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A methodology for modeling photocatalytic reactors for indoor pollution control using previously estimated kinetic parameters

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ABSTRACT

A methodology for modeling photocatalytic reactors for their application in indoor air pollution control is carried out. The methodology implies, firstly, the determination of intrinsic reaction kinetics for the removal of formaldehyde. This is achieved by means of a simple geometry, continuous reactor operating under kinetic control regime and steady state. The kinetic parameters were estimated from experimental data by means of a nonlinear optimization algorithm.

The second step was the application of the obtained kinetic parameters to a very different photoreactor configuration. In this case, the reactor is a corrugated wall type using nanosize TiO_2 as catalyst irradiated by UV lamps that provided a spatially uniform radiation field. The radiative transfer within the reactor was modeled through a superficial emission model for the lamps, the ray tracing method and the computation of view factors. The velocity and concentration fields were evaluated by means of a commercial CFD tool (Fluent 12) where the radiation model was introduced externally. The results of the model were compared experimentally in a corrugated wall, bench scale reactor constructed in the laboratory. The overall pollutant conversion showed good agreement between model predictions and experiments, with a root mean square error less than 4%.

1. Introduction

Regarding air pollution, the social concern has been usually focused on outdoor air quality problems. Nevertheless, in the past decades, along with the improvement of living standard, there has been an increasing interest in the role played by indoor or confined environments pollution in human health [1,2]. This is due to a conjunction of three main factors: (a) modern buildings tend to be designed and constructed with a high thermal insulation and air tightness in order to optimize the air conditioning processes and thus save energy and money [3]; (b) there are a large number and types of materials found indoors that may release chemical compounds into their surroundings and which can reach unhealthy concentrations; (c) the fact that, in most societies, people spend far more time doing activities indoors rather than outside [4]. In addition to the aforementioned factors, it should be added that many studies have demonstrated that for some compounds, indoor concentrations can be higher than outside [5,6]. Moreover, this indoor pollution presents a more difficult detection compared to the typically particulate-matter-related urban pollution [7].

The effects in human health of a poor air quality in a room depend on the type and concentration of pollutant, exposure times and the genetic predisposition of the occupants. A generalized clinical picture that combines headaches, nausea, dizziness, eye, nose, or throat irritations, dry cough and tiredness [8] is known as Sick Building Syndrome (SBS). This syndrome is usually associated with the presence of volatile organic compounds (VOCs) [1,3].

Indoor air pollution may be a result of in situ generation or from an exchange with the outside. Indoor chemical pollutants, particularly VOCs, are emitted from building materials, furniture and equipment [8]. Among VOCs, formaldehyde (HCHO) is one of the most dominant and has a particular interest due to its abundance in an indoor environment [4,6]. HCHO is usually the most abundant aldehyde in air and also the most studied [5].

HCHO is the simplest aliphatic aldehyde; at ordinary temperatures, HCHO is a strong smelling colorless gas. It is a widely used chemical in the industry and is present in a large number of household items, such as furnishing, carpeting, paints and cleaning products; it is also a byproduct of some combustion processes, like incense sticks and cigarettes [2,6]. Indoor concentrations of HCHO may reach up to 2 ppmv (1 ppmv = 1.23 mg m^{-3} @NTP), but are typically below 0.1 ppmv [1]. In this range, gaseous HCHO is known to

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Nomenclature

A_{cat}	photocatalytic area (cm^2)
C	molar concentration ($mol\,cm^{-3}$)
ΔF_{ij}	view factor (dimensionless)
D_{Fm}	molecular diffusivity of formaldehyde in a mixture ($cm^2\,s^{-1}$)
$e^{a,sup}$	local superficial rate of photon absorption, LSRPA ($einstein\,cm^{-2}\,s^{-1}$)
g	gravitational acceleration ($cm\,s^{-2}$)
H_{ij}	visibility factor (dimensionless)
I	specific radiation intensity ($einstein\,cm^{-2}\,s^{-1}\,sr^{-1}$)
J	diffusive molar flux ($mol\,cm^{-2}\,s^{-1}$)
K_W	kinetic parameter ($cm^3\,mol^{-1}$)
L_L	lamp useful length (cm)
N	total molar flux ($mol\,cm^{-2}\,s^{-1}$)
$\underline{n}$	unit outwardly directed normal to the catalytic plane (dimensionless)
P	pressure ($dyn\,cm^{-2}$); also lamp power output ($einstein\,s^{-1}$)
q	radiation flux ($einstein\,cm^{-2}\,s^{-1}$)
Q	volumetric flow rate ($cm^3\,s^{-1}$)
r_F	heterogeneous reaction rate ($mol\,cm^{-2}\,s^{-1}$)
r_L	lamp radius (cm)
R	homogeneous reaction rate ($mol\,cm^{-3}\,s^{-1}$)
R_λ	spectral reflectance
T_λ	spectral transmittance
v	velocity ($cm\,s^{-1}$)
x, y, z	coordinate system
X	conversion (dimensionless)

Greek letters

α	kinetic parameter ($cm^3\,einstein^{-1}$)
ρ	density ($g\,cm^{-3}$)
η_λ^{abs}	fraction of spectral radiation absorbed (dimensionless)
κ_F	kinetic parameter ($cm^3\,mol^{-1}$)
λ	wavelength (nm)
$\underline{\underline{\tau}}$	viscous stress tensor
ϕ, θ	spherical coordinates (rad)

Subscripts

cat	relative to a catalytic wall
exp	relative to experimental data
mod	relative to model
non-cat	relative to a non catalytic wall
F	relative to formaldehyde
Fi	relative to a radiation filter
W	relative to water
w	relative to wall
wi	relative to reactor window
λ	wavelength dependence

Superscripts

abs	absorption of radiation
in	relative to reactor inlet; also, relative to incoming radiation flux
out	relative to outgoing radiation flux

Special characters

_	denotes a vector
⟨ ⟩	indicates an averaged property

produce headache, nausea and chest tightness; it can also irritate the eyes and the respiratory tract and skin [4]. This concentration range, unfortunately, is in perfect accordance with the odor threshold of HCHO. For higher levels, between 5 and 30 ppmv, HCHO can produce irritation of lower airway and pulmonary effects [1,4]. Furthermore, HCHO was recently categorized as a human carcinogen [9].

Due to the unhealthy impact of HCHO presence inside buildings and its ubiquity, there is a serious need to attain its abatement. Traditional approaches to reduce exposure are related to source control, increasing of air renewal rates and air cleaning. When the two first are not possible to carry out, an air treatment technique must be applied. Conventional control processes, such as filtration and adsorption, have major drawbacks, mainly due to the low concentrations of pollutants and also the final disposal requirements. In this context, gas phase heterogeneous photocatalysis appears as an emerging technology for indoor air purification.

Photocatalytic devices for purification of indoor air have already been probed with success in the elimination of a wide range of organic and inorganic pollutants [10–13]. The technology relies on the properties of TiO_2 nanoparticles, a semiconductor that, under the illumination of UV light, can start a series of surface reactions leading to the complete mineralization of the pollutant. The main advantages of this technology also include: the operation at room temperature and atmospheric pressure, the use of an inexpensive catalyst and the possibility of combination with conventional control devices [2,3,14].

Photocatalytic processes have been intensively investigated, addressing issues such as reaction kinetics, doping and deactivation of photocatalyst, and reactor design [14]. Among the pollutants studied, HCHO is not an exception. The photocatalytic degradation of gaseous HCHO has already been addressed in a number of works that probed the feasibility of its elimination [2,3,10,15].

Chemical processes involving simultaneously momentum, heat, mass and radiation transfer usually need an optimization of the reaction unit in order to obtain the best result regarding overall performance, space and economic restraints and radiation usage. The recognition of the scale dependency of these processes is crucial. The mathematical simulation and prediction of otherwise expensive and time consumptive physical prototypes is a very helpful tool. This is especially true nowadays that the computational capabilities are sufficiently large to provide a detailed approach of every phenomena involved. In particular, CFD tools have been increasingly used to model very different kinds of processes, including photocatalytic reactions. In particular, there have been valuable contributions in the CFD modeling approach for gas phase photocatalytic reactors [16–18].

In this work, we deal with the study of photocatalytic reactors for their application in air pollution remediation. The target pollutant selected was HCHO. The study approach is based on the application of experimentally determined kinetic parameters in the modeling of a complex geometry reactor. To this aim, the first step consists in the construction and operation of a small, simple geometry reactor to perform a series of experiments and obtain the kinetic parameters. Once the kinetic parameters are known, they are able to be used in a very different reactor configuration, such as the corrugated plate type coated with TiO_2 as catalyst. The approach of radiation interchange between catalytic walls makes use of geometrical configuration factors; a study of the influence of catalyst layers optical properties on the radiation interchange was also made. The modeling of this corrugated photocatalytic reactor was performed using a commercial CFD package.