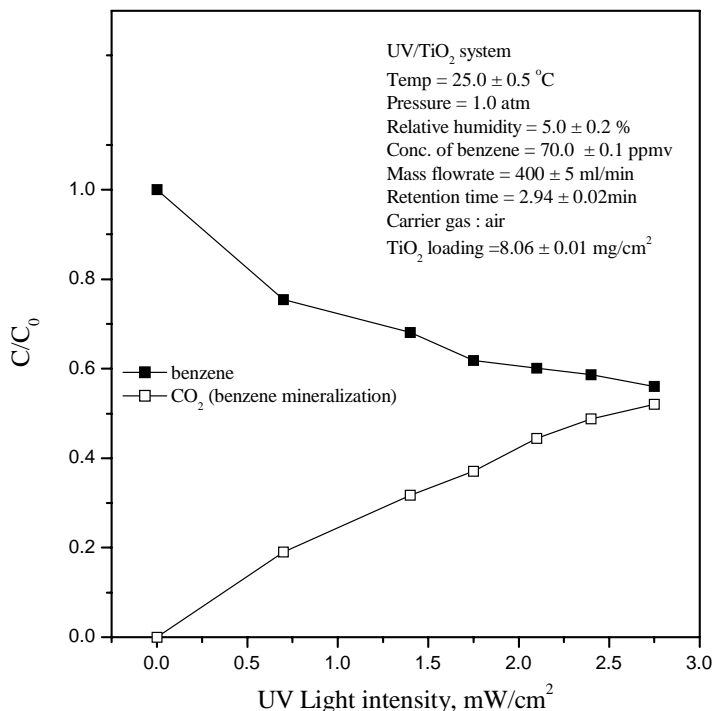


Fig. 5. The effect of UV light intensity on the decomposition of benzene by UV/TiO₂ process.

can be correlated by the L–H type rate equation considering the effects of UV light intensity for experiments conducted at constant relative humidity

$$-\frac{dC_A}{dt} = 4.47 \times 10^{-4} \times I^n \frac{0.01391C_A}{1 + 0.01391C_A} \quad (2)$$

Because the concentration of benzene employed in this study was low (less than 100 ppmv), the above equation could be reduced to be a pseudo first-order rate equation

$$-\frac{dC_A}{dt} = k_1 I^n C_A \quad (3)$$

where k_1 is the pseudo first-order rate constant determined to be $6.21 \times 10^{-6} \text{ s}^{-1}$, C_A the concentration of benzene gas in the reactor, I the illuminated UV light intensity in the range of 0.0–2.75 mW/cm², and t is the retention time (in s) of reactants in the reactor.

The effect of UV light intensity on the decomposition of benzene by UV/TiO₂ process with TiO₂ loading of 8.06 mg/cm² on the non-woven fiber surface at a residence time of 2.94 min was shown in Fig. 5. The decomposition rate of benzene increased linearly with increasing UV light intensity, for experiments conducted at UV intensity below 1.83 mW/cm². However, the reaction order to the UV light intensity was lower than unity, for experiments conducted at higher UV light intensities. Several previous studies observed similar results, i.e. the reaction order with respect to the UV light intensity was 0.5–1.0 for heterogeneous

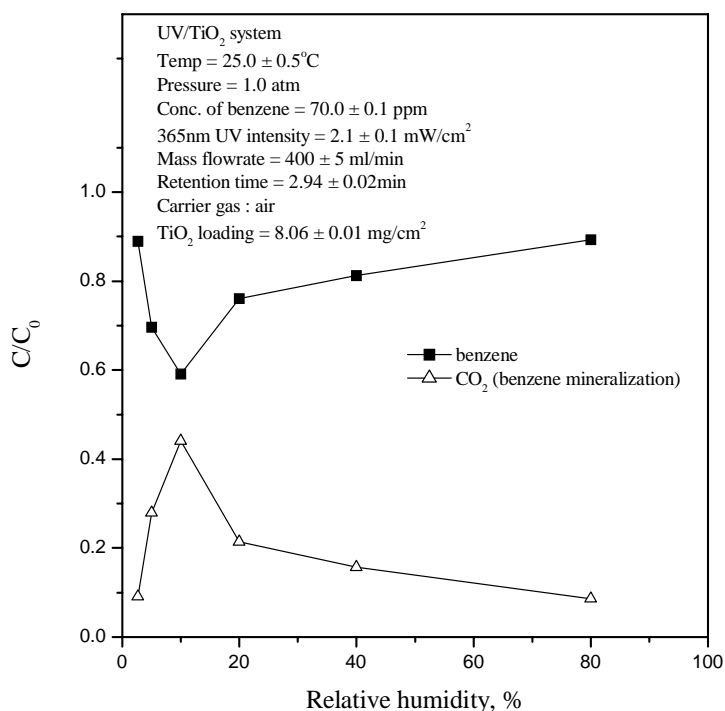


Fig. 6. The effect of relative humidity on the decomposition of benzene by UV/TiO₂ process.

photocatalysis of many organic compounds. The decomposition rate of toluene was found to be linear to the UV light intensity, employed for UV light intensity below 20.4 mW/cm^2 [18]. Choi et al. [19] reported that linearity effect of UV light on acetone decomposition existed only at low levels of light intensity. Kim and Hong [20] also stated that reaction orders with respect to UV light intensity, for the photocatalytic degradation of toluene, acetone, methanol and trichloroethylene, were all first order for experiments conducted at UV intensity below 2.0 mW/cm^2 , but lower than unity for UV light intensity above 2.0 mW/cm^2 . A common explanation for this observation is that excessive light intensity may promote the recombination of electrons and holes and decrease the efficiency of UV light applied, therefore decreasing the dependence of benzene conversion on the light intensity.

Influence of humidity content on the decomposition of gaseous benzene by UV/TiO₂ process at a residence time of 2.94 min was presented in Fig. 6. The relative humidity of air stream, used in this experiment, was in the range of 0.5–80%. The removal and mineralization of benzene increased rapidly with the relative humidity in the range of 0.1–10%. Experimental results in Fig. 6 indicate that a maximum reaction rate was obtained at relative humidity of 10%. However, the effect of increasing relative humidity changed inversely for the experiments conducted with relative humidity higher than 10%. The presence of water molecules is considered to play an important and special role in the formation of the

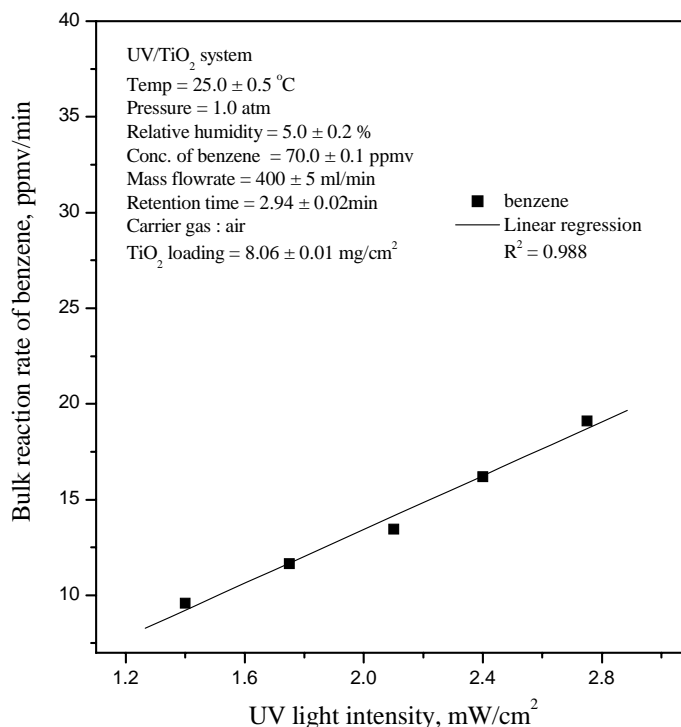


Fig. 7. The effect of UV light intensity on the decomposition rate of benzene by UV/TiO₂ process.

high reactive specie (hydroxyl radical, OH^\bullet) on the surface of photocatalyst; however, the presence of excessive amount of humidity is reported to occupy the activated surface and decrease the decomposition of benzene [9,21].

The experimental results presented in Fig. 7 indicate that bulk reaction rate of benzene degradation is linearly related to light intensity, and the regressed reaction order of UV light intensity therefore is determined to be unity. Therefore, the L–H kinetic model represented as Eq. (2) could be applied for describing the reaction behavior in this study with $n = 1$, assuming that the UV intensity profile between the inner and outer walls of the photoreactor could be expressed by Lambert's law [21], Therefore, the kinetic expression of photocatalytic decomposition of benzene is shown as

$$-\frac{dC_A}{dt} = 4.47 \times 10^{-4} \times I_0 \left(\frac{r_i}{r} \right) \frac{0.01391C_A}{1 + 0.01391C_A} \quad (4)$$

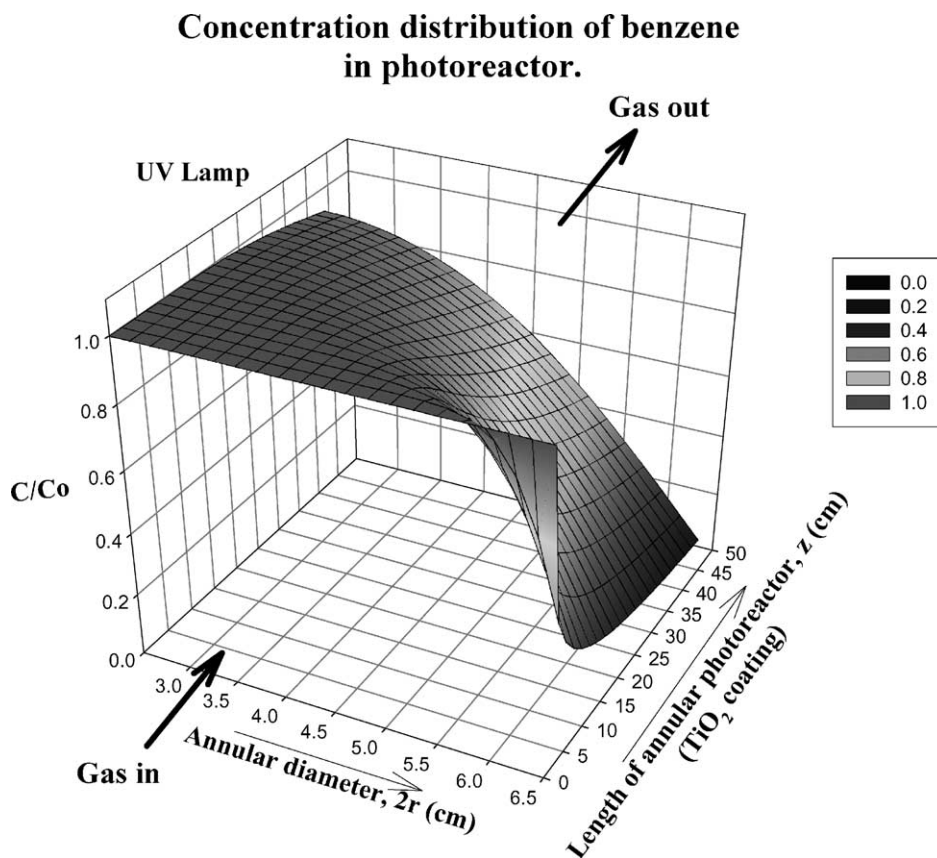


Fig. 8. The calculated concentration distribution of benzene in an annular photoreactor during photocatalytic oxidation of benzene.

Even though the geometry of the photoreactor was seldom studied in previous kinetic studies, Eq. (4) can be applied to describe the relationship between the reaction rate and the geometry of an annular reactor.

The above reaction rate equation was introduced for solving the partial differential equation of Eq. (1); the calculated results are shown in Fig. 8 for the distribution of benzene concentration in the annular photoreactor during the reaction. The depletion of benzene nearby the TiO₂ coated non-woven fiber was rapid. The decrease of benzene concentration in the axial direction is more obvious than that in the radial direction mainly owing to the mass transfer characteristics in reactor. There is a steady-state forced flowing stream in *z*-direction, but only molecule diffusion droved by concentration gradient occurred in *r* direction.

The performance of photoreactor under various conditions can be evaluated by means of kinetic behavior modeling coupled with reactor design equation. The effect of UV light intensity on the bulk decomposition rate of benzene by UV/TiO₂ process under various photoreactor dimensions is shown in Fig. 9. Reactors with thinner flowing region between the inner and outer tubes was found to be more favorable for the photocatalytic decomposition of benzene. Moreover, the drag force caused by the gas stream flow over the coated surface of the non-woven fiber textile might result in flow disturbance and enhance the mass transfer at radial direction. Therefore, it is suggested that photoreactors

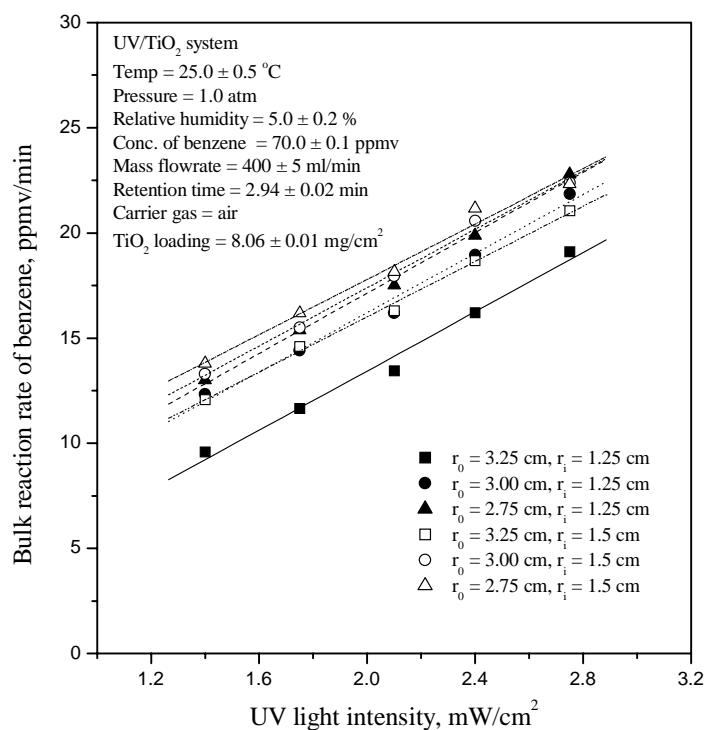


Fig. 9. Regression of UV light intensity to the bulk reaction rate by UV/TiO₂ process for experiments conducted with reactor of various dimensions.

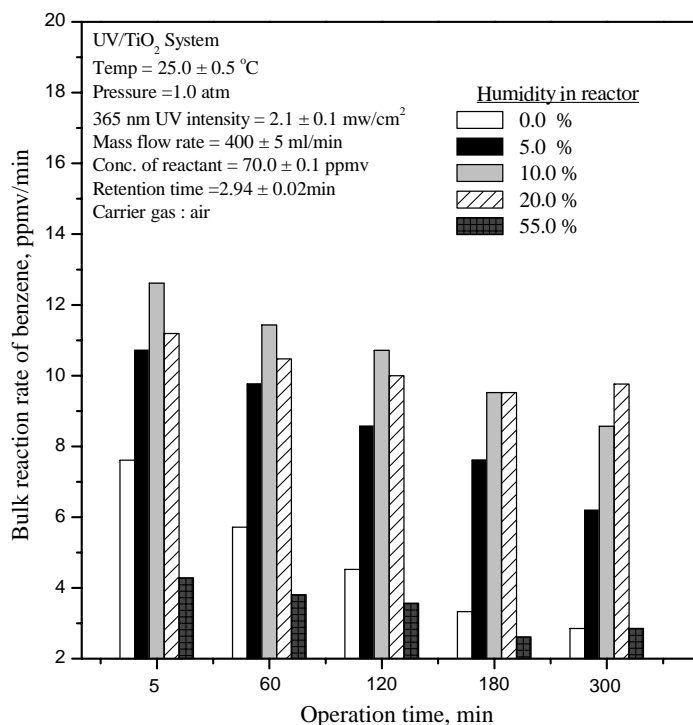


Fig. 10. Decomposition rate of gaseous benzene for experiments conducted at different operation times in the presence of various humidity contents.

with thinner flowing region such as multi-lamps configuration can effectively improve the performance of photoreactors.

The main drawback for the application of photocatalytic process is the deactivation of catalyst during the course of reaction, especially for experiments conducted with the absence of humidity, which was firstly reported by Cunningham and Hodentt [22] for the photocatalytic decomposition of 2-butanol. The decrease of catalyst activity was considered to be mainly attributed to the decrease of active surface, because the irradiated surface of catalyst was coated by the reaction intermediates especially in absence of humidity. For instance, the intermediates adsorbed on TiO₂ for the photocatalytic oxidation of benzene were identified to be phenol, maloinic acid, hydroquinone, benzoic acid and benzoquinone [23,24]. Fig. 10 shows the decomposition rate of benzene for experiments conducted in the presence of various humidity contents at different operation times. The bulk reaction rate of benzene in the absence of humidity was decreased to less than half of the initial reaction rate after 5 h of operation. The deactivation of photocatalyst was not apparent for experiments conducted at a humidity of 5–20%. However, the decomposition of benzene seems to be inhibited obviously for experiment conducted at a humidity of 55%. It is suggested that the active sites on TiO₂ were covered by the presence of excessive water molecules [25].

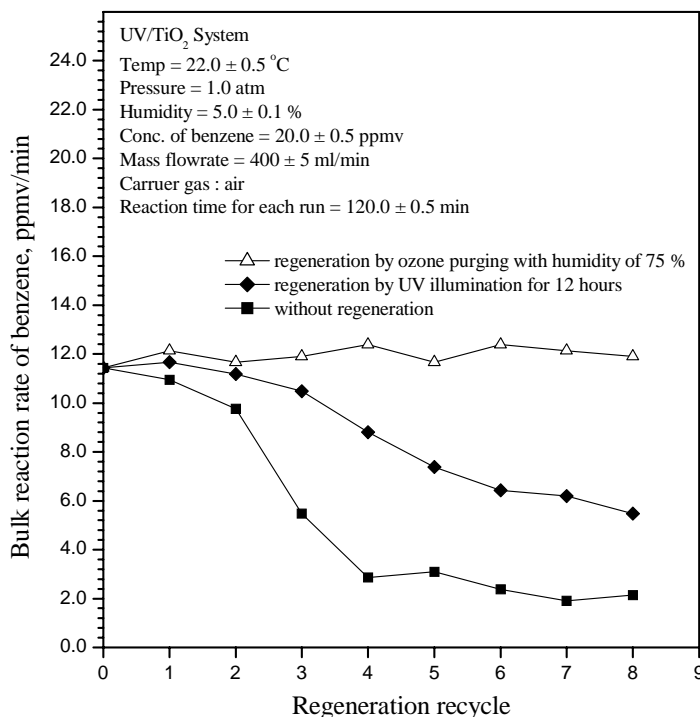


Fig. 11. Effects of regeneration cycle on the photocatalytic decomposition rate of benzene.

The deactivated photocatalysts could be regenerated by either UV illumination with high levels of humidity [24] or high temperature desorption [26]. However, both methods were time-consuming (at least 4 h) for recovering the activity of catalyst. In this study, humidified airflow containing 20.0 mg/l of ozone was introduced to the reactor for 30 min with UV irradiation for regeneration. The color of the TiO₂ coated surface was observed to be transformed from yellowish to white during the regeneration process. Fig. 11 shows the bulk reaction rate of benzene decomposition after various regeneration cycles. The activity of catalyst was totally recovered by the ozone regeneration process for two or three regeneration cycles. The activity of catalyst was reduced to almost half of the initial activity after seven regeneration cycles.

4. Conclusion

The decomposition rate of benzene by UV/TiO₂ process in an annular flow reactor was found to be increasing linearly with UV intensity, for experiments conducted with UV intensity below 1.8 mW/cm². However, the reaction order with respect to UV intensity was reduced for experiments conducted with UV intensity greater than 1.8 mW/cm². The humidity contained in the airflow strongly influenced the decomposition behavior for benzene;

a maximum decomposition rate being obtained for experiment conducted at relative humidity of 10%. A design equation coupled with L–H kinetic model can reasonably describe the concentration distribution of pollutants during the course of photocatalytic decomposition in annular reactors with different dimensions. Deactivation of TiO₂ catalyst relied heavily on the humidity contained in the airflow. Purging of ozone-containing air rapidly decomposed the organic residues adhered on the TiO₂ surface and regenerated the deactivated catalyst within 30 min.

Acknowledgements

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