



Application of a hybrid system comprising carbon-doped TiO₂ film and a ceramic media-packed biofilter for enhanced removal of gaseous styrene

Moon-Sun Kim^a, Gang Liu^b, Hong-Kwan Cho^b, Byung-Woo Kim^{b,*}

^a Bio/Nano-Fusion Material Research Center, Sungkyunkwan University, Suwon 440-746, Republic of Korea

^b Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

ARTICLE INFO

Article history:

Received 22 July 2010

Received in revised form 16 March 2011

Accepted 22 March 2011

Available online 27 March 2011

Keywords:

Gaseous styrene

Carbon-doped TiO₂ film

Ceramic media-packed biofilter

Removal efficiency

By-products

ABSTRACT

It is difficult to efficiently remove gaseous styrene using a TiO₂ film-coated photoreactor under UV light. Therefore, we used a hybrid system consisting of a carbon-doped TiO₂ (C-TiO₂) film and a media-packed biofilter in order to enhance the removal efficiency (RE) of gaseous styrene compared to that of a pure (undoped) TiO₂ photoreactor. The C-TiO₂ was synthesized by a sol-gel combustion method, and its absorption spectrum was stronger than that of pure (undoped) TiO₂ in the UV–vis range. The resultant RE of the C-TiO₂ film was 113–200% higher than that of the pure TiO₂ film. The initial RE of the photoreactor for input styrene concentrations of 630 mg m⁻³, 420 mg m⁻³, and 105 mg m⁻³ was 20.6%, 29.8%, and 40.0%, respectively. When the biofilter was added, the RE increased to 93.3%, 97.9%, and 99.0%, respectively. Thus, application of the hybrid system consisting of both a photoreactor coated with a C-TiO₂ film and a biofilter is advantageous in terms of the removal efficiency of gaseous styrene.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Because volatile organic compounds are considered major environmental contaminants that have a harmful effect on human and ecosystem health, much effort has been focused on their removal. Styrene, for example, is used extensively in the production of plastics and rubbers, and many workers are exposed to harmful gaseous styrene in the workplace. Low concentrations of gaseous styrene are known to cause carcinogenic, mutagenic, and teratogenic diseases [1]. In USA and EU styrene exposure concentration limit is 210 mg m⁻³ (50 ppm) for an 8-h time-weighted average (TWA), while the recommended concentration ceiling exposure for styrene is 850 mg m⁻³ [2].

Gaseous styrene is usually removed using photocatalytic oxidation; however, use of a photocatalytic reactor is limited to enhance the removal efficiency (RE) of gaseous styrene at a competitive cost [2,3]. In a case employing the fluidized-bed photocatalytic system, a 1260 mg m⁻³ initial concentration of styrene was removed with efficiency greater than 80% [2]. Likewise, the use of a biofilter to remove gaseous styrene has not been effective with concentrations of gaseous styrene higher than 400 mg m⁻³. For example, the removal efficiency of styrene has been reported as greater than 95% with an empty bed resi-

dence time (EBRT) of 77 s and loading rate of 74 g m⁻³ at low concentrations [3].

Therefore, for this study, we investigated the removal efficiency of a hybrid system comprising a biofilter in addition to a photoreactor. This investigation was prompted by a previous study, which demonstrated that the RE of gaseous styrene could be enhanced by first mineralizing the styrene using a photoreactor and then treating the system with a biofilter [4,5].

Titanium dioxide (TiO₂) is used extensively as a photocatalyst for the degradation of organic compounds with a UV wavelength range from 380 nm to 410 nm [6]. Because gaseous styrene cannot be removed completely by pure TiO₂, modified TiO₂ has been studied. Falconer and Magrin-Bair [7] found that the photodegradation efficiency of acetaldehyde by platinum (Pt)-doped TiO₂ was 2.8 times higher than that of pure TiO₂. Ohno et al. [8] showed that the absorption range of C-S-TiO₂ – that is, TiO₂ doped with carbon (C⁴⁺) and sulfur (S⁴⁺) ions – increased from 400 nm to 700 nm. Hong et al. [9] reported that iodine-doped TiO₂ had stronger absorption in the 400–550 nm range than pure TiO₂. A few studies have reported that carbon-doped TiO₂ (C-TiO₂) exhibited notable absorption in both the UV and visible ranges [6,10–12].

We hypothesized that the RE of gaseous styrene would be enhanced if a hybrid system consisting of both a C-TiO₂ film and a ceramic media-packed biofilter was used. It should be noted that C-TiO₂ can be obtained more easily and cheaply than other forms of metal-doped TiO₂. In addition, the biofilter filled with ceramic media contains activated organisms. For this experiment, RE was

* Corresponding author. Tel.: +82 31 299 4074; fax: +82 31 299 4079.
E-mail address: bwkim@skku.edu (B.-W. Kim).

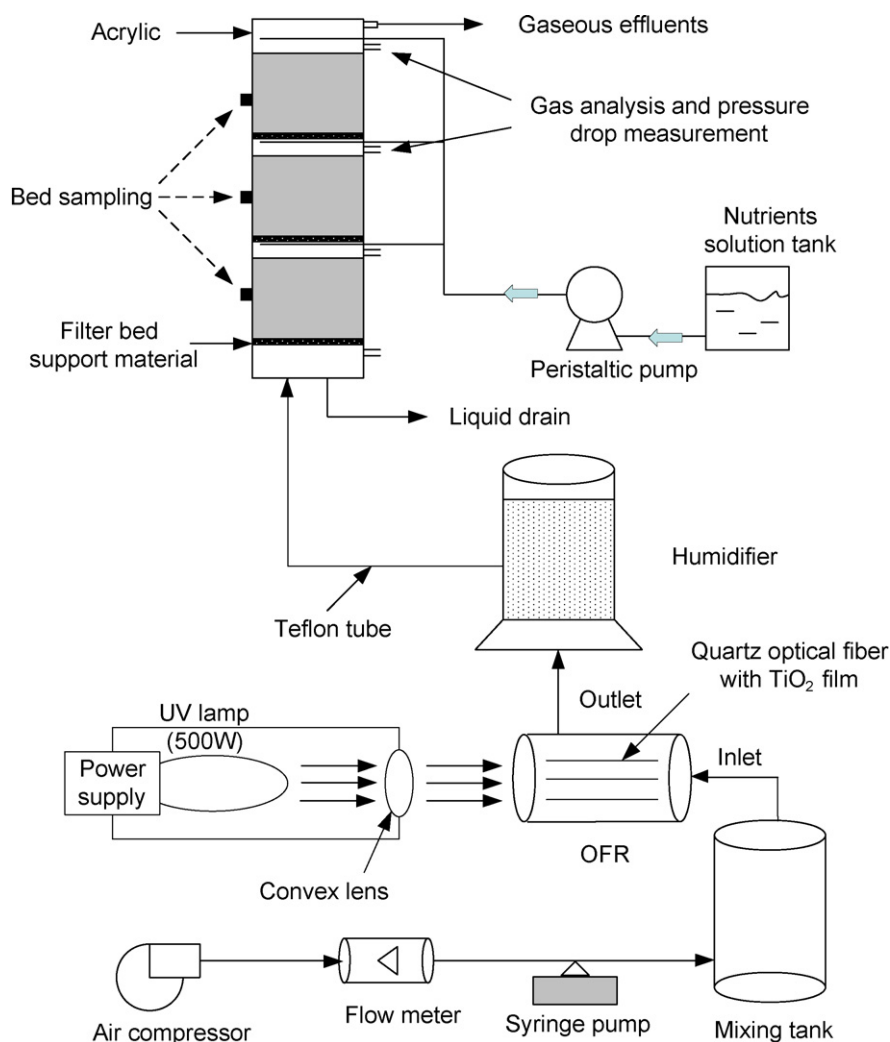


Fig. 1. Schematic diagram of the hybrid system consisting of a photoreactor and a biofilter for the removal of gaseous styrene.

evaluated by measuring the elapsed time in the photoreactor and the empty bed residence time (EBRT) in the biofilter.

2. Materials and methods

The hybrid system for the removal of gaseous styrene, comprising a photocatalytic reactor and a biofilter, is shown in Fig. 1.

In the photoreactor, air was supplied to the mixing tank at a constant flow rate of 3 L min^{-1} by an air compressor. Liquid styrene (Panto Chem, Japan) was poured into the mixing tank at 30 mL min^{-1} by a syringe pump, and the air and styrene were mixed constantly. The diluted styrene was discharged to the photoreactor at 300 mg m^{-3} at a temperature of 23°C . The photoreactor was a 1 L, 35-cm long, cylindrical-type photoreactor with immersed optical fibers. Photo-oxidation was performed in the reactor using TiO_2 film. A 500 W Hg lamp (Samil, Korea) was used as the UV light source. The system with the UV lamp was kept constant at 60°C by a circulation pump of cool air. The TiO_2 film was immobilized on the external surfaces of the optical fibers with an outside diameter of 1.5 mm [13]. Gas from the photoreactor was discharged through the humidifier to the biofilter.

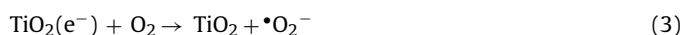
The preparation of C- TiO_2 film for photocatalytic oxidation of styrene is as follows.

After blending 15 mL of titanium tetraisopropoxide (TTIP, purity > 98.0%; Junsei, Japan) and 134.5 mL of ethyl alcohol (purity

of 99.9%; Samchun, Korea), the mixture was stirred for 30 min. Then, 0.64 mL of nitric acid (with a purity of 60.0–62.0%; Daejung, Korea) and 3 mL of distilled water were added to this mixture, and the mixture was again stirred for 90 min. Carbon particles (Aldrich, USA) with an average diameter less than 50 nm were selected as the source for carbon-doping, and 0.2 g carbon was added to the reacted titanium peroxide precursors. The mixture – including the titanium peroxide precursors and carbon particles – was finally stirred in an ultrasonic generator for 10 min.

The coating solution was immobilized on the optical fibers (BFH37-1000, Thorlabs, USA) by a dip-coating method [14]. The coated TiO_2 film was dried at room temperature for 12 h and again sintered at 600°C for 2 h [12]. Previously, we had found that a 2.28–2.98 μm -thick TiO_2 film was optimal for the photodegradation of organic compounds. The thickness of the coated TiO_2 film was measured using a surface profilometer (Alpha Step 500, KLA Tencor Co., CA, USA).

Note that the C- TiO_2 film absorbs photo-energy from an energy source, from which hydroxyl and superoxide radicals are generated, as shown in Eqs. (1)–(3) [15]. The generated hydroxyl radicals and superoxide radicals subsequently degrade styrene to CO_2 and H_2O .



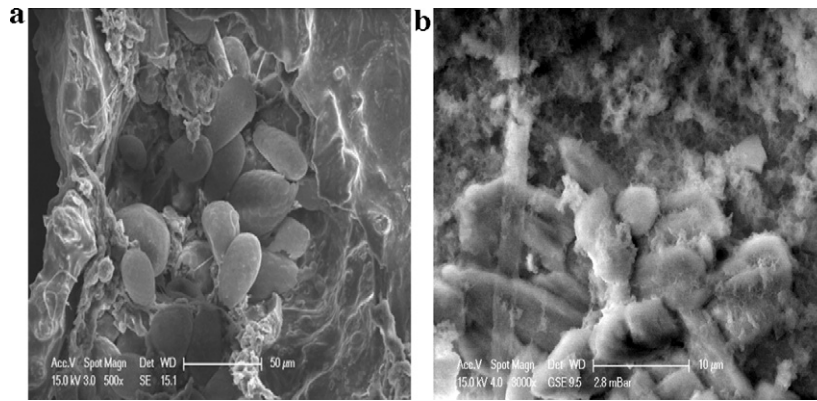


Fig. 2. SEM images of the biofilm on the surface of the media used to remove gaseous styrene at magnifications of (a) 500 \times and (b) 3000 \times .

The bottom of the biofilter reactor was arch-shaped for easy dumping of the drained liquid, and each stage had a sample port. A nozzle was located at the top of the biofilter to supply the nutrient solution via a peristaltic pump (EHC-R220 C, Iwaki, Japan). The biofilter consisted of three stages with an internal reactor diameter of 0.1 m, a stage height of 0.3 m, and a bed volume of 5 L. Both the temperature and humidity of the input gas were controlled by a humidifier with a temperature controller. The sample was collected from a port on each stage using a mini-vacuum pump (MP Sigma 300, SIBATA, Japan) and a 1 L adsorption tube. The concentration of the styrene and the by-products derived from the styrene were then determined by gas chromatography/mass spectrometry (GC/MS; Agilent 6890 GC/5975N MSD).

The biofilter bed was packed with an inorganic, porous ceramic material (Enbion Co., Korea) to minimize the pressure drop for an extended period of time. The inorganic medium was composed of 48.5 wt% SiO₂ and 28.6 wt% CaO and had a porosity of 60%, a specific gravity of 0.55, and a specific surface area of 61.03 m² g⁻¹.

SEM images of the biofilm on the biofilter media are shown in Fig. 2.

The organisms used in the biofilter were obtained by activating wastewater sludge from a sewage treatment plant in Ansong city, Republic of Korea.

The biofilter was designed to optimize major parameters such as humidity, temperature, pH, and EBRT in preliminary experiments. The humidity was regulated to 80.9–92.5 RH% while the temperature remained between 23.2 and 28.0 °C. The pH was controlled within the range of 6.3–7.1.

The RE (%) of gaseous styrene obtained using the photoreactor and the biofilter was calculated as shown in Eq. (4) [5,16]:

$$RE (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (4)$$

where C_i and C_f are the concentrations of the input and output gaseous styrene, respectively.

3. Results and discussion

3.1. Characterization of pure TiO₂ and C-TiO₂

3.1.1. XRD measurements of pure TiO₂ and C-TiO₂

The X-ray diffraction (XRD) patterns of the C-TiO₂ and pure (undoped) TiO₂ films synthesized by a sol-gel combustion method are shown in Fig. 3.

We observed that the diffraction peaks of pure (undoped) TiO₂ (1) at 25.2°, 37.8°, and 47.9° of 2θ were anatase-type TiO₂, while the peak at 28° was a rutile-type TiO₂ [14]. After doping with carbon by sintering at 600 °C, the diffraction peaks of C-TiO₂ (2) were typical anatase-type TiO₂ peaks, while the diffraction peak at 28°

disappeared. Thus, we used carbon doping to ensure the formation of anatase-type TiO₂ without any other crystal forms [11].

3.1.2. X-ray photoemission spectroscopy of C-TiO₂

The composition of the C-TiO₂ film was measured by X-ray photoemission spectroscopy (XPS) to determine the photocatalytic components, as shown in Fig. 4.

XPS signals of C 1s were observed at binding energies of approximately 285.1 eV and 288.0 eV, as shown in Fig. 4(a). The three forms of carbon were elemental carbon, Ti–C bonds substituted with oxygen atoms, and carbonate species [10,17]. Most of the carbon incorporated in the TiO₂ matrix was elemental carbon (C–C); only a small amount of the carbonate species (C–O) was present. Nevertheless, the peak at 288.0 eV indicates the presence of C–O bonds. This carbonated species incorporated into the bulk phase of TiO₂ [8], and its presence indicated that the Ti–O–C structure was present in C-TiO₂ because some of the lattice titanium atoms had been replaced by carbon [12,18]. As shown in Fig. 4(b), XPS signals of Ti 2p were observed at binding energies of 458.7 and 464.4 eV, which were assigned to Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2}, respectively. These Ti 2p peaks are consistent with those of pure TiO₂ and indicate the binding of the titanium atom to the oxygen molecule. The XPS signal of O 1s was at a binding energy of 529.9 eV, corresponding to Ti⁴⁺–O. Note that we attribute the broadening of the O 1s peak to the left (Fig. 4(c)) to the presence of O–C in the bulk phase of TiO₂ [19].

3.1.3. UV-vis absorption of pure TiO₂ and C-TiO₂

The UV-vis absorption spectra of C-TiO₂ and pure (undoped) TiO₂ are shown in Fig. 5.

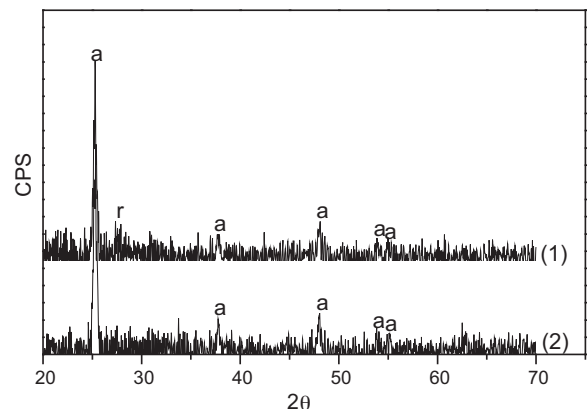


Fig. 3. XRD patterns of (1) pure (undoped) TiO₂ and (2) carbon-doped TiO₂.

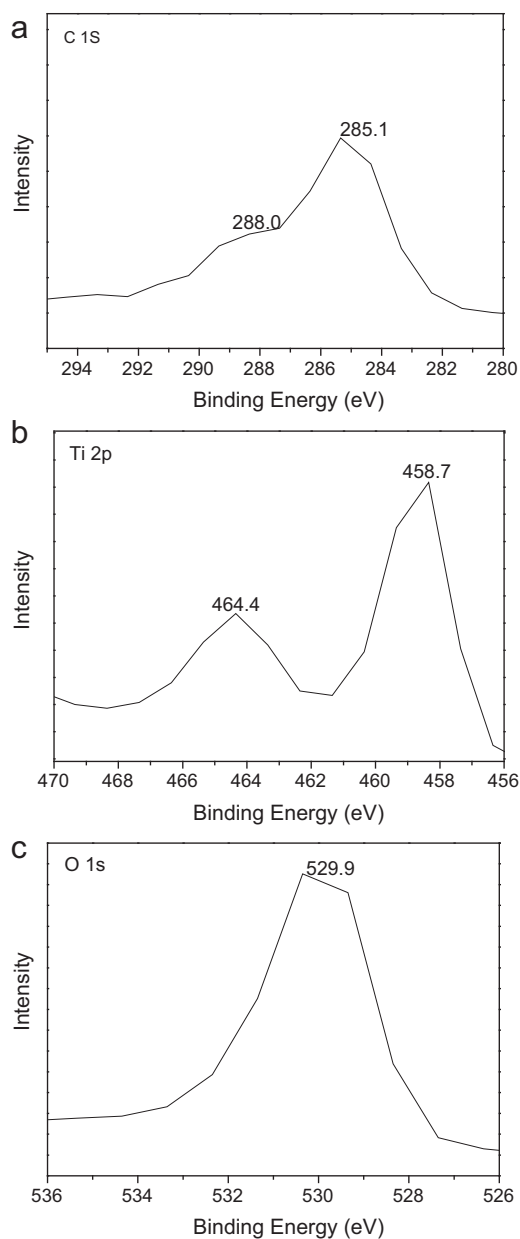


Fig. 4. XPS spectra of (a) C 1s, (b) Ti 2p, and (c) O 1s in the carbon-doped TiO₂ film.

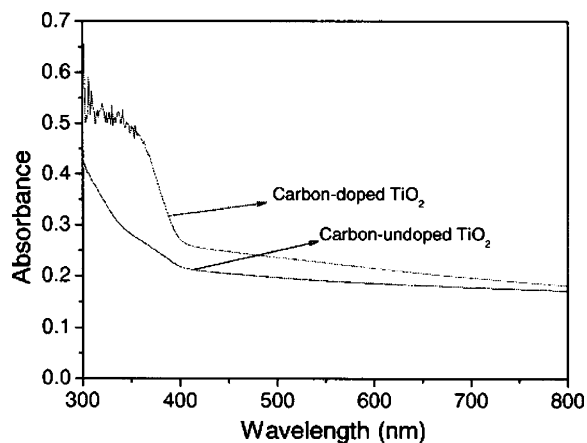


Fig. 5. UV-vis absorption spectra of pure (undoped) TiO₂ and carbon-doped TiO₂.

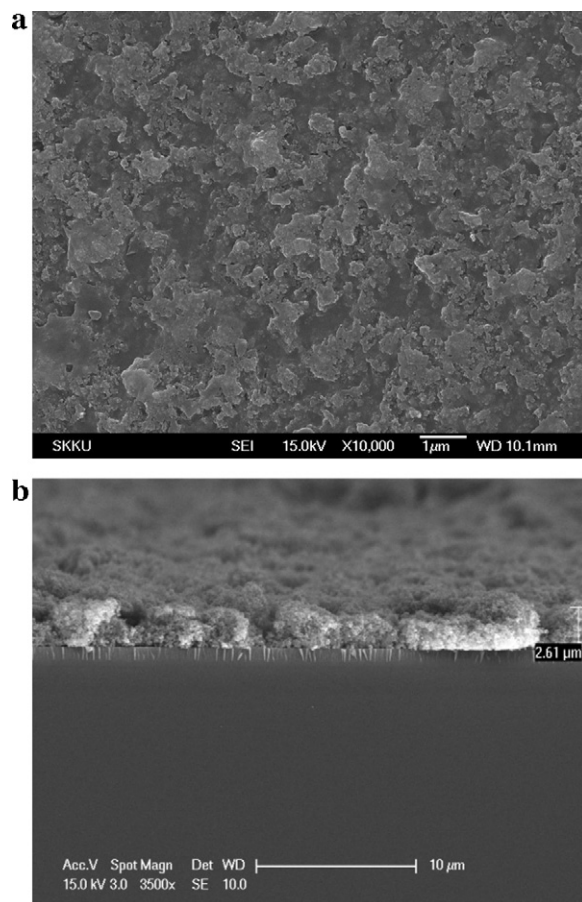


Fig. 6. SEM images of (a) the surface and (b) the thickness of the carbon-doped TiO₂ film on the optical fibers (magnification: (a) 10,000 \times and (b) 5000 \times).

The onset of the absorption spectrum of C-TiO₂ was higher than that of pure (undoped) TiO₂, as shown in Fig. 5. Additionally, the absorption spectrum of C-TiO₂ was stronger than that of the undoped TiO₂ in the UV-vis range. The onset of the absorption spectra of anatase-type and rutile-type TiO₂ appeared at about 387 nm and 413 nm, with a band gap of 3.2 eV and 3.0 eV, respectively [6].

3.1.4. Preparation of C-TiO₂ film

The C-TiO₂ film was immobilized by dip-coating, as shown in Fig. 6.

The C-TiO₂ film was prepared by a sol-gel combustion method and then coated onto the optical fibers. As shown in Fig. 6(a), the diameter of the TiO₂ particles was about 0.5–0.8 μm and some coagulation of TiO₂ was observed. In Fig. 6(b), the thickness of the TiO₂ film has been increased to 2.61 μm by dip-coating three times. Note that the RE was affected by the dispersion properties of the TiO₂ particles and the thickness of the TiO₂ film, which were controlled by the synthesis conditions, the coating method, and the sintering temperature.

3.2. Removal of gaseous styrene by the photoreactor with the C-TiO₂ film

Fig. 7 shows how the RE varied as a function of elapsed time while using the photoreactor containing the C-TiO₂ film.

The experiment was performed at 23 °C and 42 RH% and the input styrene concentration was kept constant at 490 mg m⁻³. The RE of the C-TiO₂ film was 80.1%, 82.3%, and 85.2% at 0.5 h, 1 h, and

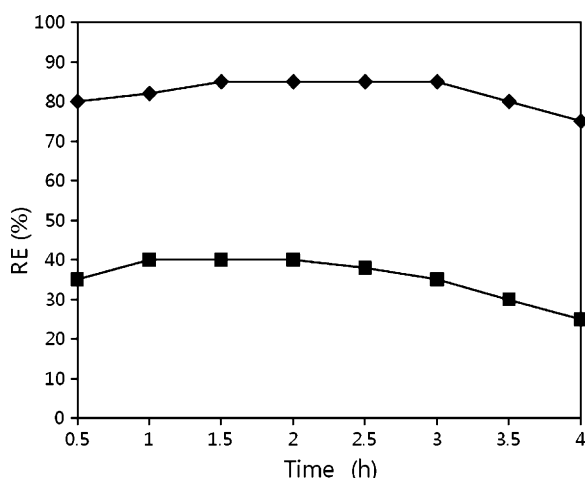


Fig. 7. Removal efficiency (RE) of gaseous styrene according to time in the photoreactor containing carbon-doped or pure (undoped) TiO₂ film at 42 RH% and 23 °C (◆: carbon-doped TiO₂ film; ■: pure (undoped) TiO₂ film).

1.5 h, respectively. After 1.5 h, it remained constant at 85.2% until 3 h, but then decreased to 80.2% at 3.5 h and further decreased to 75.1% at 4 h. For comparison, the RE of pure (undoped) TiO₂ film was 35.3% and 40.1% at 0.5 h and 1 h, respectively, after which it remained constant at 40.1% until 2 h. However, it then decreased to 38.3%, 35.1%, 30.2%, and 25.4% at 2 h, 3 h, 3.5 h, and 4 h, respectively. The average standard deviation (ASD) of the RE for pure TiO₂ film is 1.2% while it is 1.6% for C-TiO₂ film. The observed RE of the C-TiO₂ film was 113–200% higher than that of pure TiO₂ film for the period of time studied, indicating that C-TiO₂ film was more effective than pure TiO₂ film at photodegrading gaseous styrene. In other words, doping TiO₂ with carbon at a temperature of 600 °C greatly enhanced the RE and durability of the TiO₂ film. This observation follows that of another article [12] where methylene blue solution was photodegraded on carbon-doped TiO₂ sintered at temperatures of 400–800 °C, and the RE at a sintering temperature of 600 °C was found to be higher than that of any of the other sintering temperatures evaluated [12].

Nevertheless, gaseous styrene was not efficiently removed using only the photoreactor with the C-TiO₂ film. Outlet gases including styrene and by-products with a benzene ring were discharged to the biofilter. Styrene has been reported to be photodegraded to alkenes with a benzene ring [20]; more chemical compounds with a normal benzene ring (such as 2-phenylpropene, 1,3,5-cycloheptatriene, 1,4-cyclohexadiene) than with an opened benzene ring (such as 3-methylenecyclopropene) were observed in the current study. See Section 3.4 for a further discussion of the by-products.

3.3. Removal of gaseous styrene by a biofilter

The relationship between the EBRT and the RE of styrene with an input styrene concentration of 226 mg m⁻³ is shown in Fig. 8.

The REs of the gaseous styrene in the biofilter were 91.1% and 93.3% with EBRTs of 15 s and 20 s, respectively, while the ASDs of RE were 0.9%, 1.1%, and 0.7% at 15 s, 20 s, and 30 s of EBRT, respectively. The RE peaked at 95.2% at 30 s and remained nearly constant, even as the EBRT exceeded 30 s. It is, however, reasonable to recommend that one evaluate the system at an EBRT of 40 s instead of 30 s since an EBRT of 30 s is considered unstable as a point of inflection. Furthermore, a high EBRT is favorable for improving the RE because it increases the contact time between the microorganisms and the organic material [21]. Unfortunately, continuous operation of the biofilter was impeded by the fact that C-TiO₂ film

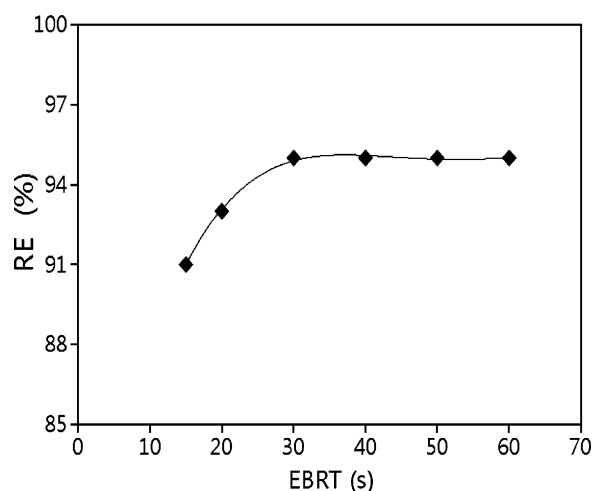


Fig. 8. Relationship between the empty bed retention time (EBRT) and removal efficiency (RE) of gaseous styrene by the biofilter.

should be changed to new one or reused by a sintering once every 2 weeks due to its sharp decline of photodegradation capability in the hybrid system comprising a reactor with C-TiO₂ film and a biofilter.

The elimination capacity (EC) at 15 s of EBRT was 22.1 g m⁻³ h⁻¹, and it increased to 25.2 g m⁻³ h⁻¹ in 20 s. However, it then decreased to 23.3 g m⁻³ h⁻¹ and then to 14.5 g m⁻³ h⁻¹ in 30 s and 60 s, respectively. That is, from the initial time until 20 s, both the EBRT and EC increased; yet, after 20 s, the EC decreased as the EBRT increased.

In the work of Rene et al. [3], the RE of styrene at 77 s of EBRT during the first 5 days was less than 20% and was reached about 100% on the 21th day. The EC was kept less than 10 g m⁻³ h⁻¹ during the period. In the study of Zilli et al. [22], the RE of gaseous styrene was nearly 100% on the 20th days at both 15 s and 7 s of EBRT. The EC was varied in the range from 24.5 g m⁻³ h⁻¹ to 48.8 g m⁻³ h⁻¹. In the article of Jung and Park [23], the RE was 94% at 120 s of EBRT and EC was less than 82.5 g m⁻³ h⁻¹. In conclusion, the RE at about 20 g m⁻³ h⁻¹ from the results was higher than those of Rene et al.'s and Jung and Park's works, however, lower than that of Zilli et al.'s work.

3.4. Removal of gaseous styrene by the hybrid system

Fig. 9 shows the styrene concentrations at the photoreactor exit and after passage through the 1st, 2nd, and 3rd stages of the biofilter, according to the inlet styrene concentration.

Three distinct inlet styrene concentrations were tested – one with 630 mg m⁻³, another with 420 mg m⁻³, and a final setup with 105 mg m⁻³. Each concentration utilized the hybrid system of a C-TiO₂ film photoreactor followed by three passes through the biofilter. In the first setup, the inlet styrene concentration of 630 mg m⁻³ decreased to 500 mg m⁻³ after passage of the styrene gas through the photoreactor. The concentration then decreased to 170 mg m⁻³, 85 mg m⁻³, and 42 mg m⁻³ after passage of the styrene gas through the 1st, 2nd, and 3rd stages of the biofilter, respectively. The RE was 20.6% through the photoreactor and increased to 93.3% after passage of the styrene gas through the biofilter. In the next setup, the inlet styrene concentration of 420 mg m⁻³ decreased to 295 mg m⁻³ after passage of the gas through the photoreactor, and then to 105 mg m⁻³, 42 mg m⁻³, and 13 mg m⁻³ after passage of the styrene gas through the 1st, 2nd, and 3rd stages of the biofilter, respectively. The RE was 29.8% after the photoreactor with the C-TiO₂ and 96.9% after the biofilter. In the final setup, the inlet styrene concentration of 105 mg m⁻³ decreased to 63 mg m⁻³ through the

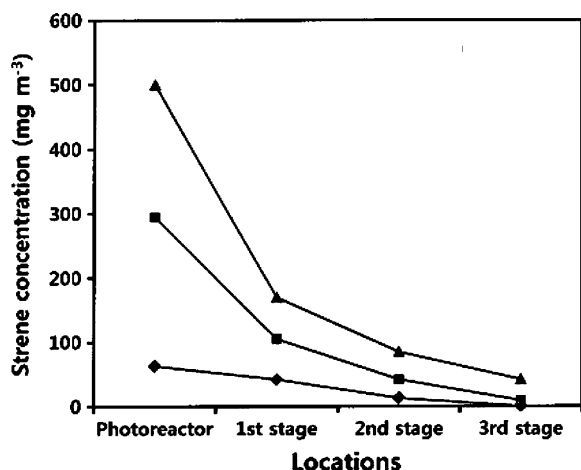


Fig. 9. Various measured concentrations of effluent styrene with respect to location in the hybrid system. Styrene concentrations in the photoreactor and in the 1st, 2nd, and 3rd stages of the biofilter are shown according to inlet styrene concentration (▲: 630 mg m⁻³; ■: 420 mg m⁻³; ◆: 105 mg m⁻³).

photoreactor, and then to 42 mg m⁻³, 13 mg m⁻³ and 1 mg m⁻³ through the 1st, 2nd, and 3rd stages of the biofilter, respectively. The RE of the photoreactor only was 40.0% whereas the addition of the biofilter resulted in 99.0% removal. The ASDs of RE were 2.2%, 0.9%, and 1.0% for inlet concentrations of 630 mg m⁻³, 420 mg m⁻³, and 105 mg m⁻³, respectively.

From this study, the hybrid system comprising a C-TiO₂ film photoreactor and a biofilter was found to have high removal efficiencies between 93.3 ~99.0% with input styrene concentrations of

630–105 mg m⁻³, keeping within the recommended TWA concentration limits of the USA and EU [2].

The by-products derived from the styrene after the photocatalytic oxidation and bio-oxidation are shown in Fig. 10.

A sample was collected from both the outlet of the photoreactor and the top of the biofilter, and the by-products derived from the styrene vapor were determined by GC/MS. Organic compounds derived from photocatalytic styrene oxidation were mostly (a) 2-phenylpropene, (b) 1,3,5-cycloheptatriene, (c) 1,4-cyclohexadiene, and (d) 3-methylenecyclopropene. The concentration of 2-phenylpropene was higher than that of any other by-products while the concentration of 3-methylenecyclopropene was the lowest. Most of the by-products from the photoreactor were organic compounds.

The major organic compounds produced by the hybrid system were (e) cyclohexane and (f) methyl alcohol. The concentration of methyl alcohol was higher than that of cyclohexane. Organic compounds with an open-ring structure produced by the photoreactor were readily degraded to CO₂, H₂O, methyl alcohol, and organic compounds with low molecular weight by the biofilter. However, unless the structure of the compounds with a closed-ring were changed to an open-ring by the photo-oxidation, they were not easily degraded to low molecular weight organic compounds such as methyl alcohol, but remained intact as compounds with a ring structure, such as cyclohexane. Therefore, the removal efficiency of gaseous styrene was more enhanced by the hybrid system composed of a photoreactor and a biofilter than by either of the two alone.

4. Conclusions

Our investigation of a hybrid system comprising a photoreactor containing carbon-doped TiO₂ film and a biofilter to remove gaseous styrene revealed the following:

The removal efficiency (RE) of gaseous styrene using carbon-doped TiO₂ (C-TiO₂) film was 113–200% higher than that of pure TiO₂ when the C-TiO₂ was prepared by a sol-gel combustion method at a sintering temperature of 600 °C.

The RE of the photoreactor with C-TiO₂ film only was 20.6%, 29.8% and 40.0% for input styrene concentrations of 630 mg m⁻³, 420 mg m⁻³, and 105 mg m⁻³, respectively. However, the RE increased to 93.3%, 97.9%, and 99.0% when the hybrid system consisting of a photoreactor and a biofilter was used.

Organic compounds derived from styrene after photoreaction were mostly 2-phenylpropene, 1,3,5-cycloheptatriene, 1,4-cyclohexadiene, and 3-methylenecyclopropene. In contrast, the main organic compounds produced in the hybrid system were cyclohexane and methyl alcohol.

Acknowledgement

This research was supported by a grant from Construction Technology Innovation Program funded by Ministry of Land, Transportation and Maritime Affairs of Korean government (Project No. 08-CTIP-B01).

References

- [1] R. Jothiralingam, M.K. Wang, Synthesis, characterization and photocatalytic activity of porous manganese oxide doped titania for toluene decomposition, *J. Hazard. Mater.* 147 (2007) 562–569.
- [2] M. Lim, V. Rudolph, M. Anpo, G.Q. Lu, Fluidized-bed photocatalytic degradation of airborne styrene, *Catal. Today* 131 (2008) 548–552.
- [3] E.R. Rene, M.E. Lopez, M.C. Veiga, C. Kennes, Performance of a fungal monolith bioreactor for the removal of styrene from polluted air, *Bioresour. Technol.* 101 (2010) 2608–2615.
- [4] O.H. Park, I.G. Jung, A model study based on experiments on toluene removal under high load condition in biofilters, *Biochem. Eng. J.* 28 (2006) 269–274.

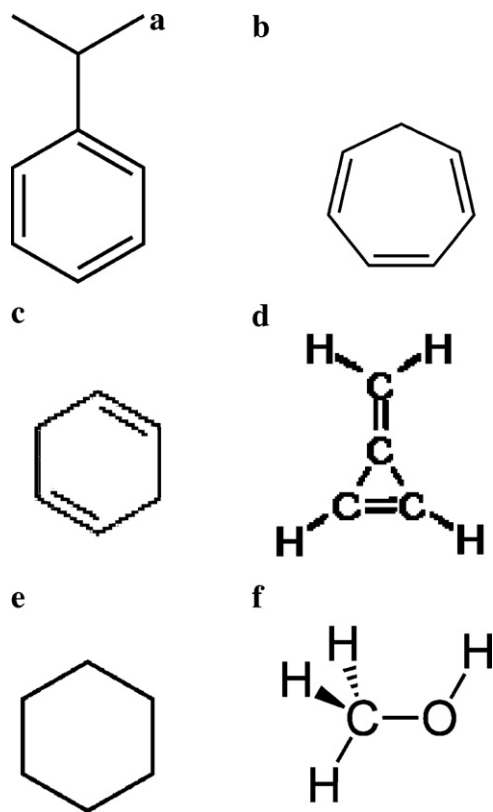


Fig. 10. By-products derived from styrene after photocatalytic oxidation ((a)–(d)) and through the hybrid system consisting of a photoreactor and a biofilter ((e) and (f)); (a) 2-phenylpropene, (b) 1,3,5-cycloheptatriene, (c) 1,4-cyclohexadiene, (d) 3-methylenecyclopropene, (e) cyclohexane, and (f) methyl alcohol.

- [5] G. Moussavi, M. Mohseni, Using UV pretreatment to enhance biofiltration of mixtures of aromatic VOCs, *J. Hazard. Mater.* 144 (2007) 59–66.
- [6] M. Shen, Z. Wu, H. Huang, Y. Du, Z. Zhigang, P. Yang, Carbon-doped anatase TiO₂ obtained from TiC for photocatalysis under visible light irradiation, *Mater. Lett.* 60 (2006) 693–697.
- [7] J. Falconer, K.A. Magrin-Bair, Photocatalytic and thermal catalytic oxidation of acetaldehyde on Pt/TiO₂, *J. Catal.* 179 (1998) 171–178.
- [8] T. Ohno, T. Tsubota, M. Toyofuku, R. Inaba, Photocatalytic activity of a TiO₂ photocatalyst doped with C⁴⁺ and S⁴⁺ ions having a rutile phase under visible light, *Catal. Lett.* 98 (2004) 255–258.
- [9] X. Hong, Z. Wang, W. Cai, F. Lu, J. Zhang, Y. Yang, N. Ma, Y. Liu, Visible-light-activated nanoparticle photocatalyst of iodine-doped titanium dioxide, *Chem. Mater.* 17 (2005) 1548–1552.
- [10] X. Wang, S. Meng, X. Zhang, H. Wang, W. Zhong, Q. Du, Multi-type carbon doping of TiO₂ photocatalyst, *Phys. Lett.* 444 (2007) 292–296.
- [11] W. Ren, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, Low temperature preparation and visible light photocatalytic activity of mesoporous carbon-doped crystalline TiO₂, *Appl. Catal. B: Environ.* 69 (2007) 138–144.
- [12] Q. Xiao, J. Zhang, C. Xiao, Z. Si, X. Tan, Solar photocatalytic degradation of methylene blue in carbon-doped TiO₂ nanoparticles suspension, *Sol. Energy* 82 (2008) 706–713.
- [13] A. Danion, J. Disdier, C. Guillard, N. Jaffrezic-Renault, Malic acid photocatalytic degradation using a TiO₂-coated optical fiber reactor, *J. Photochem. Photobiol. A: Chem.* 190 (2007) 135–140.
- [14] S.J. Jang, M.S. Kim, B.W. Kim, Photodegradation of DDT with the photodeposited ferric ion on the TiO₂ film, *Water Res.* 39 (2005) 2178–2188.
- [15] K.H. Ho, Y.C. Chung, Y.H. Lin, C.P. Tseng, Microbial population analysis and field application of biofilter for the removal of volatile-sulfur compounds from swine wastewater treatment system, *J. Hazard. Mater.* 152 (2008) 580–588.
- [16] A. Vergara-Fernandez, L.L. Molina, N.A. Pulido, G. Aroca, Effect of gas flow rate, inlet concentration and temperature on the biofiltration of toluene vapors, *J. Environ. Manage.* 84 (2007) 115–122.
- [17] Z.M. Shi, X.Y. Ye, K.M. Liang, S.R. Gu, F. Pan, XPS analysis of light elements (C, N) remaining in sol-gel derived TiO₂ films, *J. Mater. Sci. Lett.* 22 (2003) 1255–1258.
- [18] S.U.M. Khan, M. Al-Shahry, W.B. Ingler, Efficient photochemical water splitting by a chemically modified n-TiO₂, *Science* 297 (2002) 2243–2245.
- [19] G. Li, L. Chen, N.M. Dimitrijevic, K.A. Gray, Visible light photocatalytic properties of anion-doped TiO₂ materials prepared from a molecular titanium precursor, *Chem. Phys. Lett.* 451 (2008) 75–79.
- [20] S.I. Hirashima, Y. Kudo, T. Nobuta, N. Tada, A. Itoh, Aerobic photo-oxidative cleavage of the C–C double bonds of styrene, *Tetrahedron Lett.* 50 (2009) 4328–4330.
- [21] M.C. Delhomenie, L. Bibeau, N. Bredin, S. Roy, S. Broussau, R. Brzezinski, J.L. Kugelmass, M. Heitz, Biofiltration of air contaminated with toluene on a compost-based bed, *Adv. Environ. Res.* 6 (2002) 239–254.
- [22] M. Zilli, E. Palazzi, L. Sene, A. Converti, M.D. Borghi, Toluene and styrene removal from air in biofilters, *Process Biochem.* 37 (2001) 423–429.
- [23] I.G. Jung, C.H. Park, Characteristics of styrene degradation by *Rhodococcus pyridinovorans* isolated from a biofilter, *Chemosphere* 61 (2005) 451–456.