



Removal of dimethyl sulfide utilizing activated carbon fiber-supported photocatalyst in continuous-flow system

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ABSTRACT

The present study investigated the adsorptional photocatalytic decomposition (APD) efficiency of activated carbon fiber-supported TiO_2 (ACF/ TiO_2) in a continuous-flow reactor for the removal of dimethyl sulfide (DMS). The SEM analysis identified that the ACF/ TiO_2 exhibited the same tridimensional shape as uncovered ACF and that a TiO_2 photocatalyst could be embedded in the surface of the ACF. In the absence of UV light, the time-series removal efficiencies by ACF and the ACF/ TiO_2 units exhibited a similar pattern, which decreased gradually as it reached close to zero. However, the APD efficiency determined via the ACF/ TiO_2 with UV light remained at nearly 60% during the remaining courses of the 13-h period, after decreasing from a maximum APD of 80%. The APD efficiencies depended upon the weights of the TiO_2 embedded into the ACFs, the UV sources, the relative humidity, and DMS input concentrations. During a long-term (219-h) APD test, the APD efficiencies dropped from 80% to ca 60% within 1 h after the initiation of the APD process and then fluctuated between 52% and 60%. No byproducts were measurable or observable in the effluent gas or on the ACF/ TiO_2 surface. Consequently, the continuous-flow ACF/ TiO_2 system could effectively be applied to control DMS without any significant functional deterioration.

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1. Introduction

Activated carbon (AC) has been typically employed as an adsorbent for the control of various environmental pollutants because of its high pore volume and large exposed surface area to volume ratios [1–3]. However, the use of AC systems alone has a limitation in that, by adsorption, the pollutants are not eliminated but instead transferred to another phase, and the consumed AC becomes hazardous waste. Photocatalysis, which oxidizes most organic pollutants to CO_2 and H_2O , using a semiconductor such as TiO_2 , has become a promising alternative for air pollution remediation [4–6]. Still, issues remain unanswered in the application of this technique. One key issue is the dependence of photocatalytic oxidation (PCO) efficiency upon environmental conditions such as humidity and treatment concentrations [7,8]. To overcome this disadvantage, several studies [7,9,10] utilized an AC system coupled with a PCO unit and reported that a fixed-bed granular AC (GAC)-supported TiO_2 photocatalyst could enhance the removal efficiency (RE) of several organic compounds, in regards to various environmental conditions. GAC supports the TiO_2 powder by concentrating the pollutants and intermediates around the TiO_2 . These pollutants and intermediates can migrate to the surface of TiO_2 via

diffusion. GAC also reduces TiO_2 coagulation, which reduces its surface, thereby reducing its catalytic effectiveness [11]. In addition, the TiO_2 can destroy the pollutants, leading to the regeneration of GAC in situ [7,9].

AC fiber (ACF) is a newly developed type of photocatalyst support material consisting of nanographites. Compared to GAC, ACF has a larger specific surface area, a superior rate of adsorption and desorption, and a faster attainment of adsorption equilibrium. Nevertheless, the ACF-supported TiO_2 photocatalyst (ACF/ TiO_2) has rarely been used for the removal of gas-phase environmental pollutants [12]. Moreover, most adsorbent-supported photocatalytic studies were conducted in a batch or closed-circulation reactor with a residence time of at least 15 min. Unlike these studies, the present study was performed to utilize a continuous-flow reactor with ACF/ TiO_2 for the removal of dimethyl sulfide (DMS) under various operational conditions. The residence time for the continuous-flow reactor (<0.05 min) was much less than those of previous studies. The target compound, DMS, is one of the main volatile organic sulfur compounds (VOSCs) that are commonly measured in atmospheric environments adjacent to anthropogenic sources [13,14] with an odor threshold value of 0.0006–0.04 ppm [15]. DMS and other VOSCs are emitted from various anthropogenic sources such as chemical plants, tanneries, food processing operations, Kraft paper pulping processes, sewage and industrial wastewater treatment plants, and animal feces fermentation treatment processes in the livestock industry [14,16]. These emissions

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can lead to strong odors in the communities in which the sources are located [14,17], warranting the control of the malodorous DMS.

2. Experimental

2.1. Preparation and characterization of ACF/TiO₂

ACF/TiO₂ was prepared using a dip-desiccation method that has been employed for GAC/TiO₂ by other researchers [7,12,18]. Viscose rayon-based ACF (Korean Activated Carbon Fiber) in the form of felt was washed with ultra-pure water and dried at 105 °C for 3 h prior to use. A commercially available TiO₂ (Degussa P25), which is composed of nonporous polyhedral geometry with a 30 nm diameter and a specific surface area of 50 m² g⁻¹, was utilized as a photocatalyst without any pretreatment. A piece of ACF with a dimension of 59 mm × 110 mm × 1 mm was immersed in a water suspension with TiO₂ for 2 h, under ultrasonic conditions, and then dried at 105 °C for 3 h. ACFs coated with six different weights of TiO₂ (7, 11, 21, 25, 106, 429 and 451 mg ACF-g⁻¹) were prepared by immersing them in water suspensions with six different amounts of TiO₂. The amount of TiO₂ coating was determined by the weight difference of the ACFs between before and after the coating procedure. This prepared ACF/TiO₂, along with pure ACF, was characterized using a Hitachi S-4300&EDX-350 FE-SEM at an acceleration voltage of 15 kV.

2.2. Adsorption test

Adsorption tests of pure ACF and ACF/TiO₂ for DMS were performed to examine whether TiO₂ embedded in the surface of the ACF would influence the adsorption capacity of the original ACF. Either ACF or ACF/TiO₂ was placed along the annular region of a 26.5 cm long Pyrex tube with a hydraulic diameter (HD, defined as the inside diameter of the cylindrical tube minus the outside diameter of the lamp) of 0.5 cm and a cylindrical UV light source inserted inside the tube, served as the inner surface of the annular tube. The gas flowed through the ACF-loaded annular region. This design is particularly suited for research because it provides a well-characterized ACF or ACF/TiO₂ surface along the length of the Pyrex tube body and allows for uniform light distribution. Moreover, the Pyrex tube inlet was designed to direct the flow of incoming air toward the light source in order to increase the air turbulence inside the tube, thereby enhancing the distribution of the target compound onto the ACF or ACF/TiO₂ inside the tube. However, these adsorption tests were conducted in dark conditions.

Humidified air containing DMS (a concentration of 0.5 ppm) was passed, at room temperature, continuously through the ACF/TiO₂ reactor at a rate of 1 L min⁻¹. A relative humidity (RH) range between 50% and 55% was adjusted by passing zero-grade air through a humidification device in a water bath (Cole-Parmer HAAKE W26). The RH was measured just prior to the insertion of the stainless steel-tube inlet using a humidity meter (Thermo Recorder TR-72S, T & D Co.). The desired input concentration (IC) was achieved through the use of a syringe pump (KdScientific Model 210). The flow rate (FR) measurements were carried out using identical rotameters (0–10 L min⁻¹) calibrated against a dry test meter (URG 3000-020C). The weight of the TiO₂ embedded into the ACF was 451 mg ACF-g⁻¹. Gaseous samples were collected at the inlet and outlet of the ACF/TiO₂ reactor, until a saturation of ACF or ACF/TiO₂ was noted, with an interval of either 1 or 2 h.

2.3. Removal test of DMS using ACF/TiO₂

A series of experiments were performed to evaluate the DMS APD efficiencies of ACF/TiO₂ by following the procedure applied

to the adsorption test, under various operational conditions. However, these experiments included utilizing a UV lamp in order to photo-activate the photocatalyst surface. Gaseous samples were collected at the inlet and outlet of the ACF/TiO₂ reactor over either a 9- or 20-h time period, with an interval of either 1 or 2 h. The operational parameters tested in this study included the weights of TiO₂ embedded in the ACFs, UV sources, RH, and DMS ICs. Six weights of TiO₂ (7, 11, 21, 25, 106, and 429 mg ACF-g⁻¹) were tested for the DMS removal of ACF/TiO₂. The UV radiation was supplied by either an 8-W germicidal lamp (Sankyo Denki, F40T8GL) with a maximum spectral intensity at 254 nm or an 8-W fluorescent black light (Sankyo Denki F8T5/BLB) with a maximum spectral intensity at 352 nm. The RH ranges for the experiments were 20–90% (20–25%, 50–55%, and 85–90%). The ICs surveyed for this study included 0.1, 0.5, 1.0, 5.0, and 10 ppm. For each parameter test, the other parameters were all fixed at representative values: weight of TiO₂, 7 mg ACF-g⁻¹; RH, within the American Society of Heating, Refrigerating and Air Conditioning Engineers comfort range (50–55%); DMS IC: 0.5 ppm; HD: 0.5 cm; and FR: 1 L min⁻¹. In addition, the representative UV-light source was an 8-W fluorescent black light. The representative values of HD and FR provided an empty bed contact time (EBCT) of 2.8 s. The experiments were repeated three times for each experimental condition, and the repeated experiments showed similar patterns. Thus, average values were presented for all experimental conditions.

To test the long-term stability of ACF/TiO₂ for DMS removal, an additional DMS removal test was conducted over a 219-h time period under representative experimental conditions. This system was continuously operated for the specified survey period, and the inlet and outlet air samples were collected at time intervals between 0.5 and 24 h.

2.4. Measurements

For measurements of DMS and any reaction byproducts, which can be generated during a PCO process, air samples were collected by filling an evacuated 5-L Tedlar bag at a constant FR. Organic compounds were analyzed by coupling a three-stage cryogenic trapping pre-concentration unit (Entech Model 7100, Entech Instruments Inc.) with a gas chromatograph (Agilent 7890A Series, Agilent Technologies) with a flame ionization detector. In addition, this study attempted to determine potential chemicals adsorbed on the ACF/TiO₂ surface. The surfaces of used ACF/TiO₂, in conjunction with pure ACF/TiO₂, were characterized by using an FTIR analyzer (PerkinElmer Spectrum GX spectrophotometer, PerkinElmer).

The QA/QC program for gas measurements included laboratory blank bags and spiked samples. At the beginning of the experiment day, the laboratory blank bag was examined for any trapped contamination. No contamination was identified. An external standard was used daily to check the quantitative response. When the quantitative response differed by more than 15% from that predicted by the specified calibration equation, a new calibration equation was determined. The method detection limit was 0.001 ppm for DMS.

3. Results and discussion

3.1. Surface morphologies of ACF and ACF/TiO₂

ACFs prior to and after being deposited with TiO₂ photocatalysts were examined with SEM to investigate their surface morphology. Fig. 1 represents the SEM photograph of uncovered ACF and covered ACF with two different amounts of TiO₂ (7 and 429 mg g⁻¹). As revealed in previous studies [12,19], TiO₂ photocatalysts could be embedded into the surface of a support material (ACF) by applying the described coating method. The ACF/TiO₂ exhibited

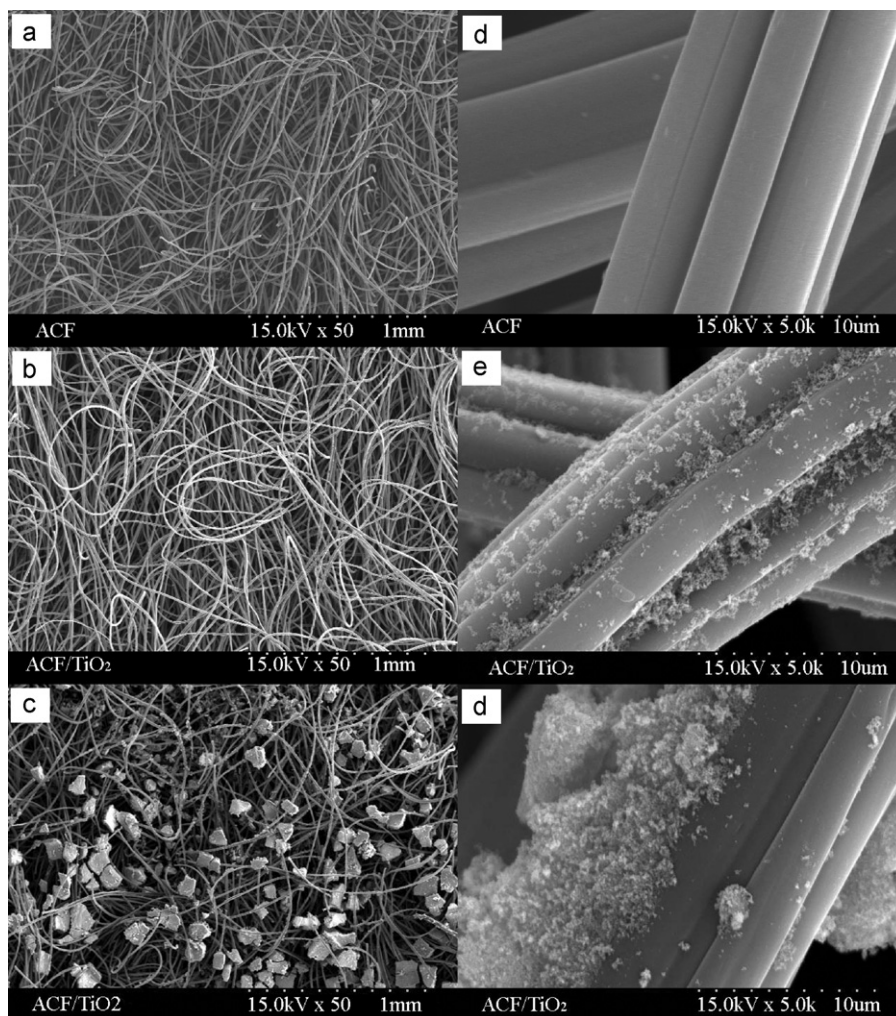


Fig. 1. Scanning electron micrographs: (a and d), AC fiber; (b and e), ACF/TiO₂ (TiO₂ coating amount, 7 mg g⁻¹); and (c and f), ACF/TiO₂ (TiO₂ coating amount, 429 mg g⁻¹).

the same tridimensional shape as uncovered ACF, and the space between adjacent ACFs appeared to be sufficient to allow the penetration of light into the felt-form photocatalysts to a certain depth. TiO₂ particles coated onto the ACF in a smaller amount were uniformly distributed compared with those coated in a larger amount.

3.2. DMS removal by adsorption and adsorptional photocatalytic decomposition

The DMS REs of the ACF alone and ACF/TiO₂ composites were examined with and without the presence of UV light. In the absence of UV light, the time-series DMS REs determined via ACF and ACF/TiO₂ units were similar during a 13-h adsorption process (Fig. 2). The maximum AEs determined using the two units of the present study were close to 80%. Around 13 h after the DMS injection, the AE decreased gradually to reach close to zero. Such evidence suggests that a DMS saturation occurred in both units during the 13-h adsorption process. The similarity in the AEs of the two units further suggests that TiO₂ particles on ACF surfaces do not significantly interfere with the adsorption capacity of ACFs. This assertion is supported by the fact that the micropore sizes of the ACFs are about 1–2 nm, while average crystal sizes of TiO₂ particles are ca 20-nm [19]. TiO₂ particles are thereby generally adsorbed onto the external surfaces of ACFs. Similarly, previous studies [12,20] reported that the adsorption capacity of a GAC unit

was almost identical to that of a GAC/TiO₂ unit for the removal of BTEX and methanol.

Unlike ACF alone and ACF/TiO₂ in the absence of UV light, the adsorptional photocatalytic decomposition (APD) efficiency of DMS via ACF/TiO₂ with UV light remained at nearly 60% during the remaining courses with a 13-h period, after dropping from

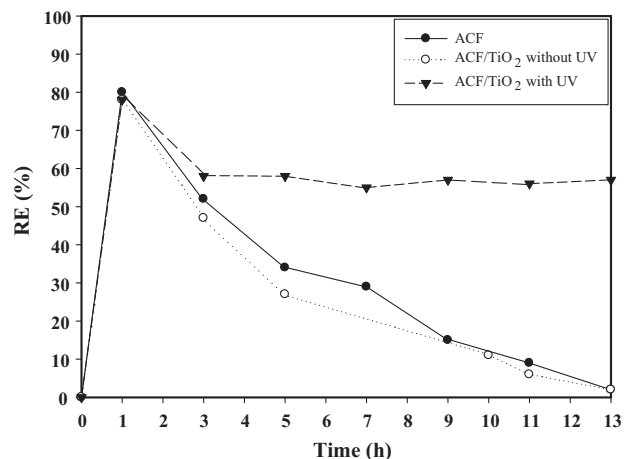


Fig. 2. Time-series DMS removal efficiency (RE, %) determined via ACF and ACF/TiO₂ with and without UV light: TiO₂ weights, 7 mg ACF-g⁻¹.

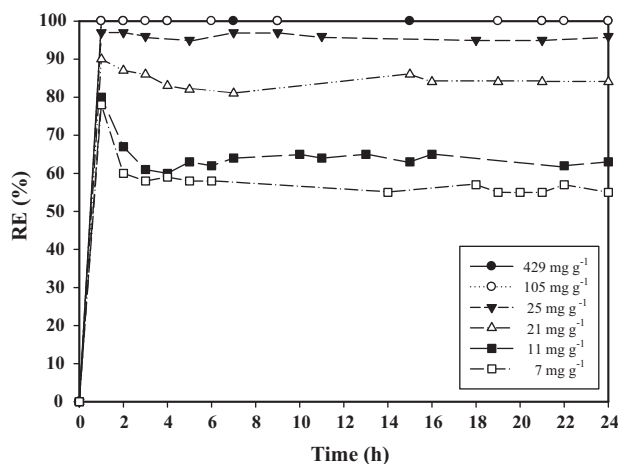


Fig. 3. Time-series DMS removal efficiency (RE, %) determined via ACF/TiO₂ with UV light, according to TiO₂ weights (mg ACF⁻¹) embedded into ACF.

a maximum RE of nearly 80% (Fig. 2). This improvement in the DMS RE suggested that the TiO₂ embedded onto the ACF could destroy DMS when in the presence of UV light, thus, at least partially regenerating the ACF in situ. The REs of the ACF/TiO₂ hybrid system are enhanced when compared to the TiO₂ alone system. This is attributed to elevated reaction areas [21]. Previous studies [12,20,21] also found that the TiO₂ embedded in the GAC could enhance the REs of BTEX, toluene and methanol, especially when compared with GAC alone and a GAC/TiO₂ unit without UV light. This APD function of ACF/TiO₂ for DMS removal encourages further experiments on this function under various operational conditions.

3.3. APD efficiency according to operational conditions

Four operational parameters (weights of TiO₂ embedded into ACFs, UV sources, RH, and DMS ICs) were tested for APD efficiencies of ACF/TiO₂. Fig. 3 exhibits the time-series DMS REs for six different TiO₂ weights between 7 and 429 mg ACF⁻¹. For the TiO₂ weights between 7 and 105 mg ACF⁻¹, the REs increased as TiO₂ weights increased, thereby suggesting that the TiO₂ weights are an important factor in APD efficiency. This result can be attributed to the presence of more catalyst surface area available in a PCO reaction with greater TiO₂ weights. However, for the two highest TiO₂ weights of 105 and 429 mg ACF⁻¹, the REs were similar to each other and were close to 100% during the entire 24-h APD process. This further suggests that there is an optimal TiO₂ weight between 25 and 105 mg ACF⁻¹ for the DMS APD process when employing the experimental conditions set forth in this study. In addition, Mo et al. [21] reported a similar photocatalyst weight dependence on gas-phase toluene removal efficiencies via TiO₂/adsorbent hybrid photocatalysts. Meanwhile, it is noteworthy that, when coating with certain great amounts, TiO₂ united in big particles (micron scale) may fall off from ACF, thereby influencing the stability of ACF/TiO₂ hybrid system.

For UV-light sources, two different lamps (8-W germicidal and 8-W fluorescent black light lamps) were evaluated for DMS RE. Fig. 4 exhibits the DMS RE profiles according to lamp type. The REs for the APD process with the 8-W germicidal lamp were higher than those with the 8-W fluorescent black light lamp during the entire 9-h period. TiO₂ is a semiconductor photocatalyst with a band gap energy of 3.2 eV. This band gap energy is exceeded with photons of less than 385 nm [22]. The wavelength of the germicidal lamp ranged from 200 to 300 nm with a maximum light intensity at 254 nm, and that of the black light lamp ranged from 315 to 400 nm with a maximum light intensity at 352 nm. Both lamps had

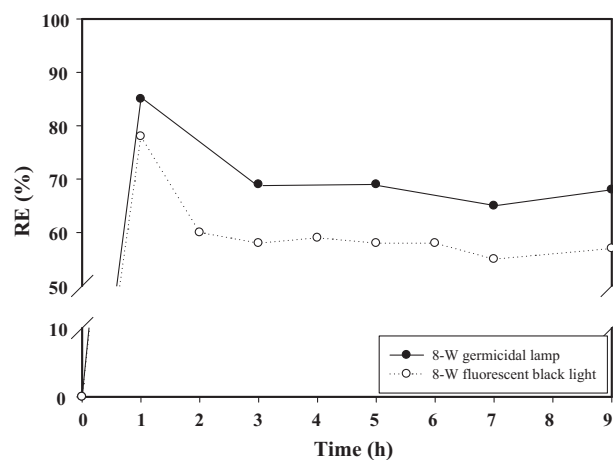


Fig. 4. Time-series DMS removal efficiency (RE, %) determined via ACF/TiO₂ with UV light, according to lamp type (8-W germicidal lamp (GL) and 8-W fluorescent black light (FBL)).

sufficient energy to promote electrons from the valence band to the conduction band of the TiO₂. However, the photon fluxes of the germicidal lamp were higher than those of the black light lamp [23]. Consequently, the higher photon flux output of the germicidal lamp was attributed to a higher APD efficiency. Similar to the present study, Kim and Hong [23] reported that, for four VOCs (acetone, methanol, toluene, and trichloroethylene), the removal rates were higher for a TiO₂ PCO unit with a 6-W germicidal lamp than with 6-W black light lamp.

The DMS RE, obtained in three different RH conditions, was plotted as a time function of a 20-h APD process (Fig. 5). The APD efficiencies were highest in the RH range of 50–55% over the entire survey period. That pattern was inconsistent with the humidity dependence of AC on adsorption efficiency in that AC adsorption efficiency of non- or semi-polar compounds decreased when the RH increased, mainly due to the competitive adsorption rate between water and contaminants on the AC surface [20,24]. It has been suggested that an APD mechanism for DMS removal, which involves a photocatalytic oxidation process as well as adsorption, differs from a pure adsorption mechanism. Compared with the RH range of 50–55%, the lower RE of ACF/TiO₂ in the RH range of 20–25% is likely due to a decrease in the hydroxyl radical population on the catalyst surface, promoting surface reaction kinetics [8,22]. Meanwhile, the drop in APD efficiency in the RH range of 85–90% appears

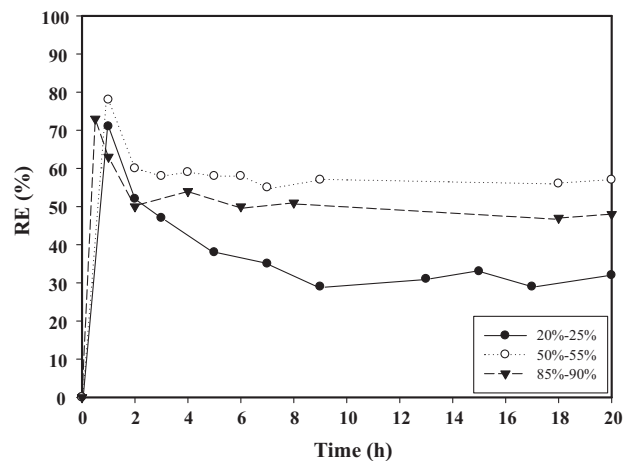


Fig. 5. Time-series DMS removal efficiency (RE, %) determined via ACF/TiO₂ with UV light, according to relative humidity (RH).

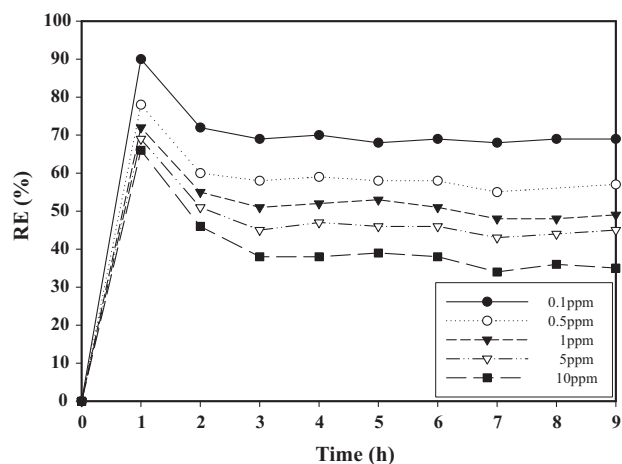


Fig. 6. Time-series DMS removal efficiency (RE, %) determined via ACF/TiO₂ with UV light, according to DMS input concentrations.

to be mainly due to the effect of the competitive adsorption rate between water and contaminants on the catalyst surface, limiting DMS adsorption on the catalyst surface [8,22]. This DMS RE dependence on humidity was also reported by Demeestere et al. [25], via the utilization a TiO₂-mediated heterogeneous PCO–UV system. This previous study reported a maximum DMS PCO efficiency at an intermediate RH (22%) for the experimental RH range of 3–75%. However, some researchers have reported an increasing PCO rate with an increasing RH for other target compounds such as chlorinated and aromatic VOCs [26–28]. In addition, other researchers [7,23] have reported a negligible or an opposite effect of RH dependence. Accordingly, different photocatalytic conditions can result in different RH dependencies.

Fig. 6 presents the time-series DMS RE determined via ACF/TiO₂ with UV light, according to DMS input concentrations. The DMS RE (%) decreased when the IC increased. For example, the DMS RE (%) observed 9 h after the experiment started was 69% at an IC of 0.1 ppm, while it was 34% at an IC of 10 ppm. This IC dependence is likely due to the increased competition between pollutant molecules for the adsorption sites of ACF/TiO₂. This assertion is supported by the fact that, generally, an adsorption capacity of AC decreases when the IC increases [29].

3.4. Long-term test

A long-term APD test was conducted for 219 consecutive hours. Although the data has not been presented in this paper because of limited article space, the estimated DMS APD efficiencies dropped from 80% to ca 60% within 1 h after initiating the APD process and then fluctuated between 52% and 60%, without significant variation. This suggests that there was not a significant functional deterioration of the ACF/TiO₂ system for DMS removal over this period. This is likely due to a lack of significant deactivation of TiO₂ embedded in ACF. In contrast, recent studies reported catalyst deactivation during the PCO processes of sulfuric compounds, mainly due to the accumulation of reaction products on the photocatalyst surface [25,30–32]. Unlike these studies that used a PCO unit alone, the present study utilized an ACF/TiO₂ composite. Although the present study does not provide documentation, these results imply that, since AC systems can effectively remove several types of airborne pollutants [1,33], the ACF would decrease the accumulation of reaction products on the TiO₂ surface, which could result in catalyst deactivation, thereby decreasing the TiO₂ deactivation processes. In addition, the DMS ICs tested in the present study were much lower. Consequently, it is suggested that the ACF/TiO₂ system sur-

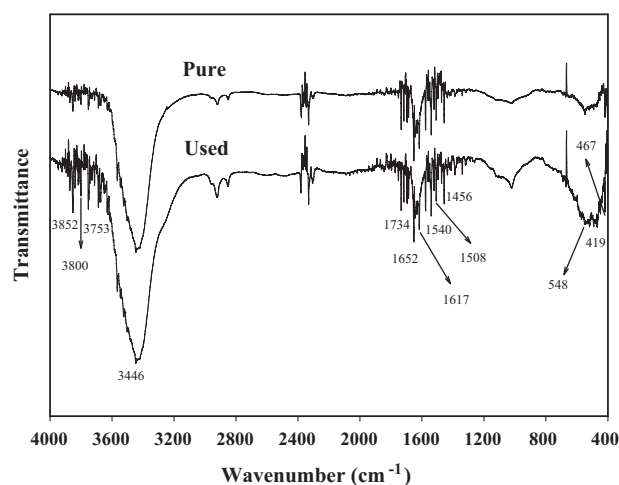


Fig. 7. Fourier-transformation infrared spectra of pure and used ACF/TiO₂.

veyed in the present study can be applied to control the DMS at treatment concentrations of less than or equal to 0.5 ppm over a long period (at least 219 h).

3.5. Byproducts in effluent gas and on ACF/TiO₂ surfaces

Potential reaction products, which can be generated through a PCO process via an ACF/TiO₂ system, were analyzed in the effluent gas and on the ACF/TiO₂ surface. This gas-phase analysis with the GC/FID did not reveal any significant formation of byproducts throughout the APD process. However, a few small GC peaks were noted but were neither qualified nor quantified since their assignment to theoretically expected intermediates was not easy. In contrast, previous studies reported the formation of methanol, DMDS, and other byproducts during PCO processes of various sulfuric compounds [25,30,31]. A possible explanation for this difference is that, even if those gas-phase byproducts were formed during the APD process of ACF/TiO₂, their concentrations would be very low and thus, undetectable or unquantifiable, and is likely due to the much lower DMS ICs in the present study (≤ 1 ppm).

In addition, qualitative information on the chemical species, adsorbed on the catalyst surface, was obtained from the FTIR spectra of pure and used ACF/TiO₂ with UV light (Fig. 7). The FTIR spectra of pure and used ACF/TiO₂ were similar to each other, and major absorption peaks appeared at bands of 3852, 3753, 3446, 1734, 1652, 1617, 1540, 1508, 1456, 548, 467, and 419 cm⁻¹. The bands of 3446–3852 and 1456–1734 were attributed to the O–H stretching vibration and the H₂O bending vibration on the ACF/TiO₂ surface [32,34]. The correspondence of the band below 1000 cm⁻¹ in the FTIR spectra of both pure and used ACF/TiO₂ could have been due to titanium crystal lattice vibrations [35]. The similarities in the FTIR spectra of pure and used ACF/TiO₂ suggest no adsorption of intermediates, which are usually generated during PCO processes of sulfuric pollutants [25,32] on the surface of used ACF/TiO₂.

It is noteworthy that the bands of 1050–1250 cm⁻¹, which have been reported during PCO processes of sulfuric compounds [25,32], did not appear in the FTIR spectra of used ACF/TiO₂. The accumulation of sulfur compounds on the surface of photocatalysts caused photocatalyst deactivation, thereby lowering the photocatalytic activities of the PCO system [25,30–32]. Consequently, it is suggested that the TiO₂ embedded in the ACF, which was employed in the present study, would not be significantly deactivated throughout the PCO processes. This assertion is supported by the finding that the PCO efficiencies of DMS did not reveal any decreasing trend over the 219-h period.

4. Conclusion

The current study evaluated the APD efficiency of a cylindrical continuous-flow ACF/TiO₂ system for the removal of DMS under various operational conditions. A SEM analysis identified that a TiO₂ photocatalyst could be embedded into the surface of a support material (ACF) by applying the described coating method. It was further suggested that TiO₂ particles on the ACF surfaces would not significantly interfere with the adsorption capacity of ACFs. The APD efficiencies obtained from the ACF/TiO₂ system exhibited a dependence on the weights of the TiO₂ embedded in ACFs, UV sources, RH, and DMS ICs. No byproducts were measurable or observable in effluent gas or on the ACF/TiO₂ surface, respectively. Consequently, it was suggested that the continuous-flow ACF/TiO₂ system could be applied to control DMS, under the operational conditions of this study, without any significant functional deterioration.

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