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# First-principles modeling, scaling laws and design of structured photocatalytic oxidation reactors for air purification

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## Abstract

First-principles, predictive engineering models provide a sound theoretical basis for quantifying the inherent light energy utilization capabilities and performance limitations of candidate commercial photocatalytic oxidation reactor configurations. In particular, these models provide insight into the similarities and differences between photoreactors based on structured honeycombed monoliths, and those based on reticulated foams or other random catalyst supports.

For honeycombed monoliths, a deterministic first-principles radiation field model provides the channel wall light intensity profile down the length of a single channel in the monolith. A three-dimensional developing flow convection–diffusion reaction model employing this radiation field submodel predicts the velocity and concentration fields. The model shows that light intensity gradients in a monolith of typical dimensions are severe, that only a fraction of the monolith can be effectively photo-activated, and as a consequence process performance is largely controlled by light distribution. For a given light source and photocatalyst combination, reactor performance scales according to the aspect ratio of the channeled monolith, the Reynolds number, and the Dahmköhler number.

For randomly structured monoliths, the radiation field must be determined by probablistic methods. Monte Carlo simulations show that the radiation field in such random porous structure scales according to the pore size distribution and the void fraction, and the photocatalyst film thickness. Reactor performance scales by the radiation field, the Peclet number, the Stanton number, and the Dahmköhler number. The complex interrelationship between the random structure of the monolith and the resulting radiation field and mass transfer behavior makes scaling of these reactor types particularly difficult.

*Keywords:* First-principles modeling; Photocatalytic oxidation; Air purification; Monolith

## 1. Introduction

A key unresolved issue in the commercial application of photocatalytic oxidation (PCO) technologies to contaminated air purification is that of optimum photocatalytic reactor design. These designs present special challenges in that a cost-effective photoreactor must simultaneously and efficiently contact the activating light, the solid catalyst and the dilutely contaminated air stream while providing high photon utilization, low pressure drop and low power consumption in a physically compact vessel. Until very recently the lack of fundamental validated design tools based solidly on reaction engineering principles has limited design processes to those largely based on Edisonian and rule-of-thumb practices. These trial-and-error

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approaches have produced relatively poor initial designs, with large margins for improvement with each subsequent design generation. Unfortunately, the poor performance behavior and, in particular, the high energy utilization of first generation designs has caused some environmental engineering professionals to conclude that PCO technology is inherently energy inefficient and not cost effective relative to competing technologies.

This situation has been changing over the course of the last several years, as several first-principles, predictive models for PCO reactors incorporating monolithic catalyst supports have appeared in the literature [1–7]. These steady-state mathematical models provide a sound theoretical basis for quantifying the inherent ultraviolet (UV) light energy utilization capabilities and purification performance limitations of candidate commercial configurations, including those employing spatially structured honeycomb monoliths [1–5] and randomly structured reticulated foam monoliths [6,7]. Detailed reactor and model analyses can ultimately provide scaling laws, and optimal designs and operating protocols. In this paper we review the state-of-the-art in photocatalytic reaction engineering for structured photocatalytic reactors and summarize the design learning gained through these efforts.

## 2. General design considerations

Economic analyses of commercial-scale prototypes unequivocally show that *light energy costs* dominate the total annual cost ($/yr) or unit processing cost ($/cfm air treated) of an installed PCO unit. Based on this observation, one can conclude that the UV radiation field is the single most important design consideration for commercial photoreactors. Because photons are valuable, the radiation field should be designed in a way that captures all photons within the active zone of the reactor and maximizes the probability that these photons will drive the desired photocatalytic reactions.

Complete photon capture implies that there will exist substantial gradients in the local rate of UV energy absorption throughout the volume of the photoreactor. The flow field must therefore be designed to ensure that there are no flow streamlines that travel exclusively through “dark” regions of the reactor. In effect, the reactor must provide sufficient residence time in the light-activated regions for all the air to be treated, i.e., flow bypassing through dark regions by a part of the air stream will unduly limit the reactor conversion performance.

These considerations have led to widespread adoption of variations on the basic modular design shown in Fig. 1. Successive alternating banks of UV lamps and structured catalyst support monoliths are mounted directly in a square or rectangular duct. A commercial prefilter is typically incorporated on the upstream side of the first lamp bank; this prefilter may or may not be impregnated with the active photocatalyst. The lamps irradiate the monolith front and back faces. The design is modular in the sense that the number of lamp bank/monolith modules can be increased or decreased to control the contaminant conversion per pass in the reactor. The monolithic nature of the catalyst support greatly simplifies construction and maintenance relative to a packed bed configuration, since the panels can be easily inserted and removed without dismantling the entire system.

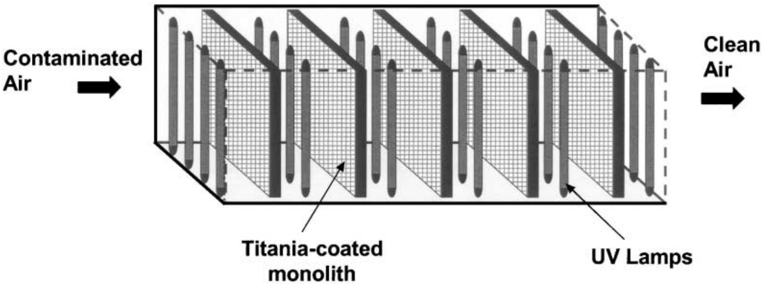


Fig. 1. Schematic diagram of a commercial-scale photocatalytic reactor for air treatment employing structured monoliths.

## 3. General modeling considerations

By “first-principles” models, we mean well-accepted conservation and accounting principles combined with physically based representations of transport and kinetic rates. In general these models combine energy conservation with momentum conservation for the fluid flow field and species mass accounting statements for the contaminant, byproduct and product concentration fields. In air purification applications, particularly for those targeted at indoor air quality improvement, homogeneous reaction rates and thermally catalyzed reaction rates are negligible. This characteristic behavior significantly simplifies the overall model framework and subsequent numerical solution, since: (i) the energy conservation statement reduces to near ultraviolet (UV) radiation field modeling through photon accounting; (ii) the radiation field model solution can be validly decoupled from the convection–diffusion reaction model for flow and concentration fields.

It is important to note that the *model framework* for spatially structured monoliths *differs substantially* from that for randomly structured monoliths. In channeled monoliths, the geometry, flow field and radiation field are well defined, and as a consequence deterministic model descriptions can be developed. In contrast, for random structures exact descriptions for these key elements cannot be readily determined. Instead, Monte Carlo simulations for the radiation field and pseudo-homogeneous models for the flow and concentration fields are more conveniently employed. Because these two model frameworks are so dramatically different, they are described separately in the sub-sections that follow.

### *3.1. Spatially structured monoliths*

#### *3.1.1. Radiation field modeling*

Fig. 2(a) is a photograph of a titania-coated and an uncoated square-channeled cordierite$^{\mathrm{TM}}$ honeycomb monolith. The channel density is 25 CPSI (cells

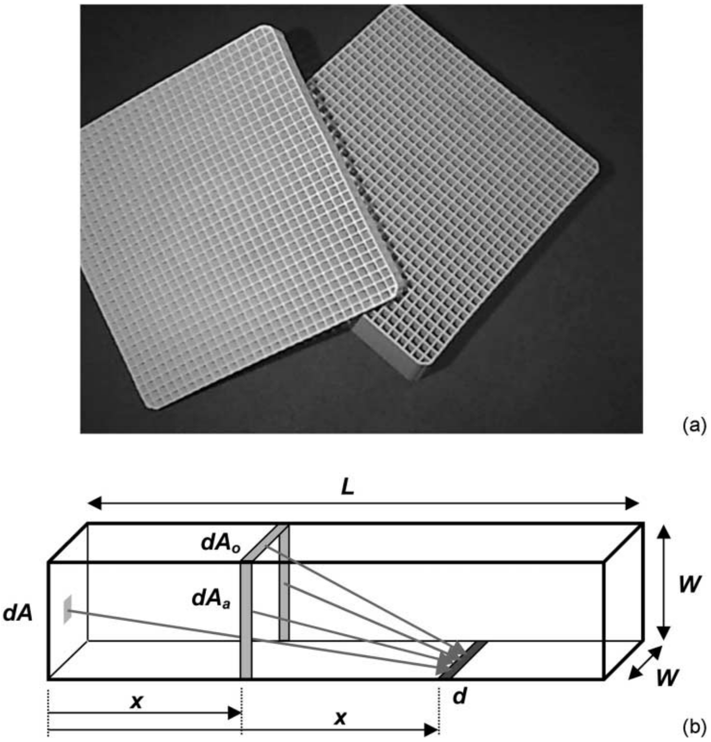


Fig. 2. Square-channeled honeycomb monoliths. (a) Photograph of a titania-coated and an uncoated cordierite monolith. The channel density is 25 CPSI. (b) Geometry of a single channel.

per square inch). This cell density is much lower than the densities employed in automotive catalytic converters, where values greater than 100 are typical. The 0.5–1.0 in. flow length of the photocatalytic monolith is relatively short, yielding channel aspect ratios in the order of 3–12. By comparison, aspect ratio values in catalytic converters are in the hundreds. The dramatically more open flow geometry in the photocatalytic system is a direct result of the nature of the UV radiation field in channeled monoliths as described in the paragraphs that follow.

Fig. 2(b) illustrates the geometry of a single square cross-section channel in the monolith. For a channel length $L$ and a width $W$, the aspect ratio $\alpha$ is defined as $L/W$. Photons enter the channel from an external source and, upon interaction with the photocatalyst coated on the channel wall, are either absorbed or reflected. Thus to determine the radiation intensity at any point in the channel, one must account for photons originating directly from the channel mouth region, photons reflecting from the opposite walls, and photons reflecting from the adjacent wall.

To provide quantitative predictions for the radiation field, Hossain and Raupp [4] have developed an incidence model that assumes the structured channel monolith is irradiated by a diffuse external polychromatic light source, that a light absorbing and diffusely reflecting catalytically active thin film is uniformly coated on the inner walls of the monolith channels, and that the film reflectivity is wavelength dependent. In the sense that the wavelength-dependent properties of the source and film can be directly measured, this polychromatic radiation field model contains no adjustable parameters.

The mathematical model representation of the light flux distribution to the monolith wall and through the cross-section of the monolith channel take the form of integral equations. For example, the UV flux $I_{\mathrm{w}}(\lambda)$ to the channel wall is given by

$$\begin{aligned} I_{\mathrm{w}}(\lambda) &= F\{\mathrm{d}A;\ A_0\}+2\rho(\lambda)\int_{A'_{\mathrm{ad}}} I_{\mathrm{w}}(\lambda)\,\mathrm{d}F\{\mathrm{d}A;\ \mathrm{d}A'_{\mathrm{ad}}\} \\ &\quad +\rho(\lambda)\int_{A'_{\mathrm{op}}} I_{\mathrm{w}}(\lambda)\,\mathrm{d}F\{\mathrm{d}A;\ \mathrm{d}A'_{\mathrm{op}}\} \qquad (1) \end{aligned}$$

where $\rho(\lambda)$ is the wall light wavelength-($\lambda$) dependent reflectivity, d$F$ the geometrically determined differential view factors, $F$ the geometrically determined integral view factor for the source (channel mouth) area, and the differential areas d$A$ are as defined in Fig. 2(b). For regular geometries, including square, circular, and triangular cross-section channels, the necessary view factors are readily available [8,9]. The equations can be solved numerically using Gauss–Legendre quadrature to give quantitative estimates of the radiation intensity profile down the length of the monolith channel for a specified incident light intensity distribution at the entrance of the channel.

Model predictions are in excellent agreement with measurements employing titania-coated monolith channels and near UV "black light" lamps emitting light primarily in the 300–400 nm range. Details of the model predictions reveal that radiation field gradients are large, with relatively little light penetrating beyond a length equivalent to three channel widths. This prediction implies that, for monoliths with aspect ratios typical of commercial thermal catalytic monoliths, a large fraction of the coated channel wall is not effectively irradiated. Moreover, the model predictions imply that the light-activated region of the monolith is limited to the *entrance region* for fluid flow development.

For a given channel type, the *dimensionless* model equations provide *scaling laws*, which reveal that light intensity profiles are controlled uniquely by channel aspect ratio $\alpha$ and film reflectivity. If the reactor designer is restricted to use of unmodified commercial titania thin films, then channeled monolith reactors scale solely by the channel aspect ratio.

### *3.1.2. Flow field and concentration field modeling*

The radiation field sub-model predictions described above indicate that neither plug flow nor fully developed laminar flow models will provide accurate description of the flow field in the active portion of the channel monolith. We have therefore developed a three-dimensional *developing flow* convection–diffusion reaction model to predict the velocity and concentration fields in a single channel [5]. Alternatively, one can employ one-dimensional convection–diffusion reaction descriptions with mass transfer coefficients [1,2], although the accuracy of such lower dimensional models relies on the accuracy of the mass transfer correlation.

Numerical solutions to the ASU three-dimensional reactor model employing the validated deterministic first-principles radiation field model are in excellent agreement with experimental measurements of formaldehyde and toluene conversion in a pilot-scale air purification system configured in a wide variety lamp/monolith combinations [5]. The validated model in dimensionless form provides scaling laws through identification of the governing dimensionless groups. These familiar parameters are the dimensionless Reynolds number *Re*, which arises through the velocity field equations, and the dimensionless Damköhler number *Da*, which arises in the concentration field diffusion reaction boundary condition at the photocatalyst surface. In summary, photocatalytic reactor performance is therefore uniquely determined by the channel geometry type, channel aspect ratio $\alpha$, the *Re* number and the *Da* number.

The model reveals several key insights into the behavior of a channeled monolith photocatalytic reactor design. Overall, the model shows that in a monolith of typical dimensions, process performance is largely controlled by UV intensity gradients. Irradiating the monolith from both the inlet and outlet sides can increase the effective length of the reactor, although the incremental increase in performance does not scale linearly with increased total irradiation intensity.

With increasing Reynolds number conversion decreases; for a doubling of *Re*, conversion is nearly halved. For a monolith of fixed dimensions, this behavior suggests that the predicted behavior can be attributed largely to a reduction in the residence time of the contaminant molecules in the reactor with increasing flow rate. Note that this scaling law is valid only over the *Re* number range from about 50 to 2000, i.e., in the laminar flow regime and for flows sufficiently high to make axial dispersion negligible.

The effect of Damköhler number for a fixed value of *Re* is complex. To understand this behavior it is useful to recall the physical meaning of *Da*. The Damköhler number is a ratio of the *characteristic* (intrinsic) rate of chemical reaction evaluated at monolith mouth conditions, and the *characteristic* rate of diffusional mass transfer evaluated for a linear concentration gradient where the surface concentration of the reactant is zero. At low *Da* values, rates of photocatalytic reaction are inherently low relative to mass transfer, and the process is largely kinetically controlled. As *Da* increases from low values, the exit contaminant conversion increases nearly linearly. As *Da* increases further, diffusional mass transfer limitations become important, until for values greater than about 10 the process is dominated by mass transfer limitations. In this regime increasing *Da*, as could be achieved in a given application by developing a more active photocatalyst, will have a limited return on process performance enhancement. For example, a catalyst improvement that doubles the activity such that *Da* is increased from 40 to 80 leads to only about a 10% absolute increase in reactant conversion.

### *3.2. Randomly structured monoliths*

#### *3.2.1. Radiation field modeling*

Randomly structured monoliths include paper, fiber or ceramic filter elements and reticulated foams. Fig. 3 is a photograph of two reticulated foam alumina monoliths manufactured by Hi-Tech ceramics. These particular monoliths shown for illustrative purposes were manufactured in a configuration suited for an annular photoreactor; manufacture in a panel-type configuration suitable for the reactor type shown in Fig. 1 is straightforward. The manufacturer classifies these reticulates by pores-per-inch (PPI), a value that only roughly corresponds to the actual number of pores found in a linear inch of monolith. The mean pore sizes for the 10 and 30 PPI reticulates are 1.5 and 0.75 mm, respectively, while the surface areas per volume are approximately 2300 and 4400 $m^2/m^3$, respectively.

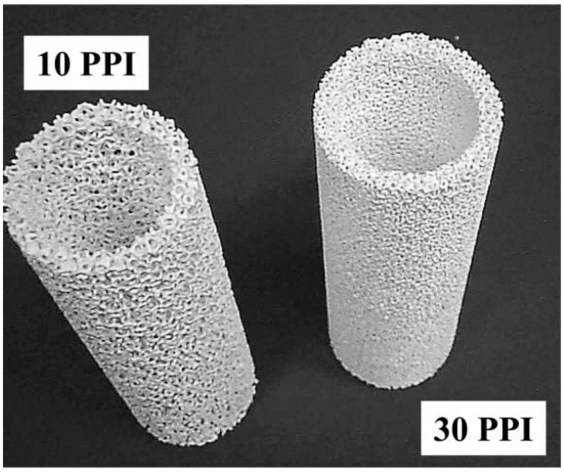


Fig. 3. Photograph of two alumina reticulated foam monoliths fabricated for an annular photocatalytic reactor.

The complex, random nature of the reticulate precludes the use of a deterministic radiation field model structure that employs well-defined geometric view factors. Instead, a probablistic model structure and Monte Carlo simulation is adopted. Changrani and Raupp [6] described two alternative approaches that yield equivalent results. In the "spatial" approach, the random pore structure of the monolith is generated by using Monte Carlo methods to randomly choose pore locations and pore sizes, consistent with the reticulate physical parameters (e.g., porosity, pore size distribution). This generated porous structure is stored in memory, and photons randomly generated from the lamp surface fly into the structure, where their paths are tacked analytically to determine the locations of solid scattering. In the "temporal" approach, the reticulate pore structure is virtually generated as the photon flies through it. The flight length is determined stochastically based on the reticulate void fraction. With this approach, each photon effectively "sees" a different random structure. The temporal approach requires substantially lower memory and CPU time than the spatial approach, without loss of simulation accuracy.

Simulations for the UV light profiles are in close agreement with experimental measurements for titania-coated 10, 20 and 30 PPI alumina reticulates. The simulations reveal that the magnitude of the local volumetric rate of energy absorption (LVREA) in the reticulate regions near the irradiated face increases with decreasing monolith mean pore size. However, the magnitude of the LVREA gradient also increases with decreasing reticulate mean pore size. For a fixed flow length, the smaller pore size reticulates capture a greater fraction of light, but at the cost of this higher LVREA gradient and existence of relatively "dark" regions at the trailing edge of the monolith. For a fixed light source and optical properties of the photocatalytic film, the model demonstrates that the radiation field is uniquely determined by the pore size distribution of the reticulate, the reticulate voidage, and the photocatalyst film thickness. Of these parameters, the LVREA profile is most sensitive to the voidage.

#### *3.2.2. Flow field and concentration field modeling*

As for the radiation field, the random nature of the flow space in the porous reticulate precludes deterministic descriptions of the flow and concentration fields. Instead "plug flow" fluid flow behavior is assumed. For the concentration field, a pseudo-homogeneous description is employed for cases when mass transfer intrusion is expected to be negligible, whereas a heterogeneous description is employed otherwise. The required dimensionality of the model is determined by the nature of the expected radiation field and concentration gradients.

Heterogeneous model representations [7] show that the magnitude of the interfacial contaminant concentration gradient depends on the magnitudes of the Damköhler number and the local value of the dimensionless radiation field profile. The interfacial gradient will be most severe for intrinsically fast reactions, catalyst supports and flow conditions that yield inherently slow mass transfer rates, and high local UV intensities.

Based on the dimensionless forms of the model equations, the resulting dimensionless concentration field $\Psi$ (and hence contaminant conversion) will take the general form:

$$\Psi = \Psi\{Pe, St, Da, \Lambda(\xi)\} \tag{2}$$

where $Pe$ is the Peclet number, $St$ the Stanton number, and $\Lambda(\xi)$ the dimensionless radiation field. This outcome highlights the difficulty in scaling the random support type photoreactor. For example, consider the following situation in which a photoreactor operates in the low $St$ regime. The dimensionless Stanton number represents a ratio of the characteristic rate of reactant mass transfer from the bulk fluid to the active surface to the characteristic rate of reactant flow by convection. For photoreactors operating in a regime influenced by mass transport, modification of the catalyst support to yield inherently higher mass transfer rates to increase $St$ will cause the conversion to increase but only as long as the dimensionless radiation field is not simultaneously adversely modified.

However, changing the Stanton number by modifying the random monolith implies a change in active photocatalytic surface area per reactor cross-sectional area. It seems highly unlikely that a different physical structure could yield similitude in the UV radiation profile. Moreover, the $Pe$ value would likewise be expected to change with changes in monolith structure. It is clear that variations in any geometric/spatial parameter simultaneously affect the catalyst distribution and the UV distribution within the active reactor volume, thus making it difficult to predict the effect of these changes on the photoreactor performance without a validated reactor model.

## 4. Simulation example for a practical reactor configuration

To illustrate several key capabilities of the models described above, we have constructed an integrated model and performed simulations for the photocatalytic reactor shown in Fig. 4. Key physical design parameters for this reticulated foam filter — lamp bank — channeled monolith configuration include number and type/intensity of lamps, lamp bank distance $h1$ to the filter and distance $h2$ to the monolith, as well as the filter and monolith width $a$ and length $b$ (generally constrained by the dimensions of the air handling ductwork). In the example documented here, $h1$ and $h2$ are both equal to 5 cm, and the filter and monolith dimensions are 32 cm × 48 cm. The key filter design parameters are a mean pore size of 1.5 mm with variance of 0.18 mm$^2$ and an overall porosity of 0.87. The triangular geometry channeled monolith aspect ratio is equal to 2.

The Monte Carlo method was employed to predict the UV light intensity field on the back face of the filter and the front face of the channeled monolith. Fig. 5 shows the smoothed LVREA profile in the first 0.2 cm layer of the back face of the filter predicted by tracking $10^8$ photons. The LVREA profile variation is substantial with three clearly identifiable maxima. These absorption maxima correspond to the incident intensity profile created by the three parallel lamps. Greater

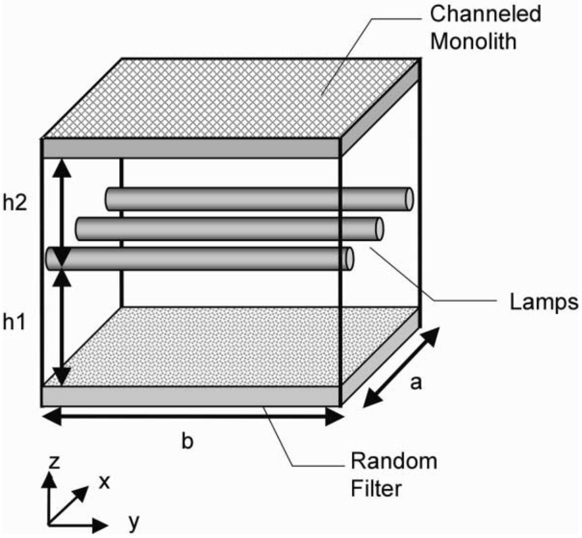


Fig. 4. Schematic diagram of a filter — lamp bank — channeled monolith photocatalytic reactor configuration indicating key physical dimensions.

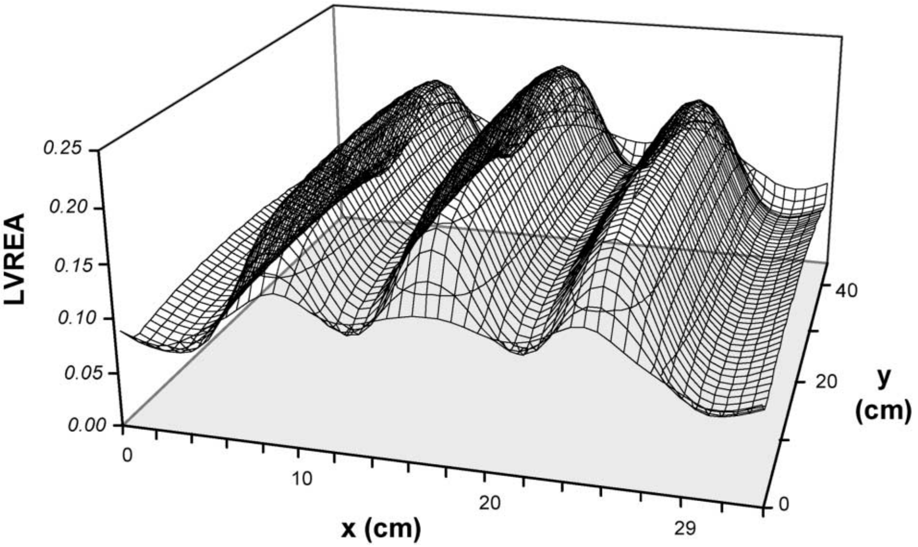
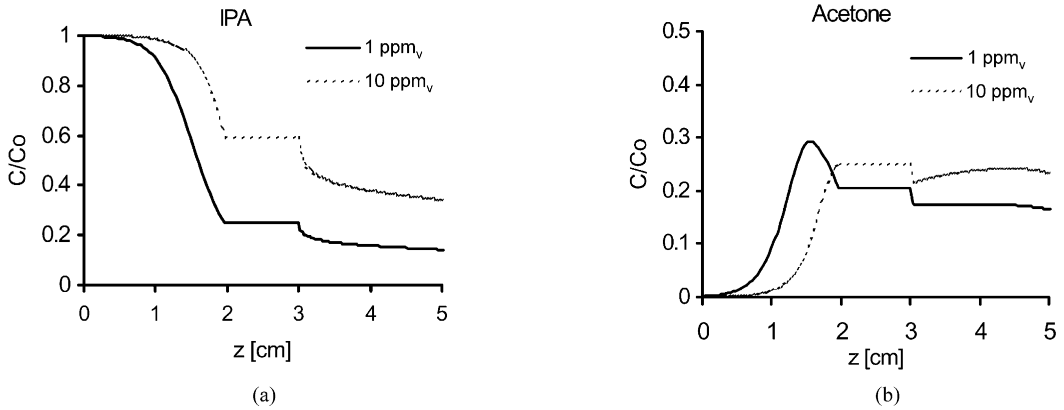


Fig. 5. Characteristic LVREA in the filter layer on the lamp side for the reactor configuration shown in Fig. 4.



(a) (b)

Fig. 6. Conversion of IPA and production of acetone for 10 ppm$_V$ (dashed lines) and 1 ppm$_V$ (solid lines) inlet IPA concentration as a function of flow length for the reactor configuration shown in Fig. 4.

uniformity can be achieved by increasing the distance between the lamp bank and the filter or monolith, but with a tradeoff of lower overall photon absorption. Greater uniformity can also be achieved by adding more lamps, but at a cost of higher energy costs.

Fig. 6(a) shows predicted fractional conversion of isopropyl alcohol (IPA) versus photocatalytic reactor flow length for inlet concentrations equal to 10 and 1 ppm$_V$ and an inlet air velocity of 1 m/s. Substantially, higher conversion is obtained for the lower inlet concentration, reflecting the substantial non-linearity of the destruction kinetics. For this example, most of the conversion occurs in the pre-filter. Analysis of the simulations reveals that this imbalance is caused largely by the greater efficiency for photon capture by the reticulated filter compared to the channeled monolith, and secondarily by the higher contaminant concentrations and hence destruction higher rates in the filter region.

In IPA destruction, it is well known that acetone is created as a volatile byproduct, which can be photocatalytically destroyed to produce complete oxidation products. In this example, acetone concentration goes through a maximum as shown in Fig. 6(b), with the location of the maximum found in the prefilter for 1 ppm$_V$ inlet IPA concentration, and found near the outlet of the monolith for 10 ppm$_V$ inlet IPA concentration. Note that in a recirculating air environment it may not be necessary to achieve complete conversion of the indoor air contaminant and byproducts in a single pass, although this design consideration depends on the hazard level of these chemical species present.

## 5. Conclusions

Models for both spatially and randomly structured monolith photocatalytic reactors reveal a complex interplay between the monolith structural details, the resulting light radiation field in the monolith, and the reactor performance. For spatially structured monoliths, scaling laws depend on the geometry and aspect ratio of the channels, as well as dimensionless groups that typically appear for conventional catalytic reactors, including the Reynolds number and the Damköhler number. Randomly structured monolith designs scale by mesoscopic physical parameters such as pore size and void fraction, along with the Peclet number, Stanton number, and Damköhler number.

Armed with this new insight into monolith PCO reactor capabilities and limitations, along with quantitative reactor modeling tools, optimal design and scale-up strategies for specific air treatment applications can now be systematically pursued.

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