REMOVAL OF FORMALDEHYDE BY AIR CLEANER WITH TIO$_2$-MOUNTED CERAMIC FILTER

E Murakami$^{1,*}$, H Kohno$^1$, T Kaji$^1$, M Hori$^2$, D Ono$^2$

1 Research and Development Center, Asahi Kogyosha Co., Ltd., Japan
2 Faculty of Engineering, Yokohama National University, Japan

ABSTRACT

The photocatalytic technology was applied to reduce formaldehyde. A photocatalytic filter used is made of the porous ceramics, is coated with TiO$_2$ and has a three-dimensional structure. The experiment to reduce formaldehyde in the air was conducted by circulating the air through the filter irradiated with UV light in a 1m$^3$ air chamber. The result showed that the formaldehyde was almost completely oxidized into carbon dioxide when the intensity of UV light is over 2.9mW/cm$^2$. The removal performance of formaldehyde was improved as the intensity of UV light increased or as one more photocatalytic unit or two were set in series.

INTRODUCTION

Within indoor environments, sensory substances such as volatile organic compounds and odorants may exist, discomforting residents and workers (Molhave et al. 1996). For harmful effects of VOC on human health, the Building Standards Law of Japan was amended in July 2003, starting to regulate timber-generating formaldehyde. For odor, the Environmental Engineering Committee of the Architectural Institute of Japan is currently discussing on the specification (Narasaki 2003). In recent years, photocatalytic technology has practically been applied as its countermeasure, however, some difficulties including the occasional generation of hazardous material have been pointed out (Hori et al. 2004). In photocatalytic reactions, there is a major technical problem on how to accelerate oxidative destruction reactions to minimize the generation of hazardous products.

In this study, focusing on formaldehyde as a removal target, which is relatively easy to oxidatively decompose and allows easy definition of reaction products, we have attempted to improve the performance of decompositional removal by increasing the irradiation intensity or installing photocatalytic units on a multistage basis.

METHODS

The photocatalytic unit adopted in the experiment was prepared by placing 16 UV lamps (Sankyo : CFL240T4/8BL) providing the dominant wavelength of 368nm and the output of 2.35 W on both sides of a photocatalytic filter (Noritake Co., Limited : standard filter), which was 240 mm in width, 125 mm in height and 13.5 mm in depth (the effective area of 0.0253 m$^2$). Each unit was used after mounted on the reactor allowing in-line multistage installation (one to five stages) in the flow direction. The irradiation intensity is adjustable by changing the number of lit UV lamps. Figure 1 shows the UV irradiation patterns and the irradiation intensity on the photocatalytic surface measured with UV meter (Minolta : UM-10, UM-360). The porous ceramic surface of photocatalytic filter is coated with 6.15 g of titania particles (the specific surface area of 290~310 m$^2$/g) from crystalline anatase in the thickness of approx. 1 μm. The pore capacity and specific surface area are 0.02 ml/g (with nitrogen adsorption method) and 11 m$^2$/g (with BET method), respectively.

The experimental procedure was as follows. First, by mounting three stages of photocatalytic units, the UV irradiation pattern was varied (among TYPE-A, TYPE-B and TYPE-C) to investigate the influence of irradiation intensity on the decomposition performance. Next, the number of mounted photocatalytic units was changed to examine the adsorption performance of formaldehyde. Then, for the UV irradiation pattern, TYPE-A, UV irradiation was performed to study the influence on the decompositional removal performance and the generation of formic acid, a product of formaldehyde oxidation. Figure 2 shows the experimental apparatus. The concentration of formaldehyde was adjusted to approx. 100 ppm by heating and sublimating 0.13 g of paraformaldehyde (Kanto Kagaku : >92.0%) with an electric plate heater in the closed acrylic chamber with the internal volume of 1 m$^3$ (1000 mm × 1000 mm × 1000 mm). The concentration of formaldehyde, 100ppm, was determined according to the observed value of residual formaldehyde after natural attenuation for 24 hours within
the formalin fumigation space.

After the start of experiment, the air with formaldehyde was circulating through a reactor in the chamber (air flow: 0.83 m³/min; air velocity at the photocatalytic filter: 0.46 m/s). The experimental apparatus was installed in the temperature-controlled testing room to keep the ambient chamber temperature at 24°C. A small circulator was installed in the chamber to achieve a uniformly diffused condition.

For the decompositional removal performance, the concentration of formaldehyde within chamber and that of carbon dioxide generated during oxidative destruction were measured with formaldehyde detector tube (Gastec: No91M, No91, No91L, No91LL) and CO₂ meter (Sibata: COX-2), respectively. From variations in these concentrations with passage of time, the removal ratio of formaldehyde ε (hereinafter, referred to as one-pass removal ratio) and the ratio of carbon dioxide conversion η (hereinafter referred to as ratio of one-pass conversion) before and after passing the reactor were calculated to evaluate the performance of decompositional removal. Neglecting the influence of adsorption on the inner surface of the chamber and the carbon dioxide meter, the one-pass removal ratio ε and the ratio of one-pass conversion η could be calculated from expressions (1) and (2), respectively. For the measurement of formic acid, the acetic acid detector tube and ion chromatograph were used.

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CHCHO = CHCHO_0 \times \exp (-F \times \varepsilon \times T/V)
\]

(1)

Where CHCHO=the concentration of formaldehyde in the chamber (ppm), CHCHO₀=the concentration of formaldehyde in the chamber before the treatment (ppm), F=the air flow rate of reactor (m³/min), T=time of measurement (min), V=volume of chamber (m³).

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CCO_2 = CCO_{2\text{max}} - CCO_{2\text{max}} \times \exp (-F \times \eta \times T/V) + CCO_2_0
\]

(2)

Where CCO₂=the concentration of carbon dioxide in the chamber (ppm), CCO₂max=the concentration of carbon dioxide on the theory when all formaldehyde in the chamber can decompose to carbon dioxide (ppm), CCO₂₀=the concentration of carbon dioxide in the chamber before the treatment (ppm), F=the air flow rate of reactor (m³/min), T=time of measurement (min), V=volume of chamber (m³).

RESULT AND DISCUSSION

Influence of irradiation intensity on the removal performance

Figure 3 shows variation with time in the concentration of generated carbon dioxide when the UV irradiation pattern was varied. The concentration of carbon dioxide for TYPE-A and TYPE-B reached 105 ppm (trial value at 24°C within chamber), which was the CCO₂max, 105 and 193 minutes after the start of experiment, respectively. Ratios of one-pass conversion were 4.0% and 2.0%, respectively. From this result, it was found that 2.9 mW/cm² or higher irradiation intensity allowed formaldehyde to be decomposed to carbon dioxide and the further irradiation intensity improved the decomposition performance. On the other hand, the concentration of carbon dioxide for TYPE-C could not reach CCO₂max even 420 minutes after the start of experiment and the ratio of one-pass conversion was also low, being 1.3% (during initial 60 minutes). This is presumably because oxidation occurred primarily in the area with relatively high UV intensity (2.9~3.1 W/cm²) near lit UV lamps due to weak photocatalyst-caused oxidative destruction in the area with lower irradiation intensity (0.9~1.2 W/cm²) as described in the report (Namiki et al. 2003). on the rapid decrease of removal ratio under 1.1 mW/cm² or lower illuminance in the experiment of ethanol removal.
Influence of the number of installed photocatalytic unit stages on the decompositional removal performance

Figure 4 shows variation with time in the concentration of formaldehyde during no UV irradiation. With one, two and three stage installation of photocatalytic units, adsorption into the photocatalytic units solely removed 22% (90→70 ppm: the initial one-pass removal ratio: 7%), 55% (90→40 ppm: the initial one-pass removal ratio: 15%) and 72% (90→25 ppm: the initial one-pass removal ratio: 30%) amount of formaldehyde, respectively, within 10 minutes after the start of process to reach the equilibrium. At this time, the equilibrium adsorption amount of 0.15 mg/g-photocatalytic filter to the initial formaldehyde concentration of 100 ppm is extremely small compared with that of activated carbon (approx. several tens mg/g).

Figure 5 shows variation with time in the concentration of formaldehyde during UV irradiation. With one, two and three stage installation of photocatalytic units, the concentration of formaldehyde decreased to 2.6 ppm (61 minutes after the start of process), 1.9 ppm (31 minutes after that) and 2.0 ppm (18 minutes after that), respectively, showing photocatalyst-caused removal effect. Here, the one-pass removal ratio (one-stage installation: 7%; two-stage installation: 15%; three-stage installation: 30%) was equivalent to the initial one-pass removal ratio during no UV irradiation. Therefore the reason for improved removal performance is supposed to be that simultaneously with the decompositional removal of photocatalyst-attached formaldehyde due to UV irradiation, the super hydrophilicity of photocatalytic surface increased adsorption capacity for formaldehyde being highly water-soluble.

Fig. 6 shows variation with time in the concentration of carbon dioxide during UV irradiation. With one, two and three stage installation of photocatalytic units, the concentration of carbon dioxide reached \( \text{CO}_2 \text{max} \) 334, 228 and 105 minutes after the start of process, respectively. Ratios of one-pass conversion at this time were 1.7%, 2.9% and 4.0%, respectively, being approx. 13−24% of previously-mentioned one-pass removal ratios. So, the removal performance might be rate-controlled at the adsorption stage before the adsorptive saturation of photocatalytic filter, while after the adsorptive saturation it might be rate-controlled at the decomposition stage of formaldehyde into carbon dioxide. Therefore, it can be said that the decomposition performance of removal target is also an important factor in the performance evaluation of photocatalyst.

Figure 7 shows variation with time in the concentration of generated formic acid upon the decomposition of formaldehyde during UV irradiation with one-stage installation of photocatalytic unit. Compared with the initial
formaldehyde amount of approx. 100 ppm, the amount of formic acid detected as vapor was as low as approx. 0.2 ppm (20 minutes after the start of process) and was sufficiently below the acceptable concentration of 5 ppm for working environment, prescribed by the Japan Society for Occupational Health (2002 edition). And this value is a hundredth of 20%, which was reported by Fujishima et al. as the generated amount of formic acid from about 75% reaction during the photodegradation of formaldehyde (Noguchi et al. 1998).

CONCLUSION
Using photocatalytic units with UV lamps placed on both sides of TiO$_2$/photocatalysts, we performed an experiment to determine decompositional removal characteristics in the circulation treatment process of formaldehyde within a closed air chamber. As a result, the following observations were obtained:

1. 2.9 mW/cm$^2$ or higher irradiation intensity allowed formaldehyde to be decomposed to carbon dioxide and the further irradiation intensity improved the decomposition performance.

The multistage installation of photocatalytic units improved the removal performance for formaldehyde. The reason for improved removal performance is supposed to be that simultaneously with the decompositional removal of photocatalyst-attached formaldehyde due to UV irradiation, the super hydrophilicity of photocatalytic surface increased absorption capacity for formaldehyde being highly water-soluble.

3. The removal performance might be rate-controlled at the adsorption stage before the adsorptive saturation of photocatalytic filter, while after the absorptive saturation it might be rate-controlled at the decomposition stage of formaldehyde into carbon dioxide.

4. Compared with the initial formaldehyde amount of approx. 100 ppm, the amount of formic acid detected as vapor was as low as approx. 0.2 ppm (20 minutes after the start of process) and was sufficiently below the acceptable concentration of 5 ppm for working environment, prescribed by the Japan Society for Occupational Health (2002 edition).

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REFERENCE