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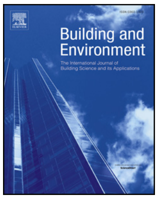

Modeling of by-products from photocatalytic oxidation (PCO) indoor air purifiers: A case study of ethanol

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ABSTRACT

Ultra-violet photocatalytic oxidation (UV−PCO) technology has been receiving extensive attention for indoor air purification in recent two decades. However, the formation of by-products during the UV-PCO process darken its prospect of providing healthy indoor air quality (IAQ). This study examines by-product generation and operational parameters from 36 UV-PCO tests using a pilot duct system with the objectives of developing reliable by-product predictive models. The statistical analysis aimed at establishing linear and non-linear regression models to predict the concentrations of formaldehyde and acetaldehyde based on factors such as concentration, RH, airflow, and irradiance. The developed linear models provided satisfactory estimations of acetaldehyde and the sum of formaldehyde and acetaldehyde (FA) levels with regression coefficients (R^2) of 0.74 and 0.84, respectively. Parametric study and bivariate analysis further confirm the statistical significance of independent variables on the acetaldehyde and FA productions. The PCO reaction pathway was proposed to explain that the presence of some strongly bounded intermediates on the surface decreased the reactivity of acetaldehyde to be further oxidized to formaldehyde.

1. Introduction

Heterogeneous ultra-violet photocatalytic oxidation (UV−PCO) based air cleaners have been receiving close attention recently due to its promising oxidation capability for a wide range of air pollutants, and thus it is capable of providing the sustainable indoor environment. An extensive body of research reports the performance of lab-scale UV-PCO air cleaners under various testing conditions and demonstrates their promising future of commercialization in a manner of stand-alone air cleaners or air cleaning units integrated into HVAC systems [1–8]. Different types of mathematical models, including analytical and numerical models, kinetic models, computational fluid dynamics (CFD) and empirical-based models, have been proposed to evaluate the UV-PCO removal efficiency of the tested compounds [9–17]. Although UV-PCO is an advanced technology for improving indoor air quality (IAQ), some researchers discovered that the operation of UV-PCO air cleaners might pose potential health risks due to the formation of carcinogenic compounds (e.g. formaldehyde, benzene) during air-cleaning processes [3,8,18–20]. Uncertain health exposure of PCO-based air cleaners in a building in terms of toxic by-product generation hinders immediate commercialization of PCO air purifiers and establishment of associated regulatory standards. In order to accelerate the progress of commercialization, there is ample need for conducting more basic research work to eliminate these technological obstacles.

At present, most research on by-product generation still relies on experimental observation. For example, a list of by-products, such as formaldehyde, acetone, acetaldehyde, hexane, cyclohexane, benzene, crotonaldehyde, benzaldehyde, formic acid, benzoic acid, CO, CO_2, and so on, has been qualitatively and quantitatively identified in the literature under different environmental conditions with diverse challenge volatile organic compounds (VOCs) [3,8,18,19,21–25]. It was experimentally demonstrated that the challenge VOC type and concentration, ozone concentration, photocatalyst type, UV irradiance, airflow rate, as well as water vapor have impacts on the formation of by-products. Hence, the by-product generation is closely related to the PCO chemo-dynamic affected by each operational condition. However, there is limited research aiming to examine the relationship between by-products and operational parameters in a modeling manner, which is increasingly recognized as an essential methodological basis to obtain fundamental knowledge on health exposure of PCO-based air cleaners. Although some researchers proposed potential pathways [18,21,23] and empirical models [26–28] to describe the mechanism of specific by-product formation and kinetics, these models are site-specific due to the facts that kinetic values (e.g., adsorption coefficient, reaction constant)

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came from specific testing system setting-up, and their predictive capabilities could be limited under varying conditions. In addition, few attempts have been made to create statistical models for the prediction of by-product generation in the air treatment, which can be a useful tool to promote the standard/code development in the healthy building industry. Compared with discrete experimental data, statistical models provide an efficient strategy to deeply and completely explore both individual and interaction effects on by-product generation, which will help us find optimal conditions to minimize by-products.

For the first time, this paper presents the by-product predictive model development using the linear and nonlinear multi-regression technique with an emphasis on prediction of formaldehyde and acetaldehyde, two common gaseous by-products, under various experimental conditions in a pilot in-duct UV-PCO unit. A small PCO database was established to facilitate the by-product analysis. Effects of VOC concentration, RH, irradiance, airflow rate, and ozone parameters on by-product formation were statistically studied. Multiple linear and non-linear models were developed and validated for aldehyde prediction. The goodness of fit for the models was evaluated by the regression coefficient (R^2), Durbin-Watson value, Kolmogorov-Smirnov test, and ANOVA F-test. Validation results indicated that the predictive models could be used to forecast aldehyde generation in a wide range of UV-PCO applications. In addition, on the basis of observation and model simulation, the potential PCO reaction pathway of ethanol was proposed to explain why acetaldehyde, rather than formaldehyde, was a dominant by-product of PCO of ethanol.

2. Materials and methods

2.1. PCO-based air cleaner

The pilot test rig used in this study (Fig. 1) was an aluminum duct system with a cross-section area of 0.3 m × 0.3 m (1 ft × 1 ft). The duct was an open–loop mode system which was able to provide 135–270 m^3/h (80–160 cfm) airflow rates by a speed-controlled fan mounted at the end. A pleated fabric pre-filter was mounted at the beginning section of the test rig to remove potential particles in the introduced laboratory air. The air mixed with evaporated VOCs in the gas mixer chamber composed of a mixing baffle and a perforated plate so that the contaminated air was fed into the duct system with a uniform distribution. The upstream and downstream of the duct were fitted with perforated stainless steel cross tubes to collect inlet and outlet air samples by sampling pumps and a photoacoustic gas monitor. Sampling tubes were connected to the sampling pumps at a sampling rate of 1.3 L/min for 1.5 h to explore the generation of by-products. After the cross tubes, sensors were installed at the centre of the duct to continuously monitor airflow, RH and temperature at upstream and downstream, respectively. At the middle section of the duct, there were three PCO filters (Saint-Gobain, France) and totally 2–6 low-pressure mercury vapor lamps (Ster-L-Ray, Atlantic Ultraviolet Corp., USA) allocated in two banks. The PCO filters were composed of the fiberglass substrate with 4.6 wt% TiO_2 loading. Brunauer–Emmett–Tele (BET) surface area of PCO filters was 106 m^2/g, and average pore diameter was 3.6 nm. There was an approximate 5 cm distance between the surfaces of the UV lamps and the PCO filters. Two types of UV lamps (UVC and vacuum UV (VUV)) were employed to examine the impacts of ozone-assisted PCO on by-product generation. An online ozone analyzer was connected to the duct system through bulkhead unions on the side of the duct system for ozone measurements. The detailed description of the duct system with regard to test rig dimensions, PCO filter characterization, and contaminant generation system can be found in the previous studies [7,8].

2.2. Chemicals

HPLC grade ethanol (99.8%), TO11/IP-6A aldehyde/ketone-DNPH mixtures (analytical standard) for the HPLC calibration and anhydrous grade acetonitrile (99.8%) for the HPLC operation were obtained from the Sigma-Aldrich Corporation (Canada). Deionized water filtered with a Milli-Q system (MilliporeSigma, Canada) was used for the HPLC calibration.

2.3. Analytical methods

The duct air quality parameters including ethanol, formaldehyde, acetaldehyde, temperature, RH, airflow, irradiance, and ozone concentration were analyzed. The inlet and outlet concentrations of ethanol were detected by a calibrated online photoacoustic spectroscopy (PAS, INNOVA 1312, LumaSense Technologies, Inc., USA). An optical filter with a centre wavenumber of 9.4 μm, which selectively measured the concentration of ethanol with the detection limit of 60 ppb, was installed in the PAS. The used optical filter was not affected by interference from carbon dioxide and water vapor and had no response for both formaldehyde and acetaldehyde. Analysis of formaldehyde and acetaldehyde in air was in compliance with the US Environmental Protection Agency Method TO11: aldehydes were trapped in a high purity silica adsorbent coated with 2, 4-dinitrophenylhydrazine (2, 4-DNPH) (Sigma-Aldrich Corp., USA) through

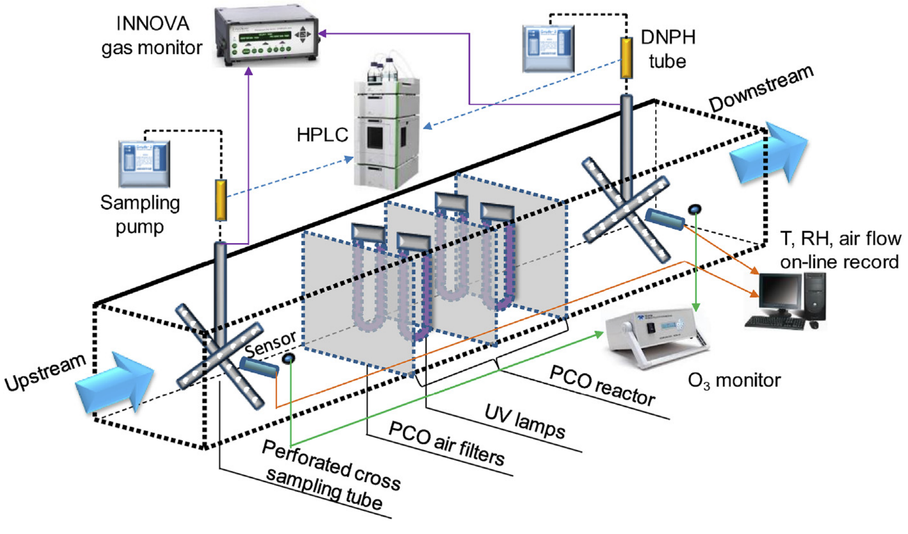

Fig. 1. Diagram of a UV-PCO duct system.