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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.

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/TiO_2

ACF/TiO_2 was prepared using a dip-desiccation method that has been employed for GAC/TiO_2 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 TiO_2 (Degussa P25), which is composed of nonporous polyhedral geometry with a 30 nm diameter and a specific surface area of 50 $m^2\,g^{-1}$, 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 TiO_2 for 2 h, under ultrasonic conditions, and then dried at 105 °C for 3 h. ACFs coated with six different weights of TiO_2 (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 TiO_2. The amount of TiO_2 coating was determined by the weight difference of the ACFs between before and after the coating procedure. This prepared ACF/TiO_2, 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/TiO_2 for DMS were performed to examine whether TiO_2 embedded in the surface of the ACF would influence the adsorption capacity of the original ACF. Either ACF or ACF/TiO_2 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/TiO_2 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/TiO_2 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/TiO_2 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 TiO_2 embedded into the ACF was 451 mg ACF-g^{-1}. Gaseous samples were collected at the inlet and outlet of the ACF/TiO_2 reactor, until a saturation of ACF or ACF/TiO_2 was noted, with an interval of either 1 or 2 h.

2.3. Removal test of DMS using ACF/TiO_2

A series of experiments were performed to evaluate the DMS APD efficiencies of ACF/TiO_2 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/TiO_2 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 TiO_2 embedded in the ACFs, UV sources, RH, and DMS ICs. Six weights of TiO_2 (7, 11, 21, 25, 106, and 429 mg ACF-g^{-1}) were tested for the DMS removal of ACF/TiO_2. 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 TiO_2, 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/TiO_2 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/TiO_2 surface. The surfaces of used ACF/TiO_2, in conjunction with pure ACF/TiO_2, 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/TiO_2

ACFs prior to and after being deposited with TiO_2 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 TiO_2 (7 and 429 mg g^{-1}). As revealed in previous studies [12,19], TiO_2 photocatalysts could be embedded into the surface of a support material (ACF) by applying the described coating method. The ACF/TiO_2 exhibited