Numerical Simulation of a UV-PCO Plate Reactor

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Abstract. Ultraviolet photocatalytic oxidation (UV-PCO) system has gained increasing attention in indoor air treatments, of which the PCO reaction kinetics mainly depend on the radiation and airflow (contaminants) fields. It is recognized that the airflow rate has a significant influence on the PCO kinetics with the balance of the VOC mass transfer process. However, there are few discussion for the airflow rate dependency in the PCO kinetic reaction model. In addition, most of the studies in the literature assumed the incident surface irradiance was the energy participating in PCO reactions, which is not accurate. Hence, a 3D Computational Fluid Dynamics (CFD) model, including catalyst photon absorption coefficient, the conservation of mass, momentum, energy, and species, as well as PCO reaction kinetics, was introduced in this study. The determined model parameters were verified by the experimental data for a plate reactor challenged with 10 ppm acetone. The airflow rate dependency was examined in conjunction with CFD providing local flow field information, and the catalyst absorbed light intensity was quantified by a validated radiation model. It was found that the PCO removal efficiency predictions from the developed mathematical model agree with experimental data.

1. Introduction

Volatile organic compounds (VOCs) are one type of the most common indoor chemical contaminants with high vapour pressures. As a promising indoor gaseous VOC elimination method, photocatalytic oxidation (PCO) technology has gained increasing attention in the past decades. CFD modelling is an effective tool to investigate the complex UV-PCO working mechanisms and provides microscopic views of the fluid/thermal/contaminant transport phenomena. It consists of three parts: the UV irradiance field model, the fluid flow simulation, and the chemical reaction kinetic model. For the irradiance field modelling, the radiation transport equation (RTE) describes the traveling of photonic rays with their corresponding photonic energy loss or gain due to absorption and scattering [1] and solved by different radiation models. The fluid flow simulation is conducted by solving a series of governing equations for mass, momentum, energy, and species. As for the kinetic reaction model, the semi-empirical Langmuir-Hinshelwood (L-H) reaction rate equation was developed based on the adsorption-reaction-desorption theory along with two lumped control coefficients k (reaction rate constant) and K (VOC adsorption coefficient) [2].

Although extensive CFD studies have been conducted for UV-PCO simulation, the radiation energy flux mechanism is not well explained, and there is no method to quantify effective (absorbed) irradiance. In addition, it is recognized under the low flow rate, the reaction rate increases with the increase of airflow rate indicating the mass transfer-controlled gas phase mass transfer for the PCO reaction [3], then plateauing while surface reaction becomes the limiting step. However, quantification of the airflow rate on the porous mass transfer is scarcely examined. Therefore, the present work employs RTE and species transport equation-based CFD model to systematically study the two aspects: (1) development of a method to determine the catalyst radiation adsorption coefficient, and (2) development of a
mathematical model to obtain the airflow rate-dependent mass transfer coefficient as well as conduction of UV-PCO CFD simulations.

2. Experimental setup of the UV-PCO system

A series of experiments were conducted in this work: the radiation measurements, dark adsorption tests, and the PCO reaction investigations. Figure 1 shows the schematic diagram of the radiation measurement setup and the reactor used in this study. The trapezoid PCO reactor (net volume = 130.19 cm³) contained a quartz-glass and a flat catalyst coating plate (103.83 mm × 83.31 mm) which located at 5.5 mm lower than the bottom surface of quartz-glass. The inlet and outlet nozzles had the diameter of 6.35 mm, length of 15.3 mm and stretched into the reactor at an angle of 15° regarding the horizontal plane. The irregular 0.15g TiO₂/diatomite (porosity ε (0.5), tortuosity τ (2.7), pore volume (0.078 cm³/g) and pore diameter (6.0 nm)) coating area was computed by the sum of discretized control surfaces, which occupied 85% ± 3% of the plate. The reactor was irradiated by two UVA lamps (JINLI T5-8W, 0.0155 m blub diameter, 0.56 m blub length and 8 W UV-A output) side by side with the maximum irradiance peak at 365 nm.

The radiation measurements were conducted under the lab environment (22°C and 50% RH). Since it was difficult to directly apply the radiometer on the catalyst surface, the light intensities of 12 different conditions before and after coating the catalyst were measured and used for model validation as well as the catalyst adsorption coefficient determination. As shown in figure 1, the radiometer was fixed on the top of quartz-glass and horizontally moved to points 1, 2, 3 and 4, while the UV lamps moved vertically at three heights, H1 (0.01m), H2 (0.025m) and H3 (0.035m) away from the catalyst plate.

The PCO removal efficiency measurements were conducted by injecting acetone under different airflow rates (1, 2 and 3L/min) at 10 ppm along with the GC-FID analysis for the inlet and outlet samples. Prior to UV light on, the reactor was continuously and steadily challenged with a VOC in the dark environment to determine the mass transfer coefficients. Then the UVA-lamps were switched on once it reached saturated adsorption (when the \( \frac{C_{out}}{C_{in}} = 1 \)). It was expected to reach the steady-state flow field after turning on the lamps, then the PCO removal efficiency was calculated from the averaged inlet and outlet VOC concentration differences for 20 minutes when the outlet VOC concentration reached stable.

3. Photocatalytic reactor model

3.1 Governing equations for CFD simulation

The fluid flow field was solved by the steady-state conservation equations with the Shear-Stress Transport (SST) k-ω model, species transport equation and DO radiation model, which are shown below [1]:

\[
\frac{\partial}{\partial x_j}\left( \rho u_j \phi \right) = \frac{\partial}{\partial x_i} \left( \Gamma_{\phi} \frac{\partial \phi}{\partial x_j} \right) + S_{\phi} \quad (1)
\]

\[
\nabla \cdot \left( \rho \nabla \phi \right) \quad (2)
\]

\[
\nabla \cdot \left( I_j \left( r, s \right) v \right) + (a_j + \sigma_j) I_j \left( r, s \right) = a_j n^2 I_{j,0} + \sigma_j \frac{4\pi}{\int_{0}^{4\pi}} I_j \left( r, s \right) \Phi \left( s \cdot s \right) d\Omega \quad (3)
\]
3.2 UV-PCO kinetic reaction model

The PCO dynamics include mass transfer and kinetic reaction processes. The mass transfer equations are shown below representing three mechanisms, the convective and diffusive transport in the concentration boundary layer, the diffusion within the catalyst pore structure and the mass transfer at the catalyst surface:

\[
\frac{\partial C_b}{\partial t} + u \frac{\partial C_b}{\partial x} = \frac{D_B}{\delta_m} \frac{\partial^2 C_b}{\partial x^2} - \frac{D_{BL}}{\delta_m} (C_b - C_p) \quad C_{b1} = C_n
\]  

(4)

\[
\frac{\partial C_p}{\partial t} = \frac{D_{peff}}{\delta_m} \frac{\partial^2 C_p}{\partial x^2} + \frac{D_{BL}}{\delta_m} (C_b - C_p) - \frac{(1 - \varepsilon)}{\varepsilon} \frac{\partial C_s}{\partial t} \quad C_{px} = 0
\]  

(5)

\[
\frac{\partial C_s}{\partial t} = D_{ad-de} a (C_p - C_s) \quad C_{sx} = 0 \quad \text{before turning on UV lamps}
\]

(6a)

\[
\frac{\partial C_s}{\partial t} = D_{ad-de} a (C_p - C_s) - \alpha k C_s \quad C_{sx}^0 = C_{px}^0 \quad \text{after turning on UV lamps}
\]

(6b)

where \(C_b\) is the gaseous bulk concentration, \(C_p\) is the catalyst pore concentration, \(C_s\) is the catalyst surface concentration, \(D_B\) is the mass transfer coefficient from the boundary layer into the catalyst pore structure, \(D_{peff}\) is the effective diffusion coefficient inside the catalyst pores, \(D_{ad-de}\) is the overall mass transfer coefficient of the adsorption-desorption at the catalyst surface, \(a\) is the surface area of catalyst per volume of catalyst and \(k\) is the kinetic rate constant. \(D_{BL}\) is determined by the turbulent concentration boundary layer theory with Sherwood number as following [4]:

\[
D_{BL} = \frac{S_h D_{ij}}{L} = \frac{0.0296}{L} \left( \frac{x U_{\infty}}{\nu} \right)^{1/5} \left( \frac{\nu}{D_{ij}} \right)^{1/3} D_{ij}\quad \text{with} \quad \frac{D_{BL}}{L} = \frac{1}{L} \int D_{BL} dx
\]  

(7)

\[
\frac{\delta}{\delta_m} = S_c^{0.3} \quad \text{with} \quad \delta = 0.37 \times Re_x^{0.2}
\]  

(8)

where \(D_{ij}\) is the mass diffusivity, \(L\) is the plate length, \(U_{\infty}\) is the freestream velocity, \(\nu\) is the kinematic viscosity, \(\delta\) and \(\delta_m\) are the velocity and concentration boundary layer thickness. With the help of CFD, flow field, the local Sherwood number, and the mass transfer coefficient were calculated to account for the nonnegligible boundary layer growth on a short plate. Furthermore, \(D_{peff}\) is determined by considering the molecular diffusion and Knudsen diffusion within the catalyst pore structure as following:

\[
\frac{1}{d} = \frac{1}{d_{st}} + \frac{1}{d_{su}} \Rightarrow d_{su} = d_p \left( \frac{8RT}{3\pi M_i} \right)^{0.5} \Rightarrow D_{peff} = \frac{\varepsilon}{d} \frac{d}{\tau}
\]  

(9)

where \(d_p\) is the pore diameter, and \(M_i\) is the molecular mass. As for the kinetic reaction model, the reaction rate equation defined in Eq. (6b) was transformed into the numerically obtained \(C_s\) as following:

\[
r_{ VOC} = -\alpha k C_s = -\alpha k \frac{C_s (\alpha k e^{-(D_{ad-de} + \alpha k) x} + D_{ad-de})}{D_{ad-de} + \alpha k}
\]  

(10)

where \(\alpha\) is the catalyst radiation absorption coefficient quantitatively computed by rigorous CFD simulations.

3.3 Numerical methodology

The flow chart of the simulation methodology is shown in Figure 2. Finite difference method (FDM) with backward time centered space (BTCS) was adopted to solve the mass balance transport equations, and Ansys Fluent 19.0 was used to simulate the flow field and UV-PCO reaction.
Accurate simulations require high-quality meshes. In this work, the tetrahedron mesh was built with the refinement in the catalyst region, which contains three layers with 1.1 height increasing ratio to 0.5 mm maximum layer size. The mesh independence was examined under three different global element seed size (4.0 mm, 2.0 mm, and 1.0 mm). It was found the mesh was convergent at 2.0 mm that was adopted here.

As for the boundary conditions. The lamp was considered as a semi-transport wall with 15 \( \frac{w}{c^2} \) emitting diffuse radiation, which was measured by applying the radiometer (UVP model UVX-38) on the lamp surface. The inlet, outlet, and space were considered as a semi-transport wall with zero-emitting radiation such that the radiation transmits freely without reflection and refraction. Furthermore, the quartz-glass was defined as a semi-transparent wall with 99.5% transmittance, which was determined by the ratio of measured radiation intensity before and after applying the quartz-glass. Other walls were considered as opaque walls with prescribed adsorption coefficients, including 0.8 for lamp base [5], 0.9 for detector [6], 0.9 for detector probe [5] and 0.8 for reactor wall [7]. The adsorption coefficients for plate and catalyst was determined by radiation simulations. With respect to the flow field boundary conditions, mixed air and 10 ppm acetone were introduced at 1, 2, 3 and 4 L/min, respectively. The outlet was set as outflow, and all other walls were set as stationary walls with no-slip boundary conditions. As for the operating conditions, the radiative properties of injected VOC were considered the same as the fresh lab air since the VOC concentration was very low. Therefore, the absorption coefficient, scattering coefficient, and refractive index of the airflow were defined as 0.000014 [8], 0.00006 [8] and 1.003001[9], respectively.

4. Results and discussion

4.1 Determination of model parameters

4.1.1 Radiation model. Associated with the characteristics of DO radiation model, sensitivity analyses were conducted to determine the angular discretization and pixilation which control the number of discrete solid angles and angular overlapping. It was concluded that the angular discretization reached convergence at N=5, while pixelation did not change the results significantly. Hence, N=5 and P=1 were used in this study. Furthermore, two-step simulations were conducted to determine the catalyst UV adsorption coefficient. Firstly, 12 radiation data were used for radiation model validation and determine the pure plate UV adsorption coefficient without catalyst coating. By varying the coefficient such that the difference between experimental and numerical results reach the minimum, the optimal coefficient (0.61) was obtained. Secondly, the validated radiation model was conducted again to determine the catalyst UV adsorption coefficient by adjusting the coefficient of the catalyst boundary. Since the effect of reflected radiation from the plate underneath the catalyst was neglected (the catalyst layer was above 1 mm), the optimal catalyst absorption coefficient was obtained (0.86). The comparisons between numerical results and experimental data without and with catalyst are tabulated in Table 1, which shows good agreements for both cases.

Table 1. Radiation intensity predictions and comparisons with experimental data at 12 spatial points

| Radiation intensity (w/m²) | Without catalyst | With catalyst |
|---------------------------|------------------|--------------|
| H1@1                      | H1@2            | H1@3        | H1@4 |
| Experimental data         | 1.241           | 1.286       | 1.434 | 1.494 | 1.095 | 1.151 | 1.332 | 1.369 |
| Numerical results         | 1.242           | 1.353       | 1.487 | 1.523 | 1.09  | 1.132 | 1.298 | 1.357 |
| Difference                | 0.08%           | 5.21%       | 3.70% | 1.94% | 0.46% | 1.65% | 2.55% | 0.88% |
| H2@1                      | H2@2            | H2@3        | H2@4 |
| Experimental data         | 0.99            | 1.045       | 1.054 | 1.084 | 0.931 | 0.978 | 0.967 | 0.981 |
| Numerical results         | 1.048           | 1.067       | 0.964 | 1.103 | 0.934 | 0.957 | 0.934 | 0.995 |
| Difference                | 5.86%           | 2.11%       | 8.54% | 1.75% | 0.32% | 2.15% | 3.41% | 1.43% |
| H3@1                      | H3@2            | H3@3        | H3@4 |
| Experimental data         | 0.759           | 0.773       | 0.73  | 0.719 | 0.691 | 0.694 | 0.64  | 0.648 |
| Numerical results         | 0.769           | 0.795       | 0.703 | 0.657 | 0.681 | 0.719 | 0.649 | 0.686 |
4.1.2 Mass transfer coefficient. With the mass transfer process in the reactor before turning on the UV lamps, the Reynolds number, Sherwood number, and mass transfer coefficient were calculated by the average of the resolved flow field provided by CFD simulation. Solving Eqs. (4)-(6) by FDM, the outlet VOC concentration was calculated and compared with the experimental data (Figure 3 and Table 2). It is shown that numerical predictions from CFD computed mass transfer coefficient agree with the experimental data and is applicable in this study. However, there are some deficiencies at the first 10 minutes of dark adsorption experiment, which might due to a better velocity estimation of the concentration boundary layer as well as the mass transfer coefficient DBL are required.

4.1.3 PCO reaction rate constant. After turning on the UV lamps, it is expected that the outlet VOC concentration decreases due to the PCO reaction and gradually reaches stable with the new mass transfer and photocatalytic reaction equilibrium. Analogous to the mass transfer coefficient determination before turning on the UV lamps with the assumption of mass transfer coefficient \( D_{BL} \) remains the same, the kinetic reaction rate constant after turning on the UV lamps can be obtained by data fitting with Eq. (6b). Figure 4 and Table 3 show the numerical predictions of the outlet VOC concentration after turning on lamps as well as the best fitted Dm and k.

4.2 Photocatalytic reaction modelling
With the resolved radiation and airflow field along with the introduced PCO kinetic reaction model, the UV-PCO reactions were numerically investigated. Since the resolved local flow field information was provided by CFD simulation, the local Sherwood number, concentration boundary layer thickness, and mass transfer coefficient were calculated at each control volume instead of using averaged one from the previous section. Taking the case 1L/min as an example, the VOC concentration fields at the catalyst surface and mid-plane are shown in Figure 5. Due to the uniform distributions of VOC and its mass transfer coefficient in the reactor before lamps on, the VOC concentration field after PCO reaction follows a similar pattern as the radiation field. Moreover, VOC concentration decreased along the flow direction since the reactions and convection propagation were irreversible. From the mid-plane view of VOC concentration field, the reaction occurred immediately after the VOC flow contacted the catalyst surface. With the effect of diffusion propagation, VOC molecules at the top part of the reactor moved down to catalyst surface and took reaction as well.

| Difference | 1.32% | 2.85% | 3.70% | 8.62% | 1.45% | 3.60% | 1.41% | 5.86% |

Table 2. Numerical calculated mass transfer coefficient at dark conditions

| | 1L/min | 2L/min | 3L/min |
|---|---|---|---|
| \( D_{BL} \) (m/s) | 0.059 | 0.071 | 0.090 |
| \( d_{peff} \) (m²/s) | \( 1.04 \times 10^{-7} \) | \( 1.04 \times 10^{-7} \) | \( 1.04 \times 10^{-7} \) |
| \( D_{ad-de} \) (m/s) | \( 1.56 \times 10^{-4} \) | \( 9.25 \times 10^{-5} \) | \( 6.15 \times 10^{-5} \) |

Table 3. Data fitting obtained mass transfer coefficient and kinetic rate constant in PCO

| | 1L/min | 2L/min | 3L/min |
|---|---|---|---|
| \( D_{BL} \) (m/s) | 0.059 | 0.071 | 0.09 |
| Reaction rate constant (s⁻¹) | 0.020 | 0.027 | 0.038 |
Figure 5. The VOC concentration field at catalyst surface (a) and mid-plane (b) after turning on the UV-lamps

The predictions of overall VOC removal efficiency for three different airflow rates are tabulated in Table 4. It is noted the model predictions agree well with the experimental data, although some deficiencies exist due to the residuals from the data fitting in the determination of model parameters.

| VOC removal efficiency | 1L/min | 2L/min | 3L/min |
|------------------------|--------|--------|--------|
| Experimental data      | 0.523  | 0.309  | 0.245  |
| Model predictions      | 0.512  | 0.327  | 0.258  |
| Experimental/model difference | 2.14% | 5.86% | 5.31% |

5. Conclusion
A CFD-based method was introduced in this study to evaluate the role of porous mass transfer in the UV-PCO reactions. A comprehensive PCO kinetic reaction model was introduced in which the influence of the airflow rate was evaluated. The DO radiation model was validated and employed to determine the catalyst radiation adsorption coefficient. It is found that the predictions of the overall VOC removal efficiency by the new PCO reaction model agree well with the experimental data. Future research will be conducted to include investigating the light intensity, VOC concentration, and humidity dependency as well.

Acknowledgments
The authors gratefully acknowledge the funding provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) through the Discovery Grant.

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