

Alternative Use of Light Emitting Diodes in an Activated Charcoal-Supported Photocatalyst Reactor for the Control of Volatile Organic Compounds

Sung-Bong YANG¹, Mee-Seon YU¹, Jong-Soon KIM², Wan-Kuen JO^{3,*}

¹Department of Chemistry, College of Natural Science, University of Ulsan, Ulsan, 680-749, Korea

²NGETech Inc, Busan, Korea

³Department of Environmental Engineering, Kyungpook National University, Daegu, 702-701, Korea

Abstract: The applicability of ultraviolet-light emitting diodes (LEDs) as a light source for photocatalysis using granular activated charcoal (GAC) impregnated with transition metal-enhanced photocatalysts for the control of volatile organic compounds (VOCs) was investigated. Two target compounds (toluene and methyl mercaptan) were selected to evaluate the removal activities of the TiO₂/GAC composites. The photocatalysts were prepared by a sol-gel method. Methyl trimethoxy silane was added as a precursor sol solution to bind the photocatalyst with the GAC. Metal (Zn²⁺, Fe³⁺, Ag⁺, and Cu²⁺) enhanced TiO₂/GAC composites were prepared and tested for their photocatalytic activities under 400 nm LED irradiation. The specific surface area (SSA) and the surface chemical composition of the prepared composites were investigated. The SSAs of all the impregnated composites were similar to those of pure GAC. Both field emission-scanning electron microscopy and energy dispersive spectroscopic analysis confirmed that titanium and the impregnated metals were deposited on the surface of the adsorbent. The breakthrough time for GAC toward toluene or methyl mercaptan gas increased upon photocatalytic impregnation and LED illumination. Using different binders affected the breakthrough time of the TiO₂/GAC composite and the addition of zinc oxide to TiO₂ increased the VOC removal capacity of the GAC composite.

Key words: granular activated charcoal; titania; sol-gel method; light emitting diode; surface chemical composition; zinc oxide

CLC number: O643

Document code: A

Received 22 November 2010. Accepted 24 January 2011.

*Corresponding author. Tel: +82-53-950-6584; Fax: +82-53-950-6579; E-mail: wkjo@knu.ac.kr

This work was supported by the Korea Institute of Environmental Science and Technology.

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

Volatile organic compounds (VOCs) in industrialized urban areas originate primarily from industrial processes such as petrochemical production, storage and distribution, solvent usage, and motor vehicle emissions [1,2]. These compounds are generally detected at high concentration levels in an industrialized urban atmosphere [1,3]. Many VOCs are toxic or potentially toxic to humans [4]. In addition, atmospheric VOCs act as precursors for the formation of secondary air pollutants such as ozone, aldehydes, and organic aerosols [5], and certain VOCs react with ozone to form secondary pollutants such as formaldehyde and organic aerosols [6]. These VOC characteristics require the control of emission sources to minimize health risks from environmental exposure.

Adsorption by activated charcoal (AC) has been widely used for the purification of industrial or non-industrial air streams containing VOCs because of its high pore volume and its large exposed surface area to volume ratios [7–9]. However, a limitation of the AC application to industrial

VOC controls is that upon saturation it needs to be exchanged for a new one or regenerated [10]. Recently, a photocatalytic process has been shown to be an alternative technique because it provides for the absolute reduction of environmental pollutants rather than transferring pollutants from the gas or water phase to the solid phase [11–13]. Moreover, photocatalytic decomposition is considered to be an attractive AC regeneration technique [14,15]. Because of their modular characteristics and the reactor's low pressure drop, photocatalytic reactors can easily be incorporated into existing AC systems. For example, Tao et al. [15] reported that TiO₂ loaded onto AC could be effectively applied to the regeneration of AC by methanol decomposition in pulp and paper mills as methanol is adsorbed on the surface of the adsorbent and the photocatalyst. This occurs without having a significant impact on the adsorption capacity of the AC.

Photocatalytic processes require light illumination for the activation of photocatalysts. Recently, light-emitting diodes (LEDs) have received an increasing amount of interest be-

cause they have several advantages over conventional light sources [16]. LEDs are more efficient in converting electricity into light because of their high quantum yields, which are close to unity resulting in low electricity consumption. Unlike other water pollution applications, LEDs have rarely been used for the photocatalysis of air pollutants [17,18]. Ghosh et al. [17] reported that LED performance was superior to sunlight and was similar to a conventional lamp for the photocatalytic oxidation of liquid-phase 4-chlorophenol. To the best of our knowledge, LEDs have not been used for the combined adsorption and heterogeneous photocatalysis of air pollutants. Accordingly, in this study we evaluated the application of UV-LEDs to various AC-supported photocatalysts for the removal of two VOCs (toluene and methyl mercaptan). Toluene was chosen as a model VOC because it belongs to a major VOC group that is frequently encountered in industrialized urban atmospheres [1,3]. Methyl mercaptan was investigated because it is a major odorous sulfur-containing compound with a low odor threshold value (5 ppm) and it has various adverse health effects [19,20]. We also examined the characteristics of the prepared TiO₂/GAC (GAC = granular activated charcoal) and metal-enhanced TiO₂/GAC composites using the Brunauer-Emmett-Teller (BET) method, field emission-scanning electron microscopy (FE-SEM), and energy dispersive spectroscopy (EDS).

1 Experimental

1.1 Preparation of catalyst samples

Two types of TiO₂ (TiO₂(I) and TiO₂(II)) and four types of metal-enhanced TiO₂ (Ag-enhanced TiO₂, Cu-enhanced TiO₂, Fe-enhanced TiO₂, and Zn-enhanced TiO₂) photocatalysts were prepared for this study. For the preparation of TiO₂(I) and TiO₂(II), a TiO₂ sol solution was initially prepared by hydrolyzing Ti(OPri)₄ (titanium tetraisopropoxide, Junsei, 99%). A 1.0 mol/L solution of Ti(OPri)₄ was added slowly to a deionized water/ethanol (Ducksan Pure Chem., 99.9%) solution containing 2 mol/L HCl (Junsei, 35%) or HNO₃ (Junsei, 60%–62%) while heating at 70–80 °C for 2 h. After cooling the sol solution containing the TiO₂ or metal/TiO₂ to room temperature, 0.50 mol/L methyltrimethoxy silane (MTMS, CH₃Si(OCH₃)₃, Aldrich) was added as a coupling agent. The addition of MTMS to the sol solution turned the transparent solution turbid and this solution is abbreviated as TiO₂(I). In addition, a portion of the MTMS was mixed with distilled water and alcohol and transformed into (CH₃SiO_{1.5})_n. This TiO₂ solution is designated TiO₂(II). The transformed silane acts as a binder for the preparation of the metal-impregnated TiO₂ solutions.

The four metal-enhanced TiO₂ photocatalysts were prepared following a procedure from previous studies [21–24]. Copper(II) acetylacetonate (C₁₀H₁₄CuO₄, Aldrich, 99%), iron(III) acetylacetonate (Fe(C₅H₈O₂)₃, Aldrich, 97%), zinc(II) acetylacetonate (Zn(C₅H₇O₂)₂, TCI), cobalt(III) acetylacetonate (Co(C₅H₈O₂)₃, Aldrich), and silver nitrate (AgNO₃, Junsei) were used for the impregnation of metals into TiO₂.

GAC (Hanil Green granular charcoal; 5-mm in length and 2.5-mm in diameter; before use, the GAC was oven-dried at 200 °C for 1 h) was impregnated with the prepared TiO₂(I), TiO₂(II), and metal-enhanced TiO₂ photocatalysts using a spray-coating method. A monolayer of the GAC was spread on a wide tray and a coating solution of TiO₂ or metal-enhanced TiO₂ (solid content 2%) was sprayed onto the GAC (10% by weight). The sprayed GAC was air-dried and heated in an oven at 200 °C for 1 h. Surface area and porosimetry measurements were carried out using a Micromeritics ASAP2010 apparatus. A field emission-scanning electron microscopy (FE-SEM) with energy dispersive spectroscopy (EDS) (FE-SEM, JEOL, JSM-6500F) was used to examine the surfaces of the TiO₂(I), TiO₂(II), and metal-enhanced TiO₂/GAC composites.

1.2 Experimental procedure

A schematic diagram for the experiments carried out in this study is shown in Fig. 1. A prepared photocatalyst/GAC composite was placed on the porous glass plate inside a glass cylinder (3.5-cm diameter and 20-cm height). The composite (0.1 g) was evenly spread onto the glass plate. 400-nm (MS-L510UVHU) and 365-nm (MS-C510UV-36) LEDs were used for the activation of the photocatalytic reaction. Their optical outputs are shown in Fig. 2. The 365 nm and 400 nm LEDs are 5 mm in diameter and had optical power outputs of 21–29 mW and 4–6 mW, respectively. The

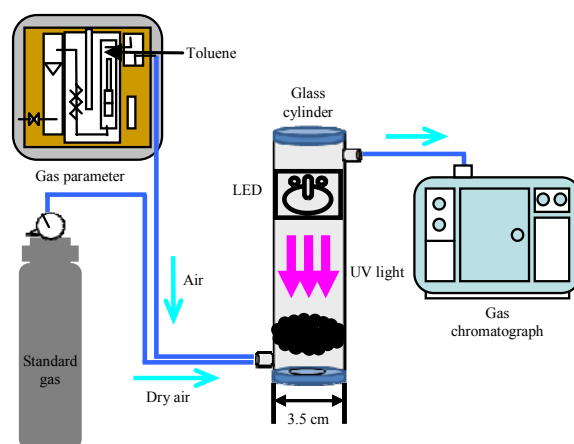


Fig. 1. Experimental setup.

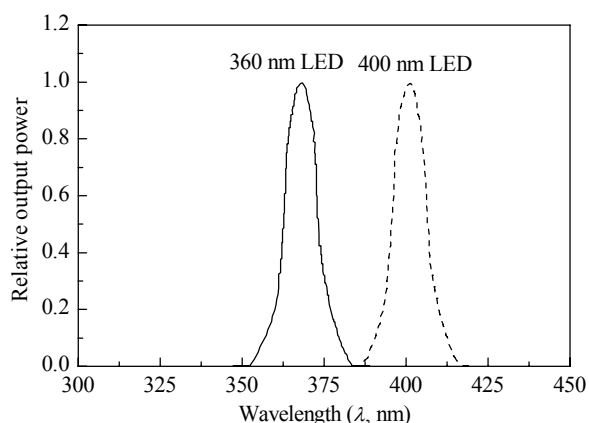


Fig. 2. Relative intensities of the UV LEDs. DC current 20 mA, temperature 25 °C.

distance from the GAC to the LED, which was suspended over the composite was 2.5 cm. The irradiative intensities were 0.6 mW/cm² and 0.12 mW/cm² for the 365-nm and 400-nm LEDs, respectively. Toluene (99.8%, Aldrich, 120 ppm) or methyl mercaptan gas (844 ppm, v/v in nitrogen, RIGAS) was supplied to the glass cylinder at a constant flow rate (220 ml/min). Toluene concentrations in the inlet and outlet air of the glass cylinder were measured using a gas chromatograph (GC)/flame ionization detector (Perkin Elmer Photovac). An aliquot of the air stream at the cylinder outlet was also taken periodically in a 1-ml gas-tight syringe for the analysis of byproducts, which were determined using a GC/mass selective detector (Varian 450GC/220MS). The concentration of methyl mercaptan in the inlet or outlet air was determined by sampling with a 1-ml gas-tight syringe and analysis by a GC/flame photoionization detector.

2 Results and discussion

2.1 Characterization of TiO₂/GAC and metal-enhanced TiO₂/GAC

The BET surface area, micropore (i.e. pore diameters < 2 nm) volume, and pore size of the TiO₂/GAC and metal-enhanced TiO₂/GAC composites are summarized in Table 1. The uncoated GAC was found to have a surface area of 1187 m²/g. The GAC composites that were obtained by spray-coating with the emulsion solution containing the catalysts and the silicone binder had slightly decreased surface areas between 1048 and 1168 m²/g, depending upon the composite type. Similarly, Tao et al. [15] reported that the surface area of a TiO₂/enhanced GAC (1380 m²/g) was less than that of pure GAC (1472 m²/g). However, they did not find that the coating process deteriorated the sorption abilities of GAC for the VOCs. The difference in surface area for the various composites can be attributed to that of the

Table 1 Physical properties of TiO₂(I)/GAC, TiO₂(II)/GAC, and the four metal-enhanced TiO₂/GAC composites

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
GAC	1187	0.58	1.97
TiO ₂ (I)/GAC	1168	0.53	1.97
TiO ₂ (II)/GAC	1048	0.50	1.90
Ag-TiO ₂ /GAC	1059	0.51	1.92
Cu-TiO ₂ /GAC	1063	0.52	1.87
Fe-TiO ₂ /GAC	1112	0.52	1.87
Zn-TiO ₂ /GAC	1077	0.44	1.80

raw GAC. The pore size and volume of each composite remained almost unchanged over the course of spraying and they showed tendencies similar to those of the above-mentioned surface areas. Therefore, considering all the data, the spray-coating solution did not influence the GAC surface area and thus the adsorption ability of TiO₂/GAC or metal/TiO₂/GAC and this ability did not decrease by spraying the sol solution onto the GAC. Similarly, Tao et al. [15] reported that the adsorption capacity of a GAC unit was almost identical to that of a TiO₂/GAC unit, which they prepared for the removal of BTEX and methanol.

The FE-SEM images suggest that the GACs that were enhanced with TiO₂(I), TiO₂(II), and metal-enhanced TiO₂ have similar porous structures (Fig. 3). The similar morphological structures of the composites are consistent with the SEM results of previous studies [15,25]. In these studies the surface characteristics of TiO₂ and TiO₂/GAC composites were investigated. Table 2 lists the weight percentages of each element in various composites as calculated from the EDS diagrams. The pure GAC mostly consisted of carbon and the detected Mg, Al, Si, Ca, and Fe come from impurities in GAC. However, for the other modified GACs the carbon percentages were lower than that found for the pure GAC. TiO₂(I)/GAC included up to 20% Ti and the other composites were composed of 1.7% to 2.8% Ti. This result suggests that TiO₂ particle aggregation increases on the GAC surface. For the TiO₂(II) composite, the reduced pore-size of methyl siloxane leads to a decrease in the particle size of TiO₂(II) compared to that of TiO₂(I), which results in a lower weight percentage of Ti. The Ag-enhanced TiO₂/GAC had the highest Ag weight percentage among the studied composites. Similarly, the Cu-enhanced TiO₂/GAC, the Fe-enhanced TiO₂/GAC, and the Zn-enhanced TiO₂/GAC had the highest Cu, Fe, and Zn weight percentages, respectively. This result is supported by the results of previous studies where the characteristics of metal-enhanced TiO₂ were determined [21–24].

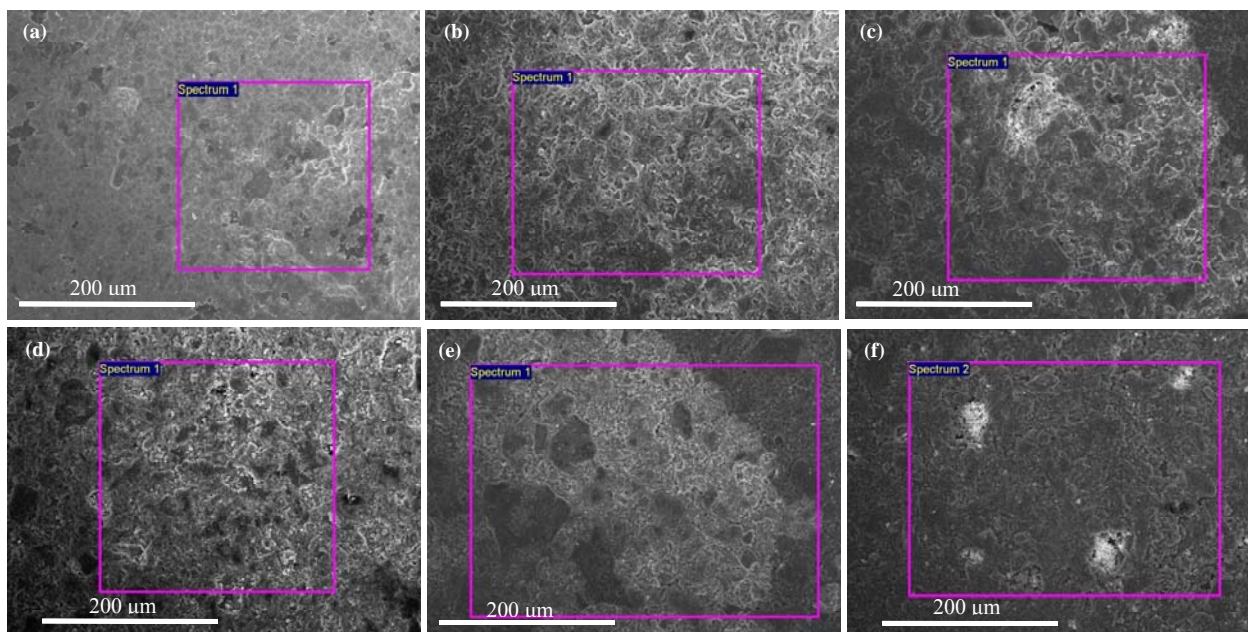


Fig. 3. FE-SEM photographs of different samples. (a) TiO₂(I)/GAC; (b) TiO₂(II)/GAC; (c) Ag-TiO₂/GAC; (d) Cu-TiO₂/GAC; (e) Fe-TiO₂/GAC; (f) Zn-TiO₂/GAC.

Table 2 Elemental composition of the GAC and the composites as measured by EDS

Sample	Elemental composition (%)										
	C	O	Mg	Al	Si	Ti	Ca	Fe	Ag	Cu	Zn
GAC	93	4.4	0.3	0.3	0.6	0	0.7	0.7	0	0	0
TiO ₂ (I)/GAC	51	28	0.3	0.3	0.2	20	0	0.2	0	0	0
TiO ₂ (II)/GAC	72	21	0.2	0.3	3.7	2.8	0	0	0	0	0
Ag-TiO ₂ /GAC	86	10	0.3	0.2	0.4	2.7	0	0	0.4	0	0
Cu-TiO ₂ /GAC	81	12	0.5	0.4	0.8	2.5	0.9	0.5	0	1.4	0
Fe-TiO ₂ /GAC	91	5.7	0.2	0.3	0.5	1.7	0	0.6	0	0	0
Zn-TiO ₂ /GAC	77	17	0.5	0.5	0.7	2.4	0.8	0.5	0	0	0.6

2.2 Removal efficiencies

To examine the photocatalytic activities of the TiO₂/GAC, the efficiency of toluene removal using the pure GAC and the TiO₂/GAC were determined (Fig. 4). At $t = 0$, the outlet toluene concentrations indicate a range of 38% to 50% of the inlet concentration (120 ppm), which means that about half the toluene passed through the cylinder without contacting the adsorbent. One reason that C at $t = 0$ was not equal to zero is that the adsorbent was spread loosely over the glass plate. Because photocatalytic oxidation occurs on the surface irradiated by UV-rays and to increase the adsorption capacity of each unit amount of the composite, the quantity of the composite used was minimized to just cover the surface of the glass plate; i.e., the GAC was not allowed to pile up. This procedure is supported by previous studies [15,25] wherein UV irradiated TiO₂ effectively regenerated the adsorption sites on the activated carbon.

Without illumination, both the GAC and TiO₂/GAC

composites gave immediate breakthroughs and about 1 h later these adsorbents were depleted. Upon 400 nm radiation with one LED lamp on the TiO₂(I) composite, the adsorption capacity increased and the breakthrough as well as depletion times of the absorption curve were extended to about 0.5 and 2.5 h, respectively. This confirmed that the TiO₂ catalyst on the surface of the GAC was activated by near UV (400 nm) radiation. By increasing the number of 400 nm LEDs from one to four, an increase in the depletion time was found for the composite and upon replacing binder I with binder II led to an increase in the lifetime of the composite. Smaller particle size TiO₂ has been postulated to be more photoactive than larger particle size TiO₂ because of a larger surface area [25].

Upon irradiation with a 360-nm LED lamp, the TiO₂(I)/GAC composite increased its adsorption capacity dramatically. The TiO₂(II) composite showed an adsorption curve similar to that of TiO₂(I). The price of LED lamps that emit wavelengths around 360 nm are about 10 times higher

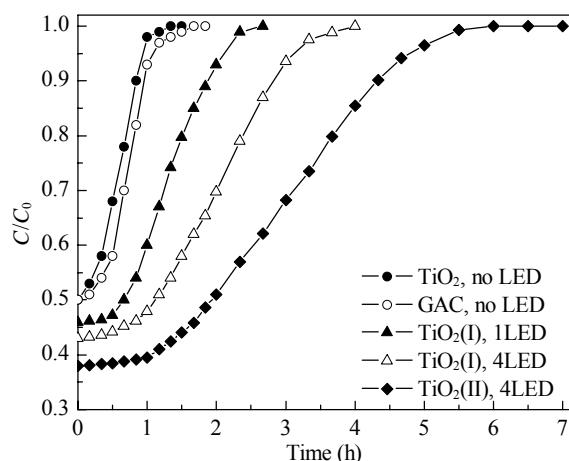


Fig. 4. Comparison of toluene removal by GAC and TiO₂/GAC under the 400 nm irradiation. C₀ and C represent inlet (120 ppm, ca. 220 ml/min) and outlet concentrations of toluene, respectively.

than those that emit around 400 nm. Although LED lamps are very useful for the fabrication of small abatement equipment and for maximizing the efficiency of VOC photooxidation, the high cost of shortwave LEDs prohibits their application in industry [26,27]. Therefore, in this study we investigated the maximum reactivity of TiO₂ at 400 nm instead of at < 380 nm upon the addition of transition metal ions to TiO₂. This wavelength shift is supported by previous studies wherein the UV-Vis diffuse reflectance spectra of metal-doped photocatalysts were obtained [21–24,28].

Figure 5 shows the toluene concentrations in the outlet stream from the cylinder filled with the different element-enhanced TiO₂/GAC under 400 nm LED irradiation. The addition of Fe³⁺, Cu²⁺, and Ag⁺ to TiO₂ had a negative effect on the adsorption capacities of the composite and for Zn²⁺, the Zn-enhanced TiO₂/GAC composite had almost the

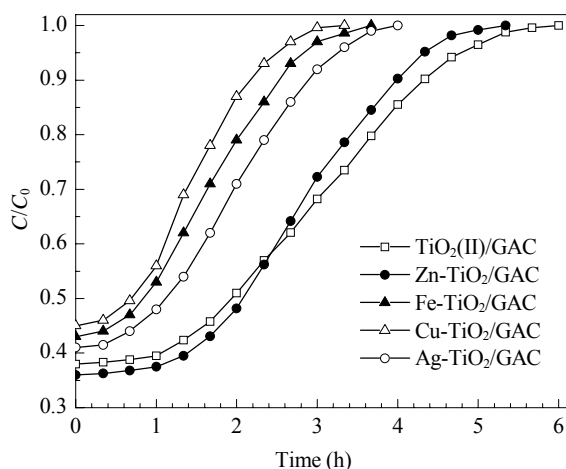


Fig. 5. Toluene concentration ratios of the inlet streams to the outlet streams upon passing through the metal-assisted composites upon 400 nm irradiation.

same adsorption curve as that of TiO₂(II)/GAC. Fe³⁺ and Cu²⁺ resulted in a red shift [29] and did not show such an effect. A few studies claim that the transition metals added to TiO₂ move the absorption edge to a longer wavelength [30–32]. The negative effects of transition metal addition on the adsorption capacities of the composites suggest that our metal doping procedure is different to that found in the literature [22]. Only zinc was found to improve the removal efficiency of the TiO₂/GAC composite. Although the reason is unclear, this pattern is likely due to the combined effects of the physical properties of the four types of metal-enhanced TiO₂/GAC (Table 1) and the elemental weights in the composites (Table 2). Previous studies [33,34] have reported an effective photocatalytic degradation of airborne toluene under conventional UV-lamp irradiation.

To evaluate the removal efficiencies of the prepared composites toward an odorous gas, methyl mercaptan was used as a model compound for the photoreaction. This compound is known to cause malodor in food waste and industrial wastewater [19,20]. Figure 6 shows that a certain ratio of outlet per inlet concentration of methyl mercaptan passed through the glass cylinder. The silver-enhanced TiO₂/GAC composite had the lowest adsorption capacity among the photocatalyst composites that were irradiated at 400 nm. Upon the addition of Fe or Cu, the depletion time of the corresponding composite was shortened slightly and we suggest that zinc increases the breakthrough time of the zinc-enhanced TiO₂/GAC composite. These results are likely due to the different characteristics of the surveyed transition metals (Ag, Fe, Cu, and Zn) as reported in previous studies [21–25]. Another possible cause is a photoadsorption effect of the composites. Nevertheless, further study is required to verify this assertion because various

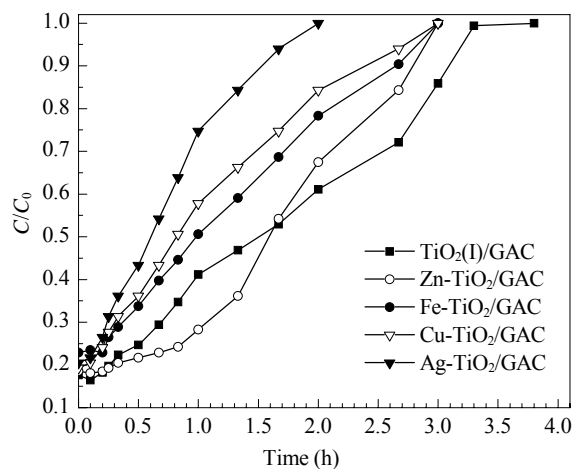


Fig. 6. Methyl mercaptan concentration ratios of the inlet streams to the outlet streams upon passing through the metal-assisted composites under 400 nm irradiation.

factors can influence their adsorption and photochemical activities.

3 Conclusions

LED lamps that emit UV wavelengths can increase the adsorption capacity of GAC upon impregnation with a TiO₂ photocatalyst or a TiO₂/co-catalyst. 400 nm irradiation is capable of activating ordinary TiO₂ photocatalysts and this dramatically increases the adsorption capacity of the adsorbent. The radiation from a 400 nm LED lamp revealed a large difference in TiO₂ photocatalytic activity depending on the crosslink agent. The particle size of the TiO₂ that was coated on the adsorbent was found to be an important parameter for the photodegradation activity of the composite. Transition metal ions added to TiO₂ could be activated with near UV radiation emitted by a low-cost 400 nm LED. However, the addition of metal ions did not have a positive effect but decreased the adsorption capacities compared with that of a simple TiO₂/GAC composite, except for zinc ion as a slight increase in the adsorption of both toluene and methyl mercaptan was found. Although impregnating the TiO₂ catalyst with transition metals did not increase the photodestruction efficiency toward VOCs with 400 nm LED radiation as much as with 360 nm irradiation, the TiO₂ impregnation of GAC increased the VOC adsorption capacity and prolonged the threshold and depletion time of the adsorbent. Further investigations into a safe, energy efficient, compact VOC abatement system are recommended to extend the renewal time to be substantially higher than that of the bare GAC using photocatalyst composites and tiny inexpensive LEDs.

Acknowledgements

The authors would like to thank the Korea Institute of Environmental Science and Technology for financially supporting this research.

References

- Cetin E, Odabasi M, Seyfioglu R. *Sci Total Environ*, 2003, **312**: 103
- Liu Y, Shao M, Fu L, Lu S, Zheng L, Tang D. *Atmos Environ*, 2008, **42**: 6247
- Roukos J, Riffault V, Locoge N, Plaisance H. *Environ Poll*, 2009, **157**: 3001
- OEHHA (Office of Environmental Health Hazard Assessment) Proposition 65 Status Report Safe Harbor Levels: No Significant Risk Levels for Carcinogens and Maximum Allowable Dose Levels for Chemicals Causing Reproductive Toxicity. California Environmental Protection Agency, OEHHA, Sacramento, CA, 2003
- Atkinson R, Arey J. *Atmos Environ*, 2003, **37**(suppl. 2): 197
- Destallats H, Lunden M M, Singer B C, Coleman B K, Dodgson A T, Weschler C J, Nazaroff W W. *Environ Sci Technol*, 2006, **40**: 4421
- Liu J, Huang Z H, Wang Z S, Kang F Y. *J Environ Sci-China*, 2004, **16**: 53
- Giraudet S, Pre P, Tezel H, Le Cloirec P. *Carbon*, 2006, **44**: 2413
- Sasaki T, Matsumoto A, Yamashita Y. *Colloid Surf A*, 2008, **325**: 166
- Yu F D, Luo L G, Grevillot G. *Chem Eng Proc*, 2007, **46**: 70
- Deveau P A, Arsac F, Thivel P X, Ferronato C, Delpech F, Chovelon J M, Kaluzny P, Monnet C. *J Hazard Mater*, 2007, **144**: 692
- Qi H, Sun D Zh, Chi G Q. *J Environ Sci-China*, 2007, **19**: 1136
- Li D P, Qu J H. *J Environ Sci-China*, 2009, **21**: 713
- Shiraishi F, Yamaguchi S, Ohbuchi Y. *Chem Eng Sci*, 2003, **58**: 929
- Tao Y, Wu C-Y, Mazyck D W. *Chemosphere*, 2006, **65**: 35
- http://en.wikipedia.org/wiki/Light-emitting_diode, 2010
- Ghosh J P, Langford C H, Achari G. *J Phys Chem A*, 2008, **112**: 10310
- Ghosh J P, Sui R, Langford C H, Achari G, Berlinguette C P. *Water Res*, 2009, **43**: 4499
- Tamai H, Nagoya H, Shiono T. *J Colloid Interf Sci*, 2006, **300**: 814
- Corrêa S M, Arbilla G. *Atmos Environ*, 2008, **42**: 6721
- Zhang X W, Zhou M H, Lei L C. *Mater Chem Phys*, 2005, **91**: 73
- Kim Y, Lee J, Jeong H, Lee Y, Umb M H, Jeong K M, Yeo M K, Kang M. *J Ind Eng Chem*, 2008, **14**: 396
- Araña J, Peña Alonso A, Doña Rodríguez J M, Herrera Melián J A, González Díaz O, Pérez Peña J. *Appl Catal B*, 2008, **78**: 355
- Melghit K, Bouziane K. *J Alloy Comp*, 2008, **453**: 102
- Ao Y H, Xu J J, Fu D G, Shen X W, Yuan C W. *Colloid Surf A*, 2008, **312**: 125
- Chen H W, Ku Y, Irawan A. *Chemosphere*, 2007, **69**: 184
- Matsumoto T, Iyi N, Kaneko Y, Kitamura K, Ishihara S, Takasu Y, Murakami Y. *Catal Today*, 2007, **120**: 226
- Yu J G, Xiang Q J, Zhou M H. *Appl Catal B*, 2009, **90**: 595
- Rehman S, Ullah R, Butt A M, Goher N D. *J Hazard Mater*, 2009, **170**: 560
- Yamashita H, Harada M, Misaka J, Takeuchi M, Ikeue K, Anpo M. *J Photochem Photobiol A*, 2002, **148**: 257
- Chen S F, Zhao W, Wei L, Zhang S J. *Appl Surf Sci*, 2008, **255**: 2478
- Zang X W, Lei L C. *Mater Lett*, 2008, **62**: 895
- Zhou M H, Yu J G, Liu S W, Zhai P C, Huang B B. *Appl Catal B*, 2009, **89**: 160
- Liu S W, Yu J G, Mann S. *J Phys Chem C*, 2009, **113**: 10712