Utilization of Element-doping Titania-impregnated Granular Activated Carbon in a Plug-flow System for Removal of BTEX

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1. INTRODUCTION

Monocyclic aromatic hydrocarbons (MAHs) such as benzene, toluene, ethyl benzene and xylene (BTEX) have been measured at high concentration levels in urban atmospheres, mainly as a result of human activities such as motor vehicle exhausts and other combustion processes utilizing fossil fuels, petroleum storage and distribution, solvent usage and other industrial processes (Brown et al., 2007; Buzcu and Fraser, 2006). Several researchers have also reported that MAH levels in urban air were higher than those of pristine or suburban air (Hoshi et al., 2008; Buzcu and Fraser, 2006). Atmospheric pollutants can penetrate indoors, thereby elevating the indoor concentration levels (Hänninen et al., 2004). Furthermore, indoor MAH levels can be further elevated by various indoor sources such as consumer products, cigarette smoke, and/or building materials (Jia et al., 2008; Kwon and Jo, 2007). Most MAHs are toxic (e.g. benzene) or potentially toxic to humans (e.g. toluene, ethyl benzene, and xylene) (IARC, 2004). These characteristics of MAHs warrant the development of controls to minimize the health risk from indoor as well as outdoor air exposure.

Activated carbon (AC) has been typically used as an adsorbent for the control of various air pollutants including MAHs because of its high pore volume and large exposed surface area to volume ratios (Sasaki et al., 2008; Giraudet et al., 2006; Lillo-Ródenas et al., 2005). However, many previous AC studies have dealt primarily with concentrations at high levels (typically more than 100 mg m⁻³), which is more typical of the air at industrial workplaces or chemical process stream than that associated with indoor air quality (IAQ). Extrapolation of adsorption performance data collected at concentrations much higher than the intended application may not be valid. This assertion suggests the need of AC application studies for the
removal of MAHs at IAQ levels.

Additionally, the use of AC systems alone has the limitation that the pollutants are not eliminated but only transferred to another phase with the consumed AC becoming hazardous waste itself. As such, the regeneration of AC is subsequently necessary for reuse of the AC thereby reducing the disposal cost. To overcome this disadvantage, an adsorbent coupled with other control methods can be utilized to remove environmental pollutants. Photocatalytic oxidation (PCO) has been considered as an attractive AC regeneration technique (Kim et al., 2006; Tao et al., 2006; Shiraishi et al., 2003). PCO provides a reduction of absolute toxicity as the gaseous products from the complete PCO of toxic hydrocarbons are carbon dioxide and water (Hunger et al., 2010; Boulinguiez et al., 2008; Han et al., 2008; Fukahori et al., 2007). Due to their modular characteristics and low pressure drop across the reactor, PCO reactors can easily be incorporated into existing AC systems. For example, Areerachakul et al. (2007) demonstrated that a granular AC adsorption-photocatalysis hybrid system resulted in higher removal efficiency of herbicides from water compared to just a photocatalysis system alone (without the pre-adsorption).

Moreover, in order to overcome the main drawback of TiO2 which exhibits photocatalytic activity only in the near UV region, other researchers (Demeestere et al., 2005; Ohno et al., 2004) have employed S-doped TiO2 to enhance light absorption and photocatalytic activity under visible-light irradiation. Besides several water pollution applications, the combined technique of granular AC (GAC) and visible light induced photocatalysis with S-doped photocatalysts of air pollutants has rarely been reported (Areerachakul et al., 2007). Consequently, the present study investigated the feasibility of applying the combined system of GAC with S-doped visible-light-induced TiO2 (GAC/S-doped TiO2) to clean gas-phase MAHs. This was done with concentrations at \( \leq 3 \text{ mg m}^{-3} \), using a plug-flow reactor (annular-type reactor), which provides a well-characterized reactive catalyst surface along the length of the reactor body and allows for uniform light distribution (Mo et al., 2005).

2. EXPERIMENTAL METHODS

2.1 Experimental Set-Up

The experimental set-up consisted of a pure dried air supply system, a humidification unit, a standard injection unit, and a plug-flow Pyrex reactor (Fig. 1). Dried air was supplied from a zero-grade air cylinder with a two-stage pressure regulator. This air was further cleaned for hydrocarbons by passing it through an activated carbon filter normally used for gas chromatograph (GC). The pure dried air was humidified by passing the zero-grade air through a humidification device in a water bath (Cole-Parmer HAAKE W26). The temperature of the water bath was fixed at 35°C. The relative humidity (RH) of the zero-grade air was measured, immediately prior to entering the inlet valve on the Pyrex reactor using a humidity meter (Thermo Recorder TR-72S, T & D Co.). Then, the humidified air was mixed with standard MAHs in a heated 500-mL bulb. The desired concentrations were achieved through the use of a syringe pump (KdScientific Model 210). Finally, the gas flowed through the annular region.
of the Pyrex reactor. The flow rate (FR) was measured using identical rotameters (0-10 L minute^-1) calibrated against a dry test meter (URG 3000-020C).

The Pyrex reactor had annular geometry, and a cylindrical UV light source was inserted inside the glass tube and served as the inner surface of the annular reactor. The hydraulic diameter of the PCO reactor (defined as the inside diameter of the annular reactor tube minus the outside diameter of the lamp) was 5 mm. 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 hydraulic diameter of the reactor using a Digital Lux Meter (INS Model DX-100) was 1.8 mW cm^-2. The annular region of this reactor was filled with a commercially-available GAC prepared from a coconut shell (Samchully Activated Carbon, Korea) or GAC/S-doped TiO2. Handling the GAC/S-doped TiO2 prepared using a dip-desiccation method, which was previously used for GAC/TiO2 by other researchers (Liu et al., 2007; Tao et al., 2006). The sulfur element was impregnated into the TiO2 photocatalysts (Degussa P-25) following a procedure previously described (Jo and Kim, 2008; Ohno et al., 2004). GAC was washed with ultra-pure water and dried at 105 °C for 2 h prior to use. It was immersed into water suspended with the prepared S-doped TiO2 for 2 h with sonification and was then dried at 105 °C for 3 h. The amount of coated S-doped TiO2 was determined by the weight difference before and after the coating procedure.

2.2 Study Protocol

This study consisted of three different experiments: an adsorption test of pure GAC and GAC/S-doped TiO2; a long-term adsorptional photocatalytic (AP) activity test of GAC/S-doped TiO2; and an AP activity test of GAC/S-doped TiO2 under different conditions. The adsorption or AP efficiency was calculated by comparing the concentrations measured at the inlet and outlet of each reactor. In the absence of visible-light, the adsorption test was performed for two different weights (0.9 and 4.4 g) of pure GAC and GAC/S-doped TiO2. Another adsorption test was done for 0.9 g of GAC/S-doped TiO2 in order to investigate if the adsorption efficiency varies for the three different FRs (0.5, 1, and 2 L min^-1). The individual input concentration (IC) of the target MAHs (benzene, toluene, ethyl benzene, m,p-xylene, and o-xylene) was constant at 1 mg m^-3. RH was 50-55%, which is within the ASHRAE (arts and sciences of heating, ventilation, air-conditioning and refrigeration) comfort range. The long-term test of GAC/S-doped TiO2 was conducted in both the absence and presence of visible light. For this test, IC, RH, and FR were adjusted to 1 mg m^-3, 50-55% and 1 L min^-1, respectively. The weight of the GAC/S-doped TiO2 used was 0.9 g. For the third AP activity test, three parameters were evaluated: the weights of the GAC/S-doped TiO2 (0.9, 4.4, and 8.9 g); the FRs (0.5, 1 and 2 L min^-1); and the ICs of the target MAHs (0.1, 1, 2 and 3 mg m^-3). TiO2 weights for 0.9, 4.4, and 8.9 g of GAC/S-doped TiO2 were 47, 246, and 521 mg g^-1, respectively.

2.3 Sampling and Analysis

A series of samples regarding the target MAHs were collected at both the inlet and outlet of the reactor in the absence and presence of visible-light, over specified experimental periods. Sampling was done by filling an evacuated 5 L Tedlar bag at a constant flow rate. Air was then drawn through a sorbent trap containing 0.2 grams of Tenax TA and 0.2 gram of carboxen 569, using a constant flow-sampling pump (A.P. Buck Inc. Model I.H). Sampling times varied from one to five minutes depending on the flow rate. All samples were collected at ambient room temperature (19-25°C), and the FRs were recorded at between 0.1 and 1 L min^-1. The FR range and sampling volume did not have any breakthrough problems. The target compounds collected on the sorbent trap were analyzed by coupling a thermal desorption system (Donam SPIS TD-2) to a GC (Hewlett Packard 5890) in conjunction with a flame ionization detector (HP 5890II), by using a 0.32-mm-i.d. by 60-m-length fused silica column (Supelco Co. SPB-5).

The quality assurance/quality control program regarding the measurement of the target MAHs included laboratory blank traps and spiked samples. At the beginning of the day, a laboratory blank trap was analyzed to monitor any trap contamination. An external standard, prepared by following the same procedures according to the calibration standards, was analyzed daily in order to monitor the quantitative response. When the daily quantitative response differed by more than ±15% from that predicted by the specified calibration equation, a new calibration equation was determined. The method detection limits ranged from 0.3 to 2.6 μg m^-3 depending on the target MAHs.

3. RESULTS AND DISCUSSION

3.1 Adsorption Efficiencies of Pure GAC and GAC/S-Doped TiO2

In the absence of visible-light, the adsorption effici-
for the target MAHs were investigated. Fig. 2 exhibits
the adsorption efficiencies of the target MAHs deter-
mined via both the pure GAC and GAC/S-doped TiO$_2$
reactors filled with 0.9 g in each reactor. The adsorption
efficiencies for the two reactors were similar with
around 80% and between 90 and 100% adsorption for
benzene and the other target MAHs, respectively. In
addition, for 4.4 g of GAC or GAC/S-doped TiO$_2$, the
adsorption efficiencies were also similar for the two
reactors, although they were slightly higher for m,p-
xylene and o-xylene compared to the low weight of

Fig. 2. Adsorption efficiencies (%) of target MAHs (benzene, toluene, ethyl benzene, m,p-xylene, and o-xylene) by pure granular activated carbon (GAC) and GAC with S-doped visible-light-induced TiO$_2$ (GAC/S-doped TiO$_2$) reactors filled with 0.9 g in each reactor.
GAC or GAC/S-doped TiO$_2$ (Fig. 3). The similarity in adsorption efficiencies for the two reactors suggests that the TiO$_2$ particles on the GAC surfaces do not significantly interfere with the adsorption capacity of GAC. Previous studies (Tao et al., 2006; Ao and Lee, 2003) also reported that the adsorption capacity of the GAC unit was almost identical to that of the GAC/ pure TiO$_2$ reactor for the removal of BTEX and methanol.

It is noteworthy that the adsorption efficiency of benzene was lower than those of the other target compounds. This result can be explained by the decrease in solubility and increase in molecular weight (Dai...
fullah and Girgis, 2003). Meanwhile, the adsorption efficiencies of the GAC/S-doped TiO₂ did not significantly varied with the variation of the FRs (Fig. 4). This suggests that, under the experimental conditions of this study, FR is not an important parameter for the adsorption process of GAC/S-doped TiO₂.

**3.2 Long-Term AP Efficiencies by GAC/S-Doped TiO₂**

The AP efficiencies of the GAC/S-doped TiO₂ reactor over a long-term period (185 h) were determined for the target MAHs in both the absence and presence of visible-light in order to identify if the GAC/S-doped TiO₂ reactor has any AP activities. Regardless of the

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**Fig. 4.** Adsorption efficiencies (%) of target MAHs (benzene, toluene, ethyl benzene, m,p-xylene, and o-xylene) by GAC with S-doped visible-light-induced TiO₂, according to flow rates.
availability of visible-light, the removal efficiencies for toluene, ethyl benzene, m,p-xylene, and o-xylene were all well above 90% over the 185-h time period (Fig. 5), suggesting that there was no significant AP activity for the GAC/S-doped TiO$_2$ reactor. For benzene, however, the removal efficiency of the GAC/S-doped TiO$_2$ reactor in the presence of visible-light was 70%, whereas it was 40% for those with the absence of visible-light. Therefore, for benzene, the removal capability of the GAC/S-doped TiO$_2$ reactor in the presence of visible-light was superior to that with the absence of visible-light. A possible explanation for this difference is that the S-doped TiO$_2$ embedded into GAC could photo-catalytically destroy benzene in the presence of visible light and thus at least, partially regenerate the GAC in situ. Similarly, other studies

Fig. 5. Long-term AP efficiencies via GAC with S-doped visible-light-induced TiO$_2$ in the absence and presence of visible-light.
(Tao et al., 2006; Ao and Lee, 2003) found that pure TiO$_2$ embedded into GAC in the presence of UV-light could enhance the removal efficiencies of BTEX and methanol compared to GAC alone or a GAC/TiO$_2$ unit in the absence of UV light. However, it was noted that, unlike the other target compounds, benzene concentrations decreased gradually after 70 to 80 h, even when the light source was activated. This result is supported by d’Hennezel and Ollis (1997), who reported that the photocatalytic oxidation rate of benzene was lower compared to the other compounds. Consequently, the present study performed further experiments to evaluate the AP of the other target MAHs as well as benzene with the GAC/S-doped TiO$_2$ reactor.

Fig. 6. AP efficiencies (%) of target MAHs (benzene, toluene, ethyl benzene, m,p-xylene, and o-xylene) by GAC with S-doped visible-light-induced TiO$_2$, according to the amounts filled into Pyrex reactor.
under different operational conditions.

3.3 Adsorptional Photocatalytic (AP) Activity of GAC/S-Doped TiO$_2$

The potential AP activities of GAC/S-doped TiO$_2$ for the target MAHs were further evaluated under different operational conditions. The operational parameters tested in this study included various weights of GAC/S-doped TiO$_2$, FRs, and ICs. Three different weights (0.9, 4.9, and 8.9 g) were evaluated for MAH AP efficiencies under visible-light irradiation. The time-series AP efficiencies over a 7-h period are represented, according to weight, in Fig. 6. The AP efficiency for benzene increased slightly as the weight
increased from 0.9 to 4.4 g. Generally, however, the AP efficiencies for the target MAHs did not significantly vary with an increase in weight, thereby suggesting that, under the weight range tested in this study, the weights are not an important parameter for the AP efficiency.

Fig. 7 shows the AP efficiencies of the target MAHs determined by GAC/S-doped TiO$_2$ for visible-light irradiation, according to the flow rates. Although for benzene the AP efficiency for the lowest FR (0.5 L min$^{-1}$) was higher than that for the two other higher FRs, FR dependency was not significant. In addition, the other target compounds exhibited a similar pattern to that of benzene or an increasing pattern as FR increased. This suggests that, under the FR range of this study, FR is not an important parameter for AP efficiency.

Fig. 8. AP efficiencies (%) of target MAHs (benzene, toluene, ethyl benzene, m,p-xylene, and o-xylene) by GAC with S-doped visible-light-induced TiO$_2$, according to input concentrations.
processes.

The AP efficiencies of the target MAHs determined by GAC/S-doped TiO$_2$ at four different ICs (0.1, 1, 2, and 3 mg m$^{-3}$) under visible-light irradiation are presented in Fig. 8. Generally, the AP efficiencies of the target MAHs decreased as IC increased. This IC dependency is likely due to the increased competition between pollutant molecules for the adsorption sites of AC under a high concentration input condition. This result is supported by a previous study (Giraudet et al., 2006) in that the adsorption capacity of the AC decreased with increasing IC of several volatile organic compounds.

4. CONCLUSIONS

The present study investigated the feasibility of applying a combined system of GAC/S-doped TiO$_2$ to clean gas-phase MAHs with concentration at low levels ($\leq$3 mg m$^{-3}$). An adsorption test suggested that S-doped TiO$_2$ particles on GAC surfaces do not significantly influence the adsorption capacity of GAC. In addition, the long-term AP test indicated that the S-doped TiO$_2$ embedded into GAC can photo-catalytically destroy benzene in the presence of visible light and thus at least partially, regenerate the GAC in situ. An activity test of GAC/S-doped TiO$_2$, which was performed under various conditions, exhibited that the ICs are important parameters for AP processes, whereas the FRs or the weights of GAC/S-doped TiO$_2$ are not.

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