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Photocatalytic Cleaning Performance of Air Filters for a Binary Mixture

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***Abstract*—**Ultraviolet photocatalytic oxidation (UV-PCO) technology has been recommended as a green approach to health indoor environment when it is integrated into mechanical ventilation systems for inorganic and organic compounds removal as well as energy saving due to less outdoor air intakes. Although much research has been devoted to UV-PCO, limited information is available on the UV-PCO behavior tested by the mixtures in literature. This project investigated UV-PCO performance and by-product generation using a single and a mixture of acetone and MEK at 100 ppb each in a single-pass duct system in an effort to obtain knowledge associated with competitive photochemical reactions involved in. The experiments were performed at 20 % RH, 22 °C, and a gas flow rate of 128 m^3/h (75 cfm). Results show that acetone and MEK mutually reduced each other's PCO removal efficiency, particularly negative removal efficiency for acetone. These findings were different from previous observation of facilitatory effects on the adsorption of acetone and MEK on photocatalyst surfaces.

***Keywords*—**By-products, inhibitory effect, mixture, photocatalytic oxidation.

I. Introduction

THE Urban Pollution Island (UPI) is an unwelcome consequence of urbanization [1]. Unpleasant outdoor air quality (OAQ) poses a challenge for indoor air quality (IAQ) in terms of outdoor air intake rates defined by the ventilation rate procedure [2]. In the context of comprehensive energy conservation campaigns, developments of high performance air filters have received considerable attention due to reducing the amount of outside air for a supply, saving energy for heating and/or cooling, and still providing an acceptable indoor air quality.

Nanotechnology is an emerging advanced technology that offers many opportunities towards improvement of IAQ in indoor environmental applications. One of the most highly anticipated practices is the photocatalytic oxidation (PCO) technology, which represents the newest generation of proactive air purification technology. This technology provides an alternative and energy efficient solution to air quality challenges by utilizing nano-photocatalysts under the exposure of ultraviolet (UV) light. Photosensitive semiconductors, usually titanium dioxide (TiO_2), absorb UV light to form reactive hydroxyl radicals (•OH) in the presence of oxygen and water vapor. These free radicals take a series of reactions with kinds of gaseous pollutants; ultimately pollutants can be mineralized to CO_2 and water.

Over the years, comprehensive research on the working mechanisms of PCO for treatment of air have been performed [3]-[9]. Although much research has been devoted to UV-PCO, limited information is available on the UV-PCO behavior for the mixtures in literature.

Indoor air contains hundreds of volatile organic compounds (VOCs) at ppb levels, which leads to the necessity to explore their competition effect on the catalyst surface for the same active sites and quantify their impact on UV-PCO performance. Adsorption and photocatalytic oxidation of methanol-benzene and 2-propanol-toluene binary mixtures were investigated [10], [11]. Their results indicated that relative humidity (RH) is a key parameter in competition adsorption and photocatalytic oxidation efficiency. Twesme et al. [12] observed photocatalytic degradation of a tertiary mixture of propane, isobutane and n-butane with ZrO_2-TiO_2 thin films photocatalysts under conditions of 70°C and 30% RH, and results showed n-butane has the highest photoconversion followed by isobutane and propane resulting from differences in strength of adsorption to the catalyst. Photocatalytic removal of the components for seven binary mixtures of VOCs over Degussa P-25 TiO_2 at 360 nm was investigated [13], and promotion and inhibition of removal of one component by the other were observed with explanation of competitive adsorption and chemical mechanism. Observation of photocatalytic degradation of four carbonyl compounds mixture at low level on adsorptive TiO_2/SiO_2 photocatalyst was conducted [14] and the decreasing order of PCO rates is propionaldehyde, acetone, acetaldehyde and formaldehyde. These observations indicate that competition effect has been examined for few compounds with rationalization, however, the complex interactions between mixtures frequently encountered in the indoor air in the processes of photocatalytic reactions are still not clear and need to be further explored. This study attempts to deeply expand the current understanding of competitive behaviors through comparative investigations of UV-PCO by testing a single VOC and a binary mixture. Acetone and methyl ethyl ketone (MEK) are selected as representative VOCs since their various nature properties, including solubility, molecular weight, and molecular structure, can be used to fully study the competition effect. Also, occupants are subject to exposure to these VOCs emitted from a

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variety of internal sources, such as paints, gasoline, combustion products, lacquers, vanishes, polish removers and adhesives. This project investigates UV-PCO performance as well as by-product generation in a single-pass duct system in an effort to obtain knowledge associated with photochemical mechanism, catalysis, surface adsorption and desorption processes, and surface chemistry involved in UV-PCO technology. The obtained knowledge is critical to explain the competitive UV-PCO phenomenon and may help improve the UV-PCO performance for a specific pollutant by introducing or avoiding compounds/radicals.

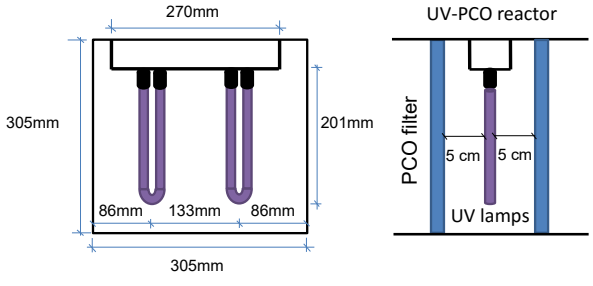
II. Experimental

A. Reactor

The experiments of photocatalytic degradation of mixtures were conducted in a pilot-scale single pass mode test rig. The detailed description of the UV-PCO test apparatus can be found in our previous work [15] and its dimensions are available in [16]. A commercial PCO filter (Quartzel® PCO, Saint-Gobain Quartz) and our prepared carbon cloth-TiO_2 PCO filter were used in this study. The commercial PCO filter was made up of long, continuous amorphous silica fibers coated with a layer TiO_2. The preparation method for carbon cloth-TiO_2 PCO filters can be found in [17]. The detailed physical properties are presented in Table I. Ultraviolet (UV) light sources used are low-pressure mercury lamps of each 18.4 W (Ster-L-Ray, Atlantic Ultraviolet Inc.) with peak output at 254 nm (UVC). The location of UV lamps inside a duct system and arrangement of UV-PCO filter banks are depicted as Fig. 1. The airflow was driven by fans installed in the UV-PCO system, one at the front of the mixing chamber and four at the end of each duct. At this study, the airflow rate was controlled at 128 m^3/h (75 cfm).

TABLE I
Technical Data of PCO Filters

Property	Fiberglass-TiO_2	Carbon cloth-TiO_2
Fibers diameter, µm	9	14
Areal weight, g/m^2	100	280-320
Specific surface area, m^2/g	120	890
Thickness, mm	15-20	2-4
Pressure drop at 0.4 m/s (75 fpm), Pa	33	450



(a) (b)

Fig. 1 (a) Arrangement of UV lamps (front view) and (b) arrangement of PCO filters (side view) in a UV-PCO reactor

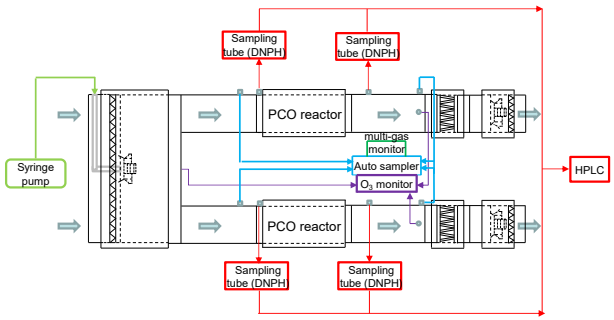


Fig. 2 Schematic diagram of the testing system

B. Chemicals

Two reagent grade chemicals were selected as model air contaminants, including MEK (99.9%) and acetone (99.5%) from Fisher Scientific Inc. (Canada). These two compounds are frequently encountered in indoor environments and possess a variety of physical properties, which is shown in Table II.

TABLE II
Physical Properties of the Selected VOCs

Property	Acetone	MEK
VOCs Class	Ketones	
Molecular Formula	C_3H_6O	C_4H_8O
Molar Mass (g/mol)	58.1	72.1
Density (g/mL)	0.7925	0.8050
Boiling Point (°C)	56.1	79.4
Vapor Pressure (mmHg)	180	78
Solubility (at 20-25°C)	miscible	28%
Dielectric Constant (at 20-25°C)	20.7	18.51

The continuous gaseous flow containing a binary mixture was generated using two syringe pumps (KD Scientific) which separately injected the selected pure liquid VOC into a chemically inert polytetrafluoroethylene (PTFE) tube at an appropriate injection rate depending on the desired inlet concentration. The injected liquid VOC was immediately evaporated by the laboratory compressed air which was used as a carried gas to bring the vaporized chemical into the UV-PCO injection port. The gaseous VOCs were fully mixed with the inlet air in a center-located mixing chamber to uniformly distribute the VOCs of expected concentrations in the four-duct system.

C. Measurement Scheme

The UV-PCO experiments were performed at 20 % RH, 22°C. The UV-PCO experiments were first performed with acetone and MEK at a concentration of 100 ppb, respectively, to observe the PCO air cleaner behavior challenged by a single gas. Then, a mixture composed of 100 ppb acetone and 100 ppb MEK was used as challenge gases to examine the competitive effect on the PCO performance. For all tests, the inlet concentration was balanced for 10 min in dark condition followed by turning on UV lights and balancing for 5 min to obtain a constant UV irradiance level. After that, DNPH impregnated silica cartridges (Supelco Inc.) were placed at both

upstream and downstream and were consecutively taken samples at a flow rate of 1 L/min for 60 min for various PCO treatment times (1, 2, 3 and 4 h). The total duration of UV-PCO tests lasted 4 hours. Upon completion of UV-PCO tests, DNPH samples were analyzed with high performance liquid chromatography (HPLC, Perkin Elmer) to quantitatively evaluate removal performance of challenge compounds and generated gaseous by-products.

D. Qualification Method

Single-pass removal efficiency of PCO is calculated from the ratio of experimentally measured decrement of a challenge VOC to its inlet concentration, which is defined by (1). By-products concentration represents the net amounts of compound produced during the PCO reaction in a certain volume and it can be obtained by (2).

$$\eta_t = \frac{Q_{air}(C_{up,t} - C_{down,t})}{Q_{air} C_{up,t}} \times 100 = \frac{C_{up,t} - C_{down,t}}{C_{up,t}} \times 100 \quad (1)$$

$$C_{bp,t} = \frac{m_{down-bp,t} - m_{up-bp,t}}{t \times Q_{sampling} \times b} \quad (2)$$

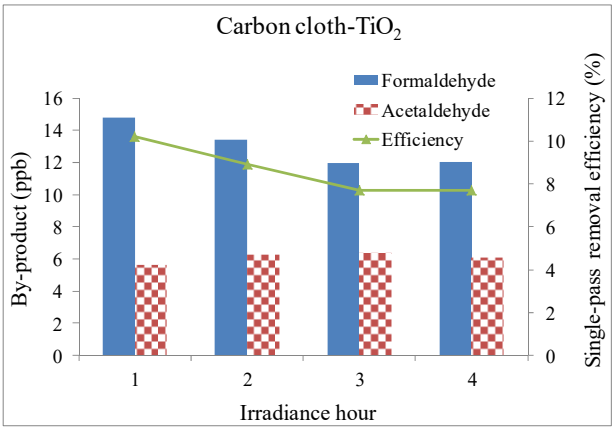
where η_t (%) is the single-pass efficiency of a VOC; $C_{up,t}$ (mg/m^3) is the upstream VOC concentration as a function of time; $C_{down,t}$ (mg/m^3) is the downstream VOC concentration as a function of time; Q_{air} (m^3/min) is the airflow rate; $C_{bp,t}$ (ppb) is the net by-product yield through PCO filters; $m_{up\text{-}bp,t}$-$m_{down\text{-}bp,t}$ (μg) is the net mass of generated by-products analyzed by HPLC; $Q_{sampling}$ (L/min) is the sampling airflow rate through a DNPH-silica cartridge; t is the sampling duration (60 min), and b is the conversion constant from μg/m^3 to ppb for a specific by-product.

III. Results and Discussion

A. Single Compound Tests

Before examination of PCO of a mixture, a single VOC was performed by the PCO technology. The observed PCO performance was regarded as a reference for comparison with that of a mixture. The temporal evolution of acetone conversion rate as a function of irradiance time for carbon cloth-TiO_2 filters and fiberglass-TiO_2 filters is presented in Fig. 3. The single-pass removal efficiency of acetone for carbon cloth-TiO_2 filters shows a slightly decreasing trend. On the contrary, the conversion rate of acetone for fiberglass-TiO_2 filters presents a slight increasing trend. In general, the average conversion rates of acetone under the experimental conditions for two filters are in the same level.

Yield of formaldehyde decreased from 14.8 ppb after 1 h PCO treatment to 12.0 ppb after 4 h treatment in the case of carbon cloth-TiO_2 filters. Yield of acetaldehyde almost kept a constant during 4 h PCO processing. Similarly, formaldehyde and acetaldehyde show the same tendency in the case of fiberglass-TiO_2 filters. It is worthy to mention that yields of formaldehyde and acetaldehyde from fiberglass filters are around twice of those from carbon cloth filters.



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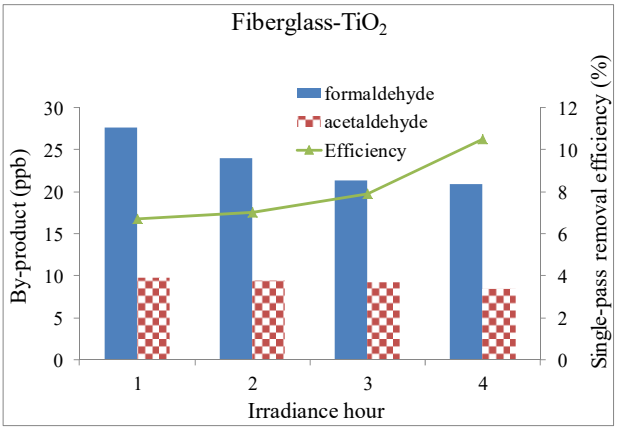
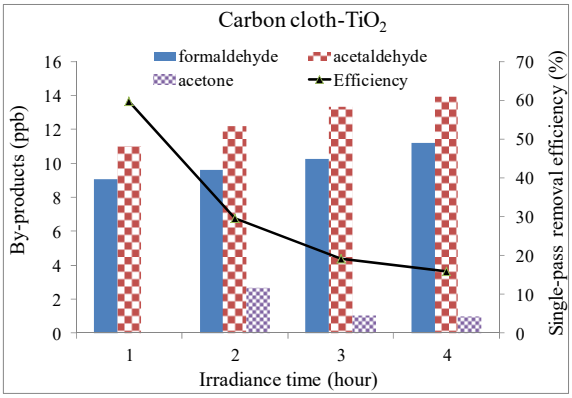


(b)

Fig. 3 PCO of 100 ppb acetone for (a) carbon cloth-TiO_2 filters and (b) fiberglass-TiO_2 filters

MEK removal efficiencies on two PCO filters and formation of gaseous by-products are shown in Fig. 4. The conversion rate of MEK on carbon cloth-TiO_2 filters rapidly decreased from 59.7% to 16.0% within 4 h PCO treatment, indicating adsorption is the dominant technology. On the contrary, PCO of MEK removal performance on fiberglass-TiO_2 filters slightly increased from 13% to 17%. Hence, it is concluded that PCO is more sustainable and durable technology than adsorption under the experimental conditions. Another obvious difference from PCO of acetone shown in Fig. 3 is that gaseous by-products of formaldehyde and acetaldehyde steadily increased during the tests, particularly in the case of carbon cloth filters. Previous studies [15]-[18] demonstrated that bond energy plays a critical role on adsorption of molecules on the adsorption sites, and it consequently impacts on PCO performance. Therefore, the PCO performance is closely related to the property of PCO filters and nature of challenge compounds.



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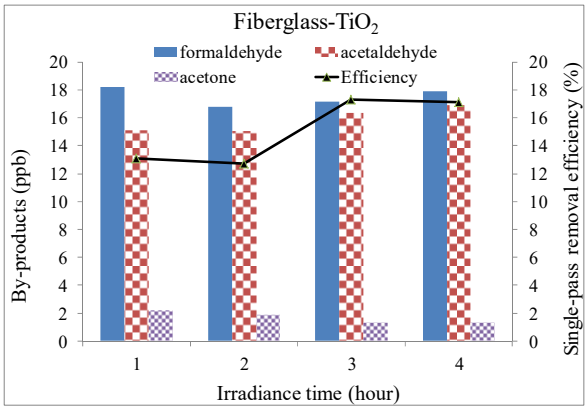
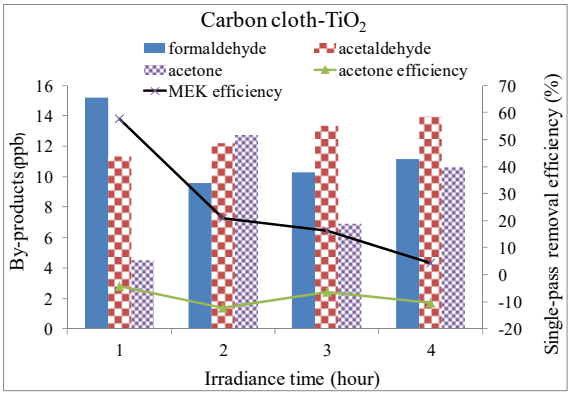


(b)

Fig. 4 PCO of 100 ppb MEK for (a) carbon cloth-TiO_2 filters and (b) fiberglass-TiO_2 filters



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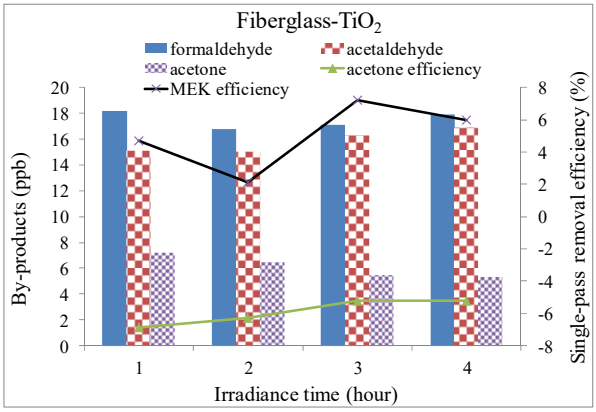

(b)

Fig. 5 PCO of a mixture of 100 ppb acetone and 100 ppb MEK for (a) carbon cloth-TiO_2 filters and (b) fiberglass-TiO_2 filters

B. Mixture Tests

Acetone and MEK with each concentration of 100 ppb were mixed and tested by PCO technology. Assuming the number of active catalyst sites remains a constant for all experiments. Fig. 5 shows the profile of removal efficiency and by products with irradiance time for two filters. The single removal efficiencies for single compound were both higher than that of simultaneous degradation of two ketones. Unexpectedly, this mutual inhibition effect was not consistent with the promotional adsorption trend of the two ketones on the TiO_2 [18]. As indicated in Fig. 4, acetone was a significant intermediate during the PCO of MEK, which resulted in the negative removal efficiency of acetone as a component of ketones. On the other hand, acetone molecules competed with MEK molecules for the adsorption sites on TiO_2, which led to a decrease of degradation performance of MEK as a single compound. However, adsorption demonstrates as a dominant technology for MEK on the carbon cloth-TiO_2 filter, and PCO of MEK was slightly affected by acetone competition. The amounts of acetone as a by-product detected from output on carbon cloth-TiO_2 filters were much higher than those from fiberglass-TiO_2, further indicating that acetone was replaced by MEK due to the major adsorption technology.

IV. Conclusion

Photocatalytic oxidation of a single gaseous acetone and MEK and their 1: 1 binary mixture using carbon cloth-TiO_2 filters and fiberglass-TiO_2 filters was investigated in a single-pass duct system. The following conclusions can be derived from this study:

1) Competitive PCO of MEK and acetone shows lower single pass removal efficiency than that of PCO of MEK or acetone, which is different from competitive adsorption of MEK and acetone on the same photocatalyst.
2) The inhibition effect on the competitive PCO is mainly resulted from transient strongly adsorbed carboxylic acids, which is the key point that differentiates competitive adsorption and competitive PCO.
3) Due to acetone is one of by-products by the PCO of MEK, the negative removal efficiency of PCO of acetone was observed when a mixture of acetone and MEK was tested.
4) More VOC mixtures with various combination ratios under different environmental conditions are needed to be explored in the future for obtaining clearer mechanism knowledge on competitive PCO.

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