

PHOTOCATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS  
FOR INDOOR AIR APPLICATIONS

by

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## Abstract

Photocatalytic oxidation (PCO) is a promising and emerging technique in controlling indoor air contaminants, including volatile organic compounds (VOCs). It has broad air cleaning and deodorization applications in indoor environments ranging from residential and office buildings to healthcare and nursing facilities as well as spacecrafts, aircraft cabins and clean rooms in the agricultural and food industry. Numerous studies have been conducted to improve the effectiveness and performance of this technology. These include development of new configurations, energy-efficient catalysts and other parameters to control the process. However, only limited research has been conducted under realistic indoor environmental conditions. One of the most recent developments in photocatalysis is the synthesis of 2% C- and V-doped TiO<sub>2</sub>, which is active under both dark and visible light conditions. However, like most research conducted in photocatalysis, the study on the reactivity of this catalyst has been performed only under laboratory conditions. This study investigated the possible application of the novel C and V co-doped TiO<sub>2</sub> in cleaning indoor air. Mathematical modeling and simulation techniques were employed to assess the potential use of some of the promising systems that utilize the catalyst (i.e., packed bed and thin films) as well as the effect of mass transfer limitations in the degradation of acetaldehyde, one of the VOCs that can be found in offices, residential buildings and other facilities.

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## List of Symbols and Abbreviations

$A_m$	Area of mass transfer
$A_p$	External surface area of a pellet
ACGIH	American Conference of Governmental Industrial Hygienists
ACH	Air changes per hour (ACH)
C	Pollutant concentration at any time, t
$C_i$	Indoor air pollutant concentration
$C_o$	Outdoor air pollutant concentration
$C_{out}$	Pollutant concentration in the gas stream coming out of the packed bed
CGS	SI units of length, mass and time in centimeter, gram and second.
CPSC	Consumer Products Safety Commission
c	Total concentration
D	Diffusivity or diffusion coefficient
$D_e$	Equivalent spherical diameter
$D_{eff}$	Effective diffusivity
$D_p$	Spherical particle diameter or nominal diameter of the pellet in the bed
$e_{CB}^-$	Conduction-band hole
$G_o$	Superficial mass velocity
$g_c$	conversion factor = $32.174 \text{ lb}_m \cdot \text{ft} / \text{s}^2 \cdot \text{lb}_f$ in the English system, otherwise equal to unity for SI unit.
$h_{VB}^+$	Valence-band hole
HEPA	High Efficiency Particulate Arresting
IAQ	Indoor air quality
$K_A$	Adsorption equilibrium constant
$K_p/K_r$	parameter for restricted diffusion defined by equation (3-12)
$k$	kinetic rate constant
$k_m'$	Mass transfer coefficient
L	Characteristic length



$L_p$	Length of cylindrical pellet
$M_p$	Molecular weight of the gaseous pollutant
$N_{Ax}$	Molar flux of substance A in the x-direction
$N_{Bx}$	Molar flux of substance B in the x-direction
$N_p$	Number of pellet per unit volume
NASA	National Aeronautics and Space Administration
NIOSH	National Institute for Occupational Safety and Health
$O_2^{\bullet -}$	Superoxide ions
$\bullet OH$	Hydroxyl radical
OSHA	Occupational Safety and Health Administration
$P$	Pressure
$p$	Number of people in the room
PCO	Photocatalytic Oxidation
PEL	Permissible Exposure Limit
ppb	Concentration in parts per billion
ppm	Concentration in parts per million
$Q$	Ventilation rate in the room equal to $V_R \cdot p$
$q$	Volumetric flow rate through the packed bed
$R_m$	Rate of removal due to mass transfer
$r_{cont}$	Molecular (equivalent) radius of the gaseous pollutant
$r_{pore}$	pore radius
REL	Recommended Exposure Limit
$S$	Area of the bed
$S_p$	Emission rate of the pollutant in $\mu\text{g/h}$ -person
SBS	Sick Building Syndrome
STEL/C	Short Term Exposure Limit (15 min)/instantaneous but up to 15 min due to sampling limitations
T	Temperature
$t$	Time
$t_R$	Residence time in the packed bed
TiO <sub>2</sub>	Titanium dioxide

TWA	Time-Weighted Average (8h)
UV	Ultraviolet
V	Volume of the room
VOCs	Volatile Organic Compounds
$V_p$	Pellet volume
$V_o$	Superficial velocity or velocity of approach
$V_R$	Ventilation rate in m <sup>3</sup> /min-person
$W_{cat}$	Weight of catalyst
$x$	Direction of flow of gas normal to the wall
$y_A$	Mole fraction of pollutant A
$z$	Bed depth

#### Greek Symbols

$\Delta$	Change or difference
$\delta$	Thickness of the hypothetical gas film at or near the wall
$\Delta P$	Pressure drop through packed bed
$\varepsilon$	Void fraction or porosity = volume of void/total bed volume
$\varepsilon_p$	Porosity factor for pellet (void fraction within the pellet)
$\Phi$	Observable modulus
$\phi$	Thiele modulus
$\Phi_s$	Shape factor or sphericity
$\eta$	Effectiveness factor
$\mu$	Viscosity of the contaminated air
$\mu\text{m}$	Micrometer
$\rho_g$	Density of the contaminated air
$\rho_{bulk}$	Bulk density of the catalyst
$\tau$	Tortuosity factor for pellet
$v_o$	Observed rate of reaction

## Dimensionless Numbers

$$N_{Re,L} \quad \text{Reynolds number for a characteristic length, } L = \frac{\rho_g V_o L}{\mu} = \frac{L G_o}{\mu}$$

$$N_{Re,p} \quad \text{Reynolds number for packed beds} = \frac{\rho_g D_p V_o}{(1-\varepsilon)\mu} = \frac{D_p G_o}{(1-\varepsilon)\mu}$$

$$N_{Sc} \quad \text{Schmidt number} = \frac{\mu}{\rho_g D}$$

$$N_{Sh,L} \quad \text{Sherwood number for a flat plate} = \frac{k'_m L}{D}$$

$$N_{Sh,p} \quad \text{Sherwood number for a spherical pellet} = \frac{k'_m D_p}{D}$$

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## Dedication

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“Education is the most important investment in life. Unlike tangible wealth that a man possesses, you can carry it anywhere you go. You won’t lose it and it cannot be stolen from you because it’s within you. It grows by time and when cultivated regularly, it will continue to bear good fruits.”

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## CHAPTER 1 - Introduction

People spend most of their time indoors. This makes the indoor environment important when addressing health risks and exposures to air pollution. Indoor environments should not pose significant risks to the health and well-being of the inhabitants. This can be achieved by maintaining an acceptable indoor air quality (IAQ) without compromising other aspects of comfort that can be achieved by keeping appropriate operating conditions indoors for temperature, humidity, lighting and acoustics.

Source control, ventilation and air cleaning are strategies that can be used in controlling IAQ. However, in source control, not all pollutants can be identified and practically eliminated or reduced (U.S. EPA, 2007). Ventilation systems have practical limitations due to the associated significant energy costs; moreover, sometimes outdoor air itself may contain undesirable levels of pollutants. Use of air cleaning devices in addition to the first two strategies has been determined to improve the overall effectiveness of the whole system in controlling IAQ. Several air cleaning devices that are tailored for specific pollutants are available in the market. For instance, for particulate removal, mechanical filters, electronic air cleaners, and ion generators can be used; and there are adsorbents and/or reactive adsorbents for gaseous pollutants. Systems are also available for controlling both particulate and gaseous pollutants.

The increasing energy costs associated with air conditioning made many people turn to enhancing energy conservation in buildings, homes, and other facilities by making them more tightly sealed (Birnie et al., 2006; Xu and Shiraishi, 1999; Tompkins et al., 2005a). Improvements in the construction of facilities, reduction in infiltration of fresh air, and use of re-circulated air have been determined as cost-effective ways to conserve energy. As a consequence, natural ventilation becomes limited that gaseous pollutants being generated indoors accumulate, and air is retained in these airtight rooms and buildings (Birnie et al., 2006; Xu and Shiraishi, 1999). Use of effective and energy-efficient air cleaning devices based on photocatalytic oxidation (PCO) is thus attractive to resolve IAQ problems.

Chapter 2 includes a literature review on volatile organic compounds (VOCs), air cleaning devices and PCO technology. VOCs are one of the major components of indoor air contaminants and can cause sick building syndrome (SBS). Acetaldehyde, a VOC, will be used

as the model pollutant in the simulation and modeling studies on the use of PCO systems in indoor air cleaning. It is therefore appropriate to include a review of literature on VOCs. Some reviews on indoor air cleaning devices are included to have a comparable understanding between them and PCO devices.

One of the most promising techniques in the field of indoor air cleaning is the use of PCO processes (Zhao and Yang, 2003; Yu et al., 2007). Considerable research has been devoted to improve this technology. Various photo-reactor designs and configurations have been explored and new photocatalysts have been developed ranging from making catalysts in the nano-size regime to doping them with other materials. One of the most recent advances in PCO, is the development of the 2% C- and V-doped TiO<sub>2</sub> (Yang et al., 2007). Results of laboratory studies revealed that the catalyst's activity under visible light and dark conditions were comparable (Yang et al., 2007), making the catalyst an attractive component of an effective and energy-efficient PCO air cleaning device. However, to test the potential of a certain device for indoor air cleaning, it would necessitate testing it in a typical indoor air setting. Preliminary calculations are needed to design a PCO system that would be a good candidate for the test study. Modeling and simulation studies can help understand the influence of various factors that would affect PCO performance in a typical indoor air environment.

The modeling and simulation studies in Chapter 3 focus on scaling up various reactor designs utilizing the photocatalyst developed in Yang et al. (2007) that would be applicable in cleaning some of the VOCs (i.e., acetaldehyde) commonly found in a typical indoor environment. The two reactor designs that are considered in the study are packed bed and thin films on the walls and ceiling, as they are the two most common PCO configurations that are being adapted by companies commercializing this kind of technology for gaseous applications (Tompkins et al., 2005a). The effects of several mechanisms and factors on the performance of these systems in a simulated indoor air environment will be assessed using mathematical models and techniques.



## **CHAPTER 2 - Literature Review**

### **2.1 Volatile organic compounds (VOCs)**

Volatile Organic compounds (VOCs) are carbon and hydrogen-containing chemicals, which evaporate readily or are gases at room temperature and pressure. They are important pollutants in indoor air (Yu et al., 2007; Wang et al., 2007). Compared to outdoors, higher concentrations of VOCs can be found indoors (Wang et al., 2007) where there is limited ventilation. The U.S. Environmental Protection Agency (EPA) Total Exposure Assessment Methodology (TEAM) studies revealed that indoor VOC levels were typically 2 to 5 times higher than outdoor concentrations (U.S. EPA, 2009; Birnie et al., 2006).

VOCs may come from gaseous emissions of household chemicals and products (U.S. EPA, 2009). There are thousands of different VOCs produced and present in our daily lives (Minnesota Department of Health, 2009). These include those coming from cleaning and degreasing agents, pesticides, air fresheners, toilet bowl deodorants, environmental tobacco smoke (second hand smoke), furniture and building materials (e.g. wood products, adhesives, carpeting, paints, varnishes, vinyl floors, moth balls, solvents, gasoline, newspaper, upholstery fabrics, sealing caulks), cosmetics, fuel oil, vehicle exhaust, cooking, photocopying, etc. (U.S. EPA, 2009; Minnesota Department of Health, 2009). Common VOCs include acetone, benzene, ethylene glycol, formaldehyde, methylene chloride, perchloroethylene, toluene, xylene, and 1, 3-butadiene. Acetaldehyde, a component of Environmental Tobacco Smoke (ETS) is one of the organic compounds that accumulate in rooms. Xu and Shiraishi (1999) and Tang et al. (2004) recognized it as key indoor air pollutant. Minnesota Department of Health (2009) listed a variety of factors that affect levels of VOCs in an indoor environment. These are volume of air in the room/building, the rate at which the VOC is off-gassed, the building ventilation rate, outdoor concentration, and the time spent by people in the affected environment.

Among those sources of VOCs mentioned above, building materials are considered to be the largest source of VOCs in indoor air (Wang et al., 2007). Thus, it is always expected that the concentration of VOCs in a new building will be higher than in old buildings. For instance,

formaldehyde, a common VOC in mobile homes is found in many indoor products, such as pressed wood, paints, insulation, coated paper products, and combustible materials.

VOC concentrations indoors are typically in the ppb to sub-ppm range (Wang et al., 2007). However chronic exposures to low levels of these compounds can increase some people's risk of health problems (Minnesota Department of Health, 2009). This is true for some people who have existing respiratory problems and higher sensitivity to chemicals. Many VOCs are toxic and considered to have carcinogenic, mutagenic or teratogenic effects (Alberici and Jardim, 1997) in both animals and humans. Long-term exposure to high concentrations of some VOCs can cause cancer and damage to vital organs of our body such as liver, kidney and central nervous system. Short term exposure to high concentrations of VOCs can cause eye, nose and throat irritation, headaches, nausea, vomiting, dizziness, fatigue, allergic skin reaction, and worsening of asthma symptoms (Minnesota Department of Health, 2009; U.S. EPA, 2009). VOCs are also considered one of the causes of Sick Building Syndrome (SBS). SBS is a situation in which the occupants experience acute and comfort effects that appear to be associated with the time spent in the building but no specific illness or cause can be determined (U.S. EPA, 2008). To eliminate SBS, building air must be cleaned or properly refreshed, and/or the sources of VOCs must be removed or modified. VOCs cannot be avoided, but concentrations indoors can be lowered by using materials and products with lower VOC emissions, proper ventilation and use of air purifiers.

The presence of these compounds from a variety of sources represents a significant burden to indoor air environments. It is therefore necessary to apply control measures that would safeguard building occupants from exposure to these harmful compounds.

## **2.2 Air cleaning devices**

Air cleaning devices are used to supplement source control and ventilation in reducing and maintaining acceptable levels of indoor air contaminants. Air cleaning devices alone cannot assure adequate air quality, particularly where significant sources are present and ventilation is inadequate. Air cleaners are classified according to their specific purposes. The type of device should be selected according to the governing cleaning mechanism. Thus, a particular control device is different from devices for gaseous pollutants.

The three general types of air cleaners for particulate removal are mechanical filters, electronic air cleaners, and ion generators (U.S. EPA, 2007).

Mechanical filters can be installed in ducts in homes and buildings with central heating and/or air-conditioning or may be used in portable devices which contain a fan to force air through the filter. Mechanical filters can be in the form of flat or panel filters, pleated or extended surface filters, or high efficiency particulate air (HEPA) filters. Flat or panel filters can be made of low packing density of coarse glass fibers, animal hair, or vegetable fibers often coated with a viscous substance (U.S. EPA, 2007).

Electronic air cleaners utilize an electrical field to catch charged particles. They can be installed in central heating and/or air conditioning system ducts or in portable units with fans. Some of the most common electronic air cleaners are electrostatic precipitators or charged-media filters. Electrostatic precipitators collect particles on a series of flat plates while in charged-media filters, particles are collected on the fibers. To attain higher collection efficiency, the particles are ionized or charged prior to collection.

Ion generators, like electronic air cleaners use static charges to remove particles from indoor air, except that they come in portable units only. The charging of the particles in the room attracts them to the walls, floors, table tops, draperies, occupants, etc. These devices come with a collector which attracts the charged particles back to the unit.

Hybrid devices contain two or more of the particle removal systems discussed above. For instance, one or more types of mechanical filters may be combined with an electrostatic precipitator or an ion generator.

There are a limited number of studies on the effectiveness of portable or residential air cleaners in removing gaseous pollutants. Adsorbents and/or reactive adsorbents can be used with particle removal devices for removing gaseous pollutants in indoor air. This is due to the fact that gaseous pollutants cannot be removed by air cleaning devices that are based on filtration and electrostatic attraction alone. The performance of solid sorbents used with these systems depends on the following (U.S. EPA, 2007):

- Air flow rate through the sorbent bed
- Concentration of the pollutants
- Presence of other gases or vapors
- Physical and chemical characteristics of the pollutants and the sorbent

- Configuration of the sorbent in the device
- Quantity of sorbent used and the sorbent bed depth

Generally, the efficiency of the above system decreases with the amount of pollutant captured and is usually rated by sorption capacity and penetration time.

The most common adsorbent material is activated carbon. It can adsorb some pollutants, mostly hydrocarbons and non-polar gases (Chin et al., 2006), even in humid conditions. One of the constraints of this type of adsorbent is that it is not efficient in adsorbing volatile, low molecular weight gases. In most cases, activated carbon is good in removing odor; however, the absence of odor alone does not guarantee good air quality. Zeolites are adsorbents that can be used for treating polar gases and vapors such as benzene, n-hexane and  $\text{CH}_2\text{O}$  from indoor air (Chin et al., 2006). At present, limited data are available on the effectiveness of this system in the removal of the low concentration range of pollutants typically found in an indoor air environment. One of the major concerns in this type of device is the useful capacity of the adsorbent as their lifetime can be short depending on the type and concentration of pollutant to be adsorbed. Other than carbon, there are also special sorbents available to treat specific pollutants, such as chemisorbents impregnated with chemically active materials to remove specific reactive gaseous materials.

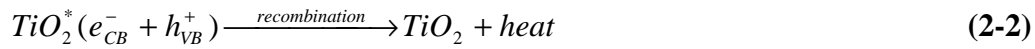
One of the most promising techniques in indoor air cleaning that is still under development is the use of the photocatalytic oxidation (PCO) process. Considerable research has been devoted to improve the technology and extend its application for specific purposes. However, most of the studies have been performed under laboratory conditions. More information regarding this technology will be discussed below.

### **2.3 Photocatalysis**

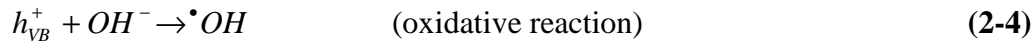
Photocatalytic oxidation (PCO), or heterogeneous photocatalysis, is carried out when a semiconductor photocatalyst is irradiated by a light photon that has energy higher than the photocatalyst's band gap energy. In the case of titanium dioxide ( $\text{TiO}_2$ ), a wavelength less than 385 nm is sufficient to exceed its band gap energy of 3.2 eV. When this happens, electron is promoted from the valence band to the conduction band leaving a hole in the valence band. The

valence band hole and the electron in the conduction band react with water and oxygen (O<sub>2</sub>) present in the surrounding air. As a consequence, two very potent oxidants, hydroxyl radicals (<sup>•</sup>OH) and super oxide ions (O<sub>2</sub><sup>•-</sup>) are produced (Frazer, 2001; Jacoby et al., 1996; Indoor Environment Center, 2006; Maness et al., 1999). Hydroxyl radicals are highly reactive and non-selective oxidizers that can attack organic materials, including those that make up living cells.

Several steps are involved in photochemical mechanisms in solid semiconductors. These steps are described in detail in de Lasa et al. (2005) and Tompkins et al. (2005a), and presented briefly herein. First, the light energy,  $h\nu$  greater than the band gap energy,  $E_g$ , strikes the surface of the catalyst and excites an electron from valence band to conduction band. A valence-band hole,  $h_{VB}^+$ , is created, which migrates to the surface and initiates a reduction reaction. The valence-band hole and conduction-band electron can recombine in the bulk material and on the surface. Tompkins et al. (2005a) proposed the following possible PCO pathway:



Production of hydroxyl radicals



Production of super-oxide

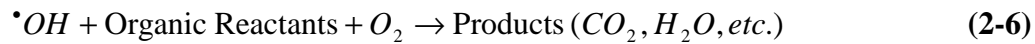
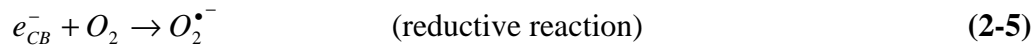
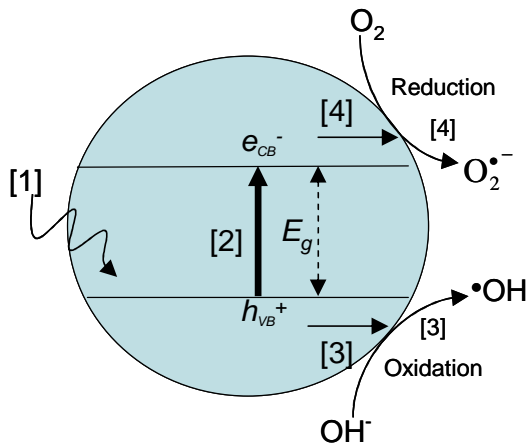


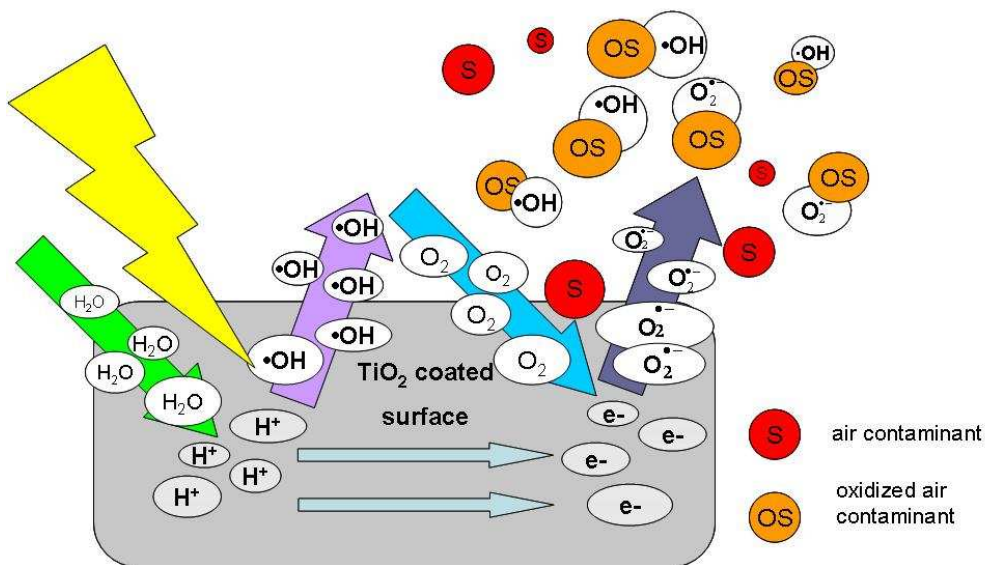
Figure 2.1 describes the primary steps of photochemical mechanisms taking place in a solid semiconductor photocatalyst (i.e., TiO<sub>2</sub>) neglecting recombination reactions.



**Figure 2-1 Steps of photochemical mechanisms in a solid semiconductor:**

[1] Light energy photon ( $h_{\nu}$ ) greater than band gap energy,  $E_g$  (3.2 eV for  $TiO_2$ );  
 [2] excites electron from valence band to conduction band leaving a hole in the conduction band; [3] valence-band hole that successfully migrates to surface initiates oxidation reaction; [4] conduction-band electron that successfully migrates to surface initiates reduction reaction. *Adapted from Tompkins et al. (2005a).*

Hydroxyl radicals and superoxide ions produced from steps [3] and [4] can attack any organic compound (S) in the air that come into contact with them to a more oxidized form, OS (see Figure 2-2).



**Figure 2-2 Photocatalytic destruction of organic compounds.**

*Adapted from The no odor and no mold network (2005).*

### ***2.3.1 PCO for environmental air quality applications***

Photocatalytic oxidation is simple, relatively new, and considered as a promising technique for air cleaning and disinfection. Kowalski (2003) listed PCO as a technology in a developmental stage that can be applied to the cleaning and disinfection of air. PCO is known to destroy most organic contaminants even at low levels and at near-ambient temperatures. Precise reaction mechanisms vary for different compounds; however, in general, PCO just needs a light energy sufficient to overcome the catalytic material's band gap energy, a high surface area of photocatalyst material  $>100\text{-}150\text{ m}^2/\text{g}$ , and an oxidizing agent such as  $\text{O}_2$ . The most commonly used photocatalyst,  $\text{TiO}_2$  is proven over the years to be excellent in breaking down organic compounds. It is relatively inexpensive, highly stable chemically, and resistant to corrosion. The photogenerated holes are highly potent to break down almost any organic compound (Frazer, 2001), including bioaerosols (i.e., bacteria, viruses). The bactericidal activity of hydroxyl radicals and superoxide ions was first demonstrated by Matsunaga (1985).

The PCO process attacks practically all gaseous species of interest in IAQ problems and effective for trace contaminants at levels on the order of ppm or below as well (Hall et al., 2000). Conversion of these organic contaminants to more benign compounds such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is attainable especially when certain conditions favor complete oxidation. Chlorinated organic compounds including dioxins (a harmful emission from inefficient incineration processes) and PCB's can be oxidized by PCO (Anpo and Takeuchi, 2003; Pridal and Pridal, 2003). Yang et al. (2007, 2008) have reviewed the literature and conducted research to modify  $\text{TiO}_2$  so that visible light can be used effectively in PCO.

Indoor air cleaning devices such as filtration and adsorption units merely transfer pollutants to another phase which requires replacement and additional disposal of used media. Because PCO cleans indoor air, it can reduce the amount of air exchange needed. The promise of minimal pressure drop, low power consumption, potentially long service life, and low maintenance are also additional factors which make PCO an attractive method for indoor air applications. It can be used to decontaminate the air (Xu et al., 2006a); combat bioterrorism/agri-terrorism; and maintain good IAQ in offices, buildings, homes, industrial premises, healthcare facilities and public transportations/vehicles (i.e. cars, ships and aircrafts). The use of PCO with

environmentally friendly photocatalysts is expected to solve environmental pollution also in a huge global scale (Anpo, 2000). Research has investigated the effectiveness of TiO<sub>2</sub> coated surfaces (i.e. building materials, roads) in removing pollutants in urban air (Berdahl and Akbari, 2008). Catalytic activity per square meter of catalytic material exposed to outdoor sunlight was measured. Results of the study showed that the use of TiO<sub>2</sub> nanoparticle surfaces is technically feasible with catalytic activities of 200 and 60 m/day for nitrogen oxides and VOCs respectively. However, Berdhal and Akbari (2008) emphasized the need to develop novel and more effective catalysts and ensure that use of these catalysts will not bring unintended harm to the environment.

### ***2.3.1.1 Odor removal***

Odors can be a big nuisance and pose adverse health effects if not controlled or maintained below acceptable levels. They are usually caused by odorous volatile compounds that are dispersed from very minute to large quantities in the air. Activated carbon adsorption, thermal oxidation, biofiltration, bioscrubbing and wet chemical scrubbing are among the conventional methods for odor control. PCO has attracted research interest for application in the control of odors. Canela et al. (1998, 1999) reported the use of heterogeneous photocatalysis in waste water treatment plants for the destruction of malodorous sulfur-containing compounds such as hydrogen sulfide (H<sub>2</sub>S), trimethylene sulfide (C<sub>3</sub>H<sub>6</sub>S), propylene sulfide (C<sub>3</sub>H<sub>6</sub>S), thiophene (C<sub>4</sub>H<sub>4</sub>S) and methyl disulfide (C<sub>2</sub>H<sub>6</sub>S<sub>2</sub>). Though formation of intermediates and catalyst deactivation were observed at certain conditions in their experiments, chemical and sensory analysis showed catalytic processes were efficient in decomposing these malodorous compounds. Canela and Jardim (2008) found the use of PCO as a viable method for the destruction of malodorous compounds from sewage. Decomposition of other obnoxious odor-causing compounds such as aldehydes and alcohols as well as pungent acids using PCO process has been reported elsewhere (Blake, 2001). Thus, PCO technology will be of growing importance where odor is of great concern such as hospitals, nursing homes, chemical manufacturing and waste treatment plants.



### ***2.3.1.2 Residential homes and office buildings***

People spend most of their time indoors. They can be mostly either at home or at their respective working places. People expect that they would feel safe and protected at least in their homes. They are unaware of the extent that they can be exposed to harmful substances and chemicals in their surroundings. Dungcan (2006) in the article entitled “Our Toxic Homes” under the major article “The pollution within” discussed the harmful and toxic chemicals that can be found in homes. Studies conducted by the U.S. EPA, NIOSH and NASA and CPSC have shown that VOCs released and off-gassed from building materials and equipment comprise a considerable portion of indoor air contaminants (Niu and Burnett, 2001). VOCs can greatly affect the quality of life of inhabitants living and working in VOC -contaminated homes and office buildings. One example that is a common problem in mobile homes is formaldehyde. It is released from building materials commonly used in mobile homes. According to several studies, bioaerosols such as fungi, bacteria and viruses can also thrive and proliferate in homes and office buildings when high humidity conditions allow them to do so. The concentration of VOCs from these organisms indoors is typically higher than outdoors. The absence of sunlight which contains some UV radiation that is deadly to the organisms and the high humidity coupled with moderate temperature in an indoor environment favor the survival and growth of these airborne microorganisms and pathogens.

PCO can destroy VOCs and microorganisms including microbial VOCs. The hydroxyl radicals produced during the process are sufficiently powerful that they can decompose most organic compounds even at low levels. VOCs can be adsorbed on the catalytic surfaces and oxidized to less harmful compounds such as CO<sub>2</sub>. PCO is a cost effective technology for removal of VOCs in comparison with adsorption, biofiltration or thermal catalysis (Wang et al., 2007). It is considered the most promising technique in the removal of VOCs in indoor air (Zhang, et al., 2003; Mo et al., 2005; Yang, et al., 2003; Zhang et al., 2007). Huang et al. (2000) described the bactericidal mode of photocatalysis with TiO<sub>2</sub>.

Kowalski (2006) indicated PCO was the most promising technology for use in an integrated building design employing both air and surface disinfection systems by creating self-sterilizing surfaces for building components such as doorknobs. In PCO, the catalytic material is excited by UV and sunlight and is not consumed in the process. This makes PCO a self-cleaning

process, requiring no regeneration. Due to their modular design, room temperature operation, and negligible pressure drop, PCO reactors can be integrated into new and existing, heating ventilation, and air-conditioning (HVAC) systems.

The technical issues associated with the use of PCO in commercial and residential applications and alternative designs will be discussed later in this paper. Some PCO-based systems are currently available in the market. In Japan, they are being sold as self-contained recirculation units made from filter materials coated with  $\text{TiO}_2$  and UV lamps (Kowalski, 2003). However, like other technologies, PCO still needs more evaluation. More improvement of the PCO process/technology in the coming years will put it in place as a component of green building designs and help society to move toward sustainable development (Pridal and Pridal, 2003).

### ***2.3.1.3 Healthcare and nursing facilities***

Kowalski (2006) defines health care facilities as all types of buildings associated with health care, such as hospitals, clinics, doctor's offices, dental offices, and homes or offices converted for health care use. Health care workers and patients are continuously exposed to airborne hazards that are commonly found in these facilities. U.S. EPA (1988) published a report entitled "Indoor Air Quality in Public Buildings." Chemicals such as chloroform, trichloroethylene, benzene, xylene and formaldehyde were found in hospitals, nursing homes and office buildings. Among these chemicals, formaldehyde concentrations in all three kinds of establishments tested were the highest. The values were  $0.106\mu\text{g/L}$  in hospitals,  $0.081\mu\text{g/L}$  in nursing homes, and  $0.173\mu\text{g/L}$  in office buildings. Infants, the elderly and sick people are more susceptible to diseases associated with airborne hazards because of low physiological functions and immune systems. Thus, maintaining acceptable low levels of air pollutants in these facilities is very important. Odor is also common in health care facilities and more significant in nursing homes due to frequent toileting, more soiled linen, widespread use of portable commodes, and pungent cleaning chemicals (Ninomura and Cohen, 1999). The demand for more nursing care will greatly increase in the coming years due to the approaching retirement of the "baby boomer" generation. In order to provide them with good quality of life, good IAQ in nursing homes should be maintained. Knowing the deodorization capability and potential to destroy most organic compounds, including bacteria, viruses and pathogens, PCO will have valuable

applications in nursing home facilities. Use of PCO for indoor air cleaning can control the spread of contagious pathogens and at the same time reduce energy costs associated with increased ventilation rates in health care and nursing facilities.

#### ***2.3.1.4 Spacecrafts and aircraft cabins***

In spacecraft environment, material off-gassing and human metabolism emissions are the primary sources of chemical contaminants. Generation rates of human emissions in spacecrafts are provided by NASA in Perry (1995). James et al. (1994) discussed the volatile organic contaminants found in the habitable environment of two space shuttles (STS-26 and STS-55). Trace chemicals from these sources, which can contaminate the spacecraft atmosphere, must be controlled to achieve an acceptable living environment.

The enclosed and isolated environment coupled with limited ventilation present a unique design challenge with respect to providing a comfortable spacecraft environment in which people can live and work (Perry, 1995). NASA crew members aboard spacecraft are continuously exposed to pollutants in the respirable air that can make them ill and unproductive. Excessive levels of pollution in spacecraft air can cause crewmembers to experience cardiac rhythm disturbances, eye and respiratory irritation, headache and disorientation, and risk of developing chronic disease such as cancer (James and Mukhamedieva, 1999; Zorn, 2003). These pollutants can also interfere with biomedical experiments being carried out in outer space.

Photocatalysis has great potential for use in a number of NASA applications. The use of self-generating and non-consumable photocatalytic materials makes the process especially attractive in moderate and long-term applications where consumable materials are to be avoided. Confined spaces like space shuttle cabins and international space stations (Zorn, 2003) are locations for the broad oxidation potential of PCO. Sufficient residence time to achieve complete oxidation of simple hydrocarbon contaminants to CO<sub>2</sub> and water is needed for PCO to purify spacecraft environments (Ollis, 1996). A suitable photocatalyst coupled with a good photoreactor design can partially or completely replace the commonly used adsorption systems in spacecrafts. PCO can be incorporated in the air revitalization system of a spacecraft to maintain safe levels of air contaminants. The use of PCO process would help in the reduction in lift-off weight of the life support system for the spacecraft, or other related applications such as in space stations (Ollis, 1996). Some kinetic studies of the conversion of oxygen-containing contaminants, aromatics, oxyhydrocarbon contaminants containing heteroatoms (e.g., sulfur, nitrogen and

silicon) and multicomponent systems that are typical in a spacecraft environment can be found in NASA research grant report (NASA-CR-203027) (Ollis, 1996). KES Science and Technology (2005) has developed the Airocide TiO<sub>2</sub>, an airborne pathogen killer. In aircraft cabins, gaseous contamination originates from human metabolic processes, off-gassing of lubricants in the engine, equipment, furnishings, detergents, and food and drinks. Excluding vapors from alcoholic beverages, VOC concentrations in aircraft cabins are generally low. However, several studies have confirmed that odor is a common problem especially in periods during and after boarding. This can be attributed to semi-VOCs from passengers, as well as hydraulic fluids, de-icing fluid, and engine oils. Transmission of disease by infectious bioaerosols aboard aircraft is also a serious concern (Ginestet et al., 2005).

The supplied air is composed of an unfiltered outside air from the engine's compressor stage and about an equal quantity of filtered recirculated air. The air ventilation system in modern aircraft is used to provide fresh air in the cabin and to remove air contaminants from confined spaces. The outside air supply controls the cabin pressure, temperature gradients, prevents stagnant areas, maintains air quality, and dissipates particulate matter, and odors in the cabin. However, the current regulatory air exchange rate in aircrafts is apparently not enough since complaints from flight attendants and passengers are still being raised. Ventilation is intended to dilute the pollutants; however, ambient air quality at busy airports may be poor, and contaminants may be introduced into the passenger cabin through the bleed air.

Consideration of power consumption, size and weight and life cycle costs of a VOC control system is important for aircraft applications. Installation of a control device such as PCO will maintain acceptable air quality inside aircraft cabins, improve the quality of fresh air being supplied inside aircrafts as well as the amount of fresh air flow, thereby reducing fuel consumption and operating costs. Moreover, the PCO process transforms the odor-causing contaminants as well as bioaerosols to CO<sub>2</sub> and water instead of being concentrated on an adsorbent bed and then purged overboard.

Ginestet et al. (2005) developed a modular and regenerable PCO air filter unit to improve the quality of recirculated air entering the cabin. The air filter used is photocatalytically active under UV light illumination. The study was considered one of the preliminary attempts to design a filter for VOC removal in cabin aircraft applications. Despite the limitations and problems (i.e.

intermediate reaction products) encountered in their study, PCO technology still appears to be a promising solution to odor and IAQ problems in aircraft.

Hall et al. (2000) developed and studied a multi-stage honeycomb monolith PCO reactor for the destruction of VOCs and bioaerosols in airliner cabins. The study showed that PCO reactors for VOC control can replace HEPA filters for bioaerosol control. The detailed life-cycle costs comparison made between PCO and carbon adsorption/HEPA showed that adsorption involves higher life cycle cost owing to the low adsorption capacity.

Yates et al. (2005) described a PCO cleaner which simultaneously removes VOC pollutants and ozone in aircraft cabins and indoor environments.

#### **2.3.1.5 Inactivation of bioaerosols**

Photocatalytic oxidation can inactivate and destroy airborne pathogenic organisms such as bacteria, fungi, viruses, as well as their spores (Vera et al., 2007a). Matsunaga (1985) pioneered this research in demonstrating the microbiocidal effects of hydroxyl radicals and superoxide ions during PCO process (Kowalski, 2006). Furthermore, he found that the extent of killing was inversely proportional to the cell wall thickness. Maness et al. (1999) also explored the bactericidal activity and killing mechanism of photocatalytic TiO<sub>2</sub> towards *Escherichia coli*. The sensitivity of microorganisms to TiO<sub>2</sub> photocatalysis is likely in the following order: virus > bacterial cells > bacterial spores (Huang et al., 2000). Huang and his co-workers found that the destruction of bacteria by PCO starts with the attack on the external cell wall followed by the oxidative damage of the underlying cytoplasmic membrane. The photocatalytic action goes deeper and deeper as the cell becomes more permeable and later on causes cell lysis and death. In their study, continued bactericidal activity was observed even after UV illumination on TiO<sub>2</sub> was terminated. Comparative studies originally done by Goswami et al. (1997) showed that PCO was more effective than ultraviolet germicidal irradiation (UVGI) in the destruction of *Serratia marcescens*. (Kowalski, 2006; Goswami et al., 1997; Vera et al., 2007b).

### ***2.3.1.6 Defense against biological and chemical terrorism***

Photocatalytic oxidation can be used in the control of biological and chemical attacks. Biological and chemical agents that are being used in terrorism attacks can be deactivated by PCO to convert them to less harmful compounds.

PCO has the potential to be used in the disposal of tons of confiscated chemical warfare agents (CWAs). In response to the call of the Chemical Weapons Convention of 1993 for the bans on the production, possession and use of chemical weapons, Hitchman et al. (1997) conducted a feasibility study on the use of PCO as a proposed method for the destruction of existing arsenals and deposits of chemical weapons.

Kozlov et al. (2003) investigated the PCO of diethyl sulfide (DES), a simulant for chemical agent mustard gas. During the experiment, some intermediates were formed, but later on DES was completely oxidized to yield CO<sub>2</sub>, water and sulfates and carbonates as final products.

Martyanov and Klabunde (2003) also reported the PCO of gaseous 2-chloroethyl ethyl sulfide, a chemical agent known to be the main component of mustard gas (HD), a chemical weapon. Oxidation of this compound resulted in the formation of intermediates of different toxicity levels that can be toxic to humans. However, further oxidation can lead to the transformation of the intermediates to compounds of lesser toxicity.

Smith (2008) listed PCO as one of the catalytic methods that can be used to destroy chemical warfare agents under ambient conditions. The author also mentioned possible incorporation of photocatalytic surfaces on protective garments and masks for the protection of emergency responders. However, the ability to use PCO during night time is of great concern for the military due to the scarcity of a light source necessary for photocatalysis to take place. There is a great possibility that terrorist attacks can be initiated at night times too, and the first responders must have their protective gadgets functioning both day and night. The 2% C- and V-doped TiO<sub>2</sub> that is active under both visible light and dark conditions (Yang et al., 2007) might solve the issue.

Use of biological agents also became a mode of terrorism attacks. The ability of PCO to deactivate bioaerosols such as bacteria, viruses, and spores makes it attractive in the mitigation of bioterrorism activities. Kau et al. (2009) studied the inactivation of anthrax spores in mice

using doped TiO<sub>2</sub> substrates by PCO under visible light illumination. Results from the study suggested that spores from the photocatalyzed group have a lower survival rate than the control group. Based on their results, Kau and his co-authors indicated that photocatalysis could directly inactivate lethal toxin, the major virulence factor of *B. anthracis*. Because of this, they envision that induced injuries of the spores might be more important than killing spores directly to reduce pathogenicity in the host. Kowalski (2003) suggested the use of PCO as another option for handling mails in the post office to protect employees in case of CBW attacks.

### **2.3.1.7 Agricultural and food industry**

Maintaining IAQ in livestock buildings is necessary to prevent the on set and spread of airborne diseases among animals and as well as those that might be contagious to humans. For safety purposes, food and agricultural products must be protected against microorganisms and harmful compounds that can contaminate them through the surrounding air. Effective air decontamination methods are therefore necessary in animal slaughter and food processing facilities. PCO is regarded as one of the air cleaning technologies that can help in maintaining good air quality in these facilities and as well as in preventing contamination and microbial spoilage of food and dairy products. To decompose harmful products in food processing and packaging plants, photocatalytic devices, surfaces and coatings can be installed (Vera et al., 2007b). PCO process can be used to prevent premature aging of flowers and fruits by maintaining low levels of ethylene gas that is naturally produced in storage areas (Pridal and Pridal, 2003). Cho et al. (2007) reported use of PCO in the nonthermal disinfection of fresh vegetables by inactivating foodborne pathogenic bacteria such as *E. Coli*, *Salmonella Typhimurium* and *B cereus* in fresh carrots. Maneerat and Hayata (2006) demonstrated the antifungal activity of PCO with 7 nm TiO<sub>2</sub> particles against *P. expansum*, an organism responsible for postharvest rot development in fruits such as tomatoes and lemons.

### **2.3.2 Recent advances on PCO**

Most suitable photocatalysts are the metal oxide semiconductors, because of their resistance to photo-corrosion. To increase the photocatalytic power of semiconductor photocatalysts like TiO<sub>2</sub>, researchers and other manufacturers have been continuously modifying their structure. This includes changing its size, use of another method of synthesis or doping it

with other metals, metal ions and mixed-metal oxides. Nanosize regime as defined by Klabunde (1994) deals with particles of 1 to 100 nm or about  $10^4$  to  $10^6$  atoms or molecules per particle. Anpo and Takeuchi (2003) found that nanosized  $\text{TiO}_2$  particles of less than 10 nm showed enhanced photocatalytic reactivity due to the quantum size effect. This phenomenon is due to electronic modification of the photocatalysts as well as the close existence of the photoformed electron and hole pairs and their efficient contribution to the reaction, resulting in a performance much enhanced over that of semiconducting  $\text{TiO}_2$  powders. The size of nanoscale particles influences many physical and chemical properties such as binding energy, melting points, and optical and electronic properties (Gupta et al., 2004; Gupta, 2003). Nanosize  $\text{TiO}_2$  has more surface area and active sites for adsorption thereby increasing its photocatalytic activity. In terms of photochemical characteristics, ultra-fine particles like nanosized particles have some advantages relative to macroparticles such as P25  $\text{TiO}_2$  (Zhao and Yang, 2003). Zhao and Yang (2003) provided the following explanations for this claim. First, smaller particles (1 – 10 nm) exhibit characteristics between molecular and bulk semiconductors. Second, blue shifts of the band gap in UV absorption for these particles enhance redox potential of the photogenerated electrons and holes. Lastly, the high surface-area-to-volume ratios improve effectiveness for surface-limited reactions. In inactivation of bacteria via photocatalysis, smaller  $\text{TiO}_2$  particles are reported to cause quicker intracellular damage (Huang et al., 2000).

Several PCO reactor configurations and designs have been explored. Catalyst supports can be used to maximize active surface area (Anpo and Takeuchi, 2003). Catalysts can be fixed (anchored) on supports by means of physical surface forces or chemical bonds. Typical supports for PCO photocatalysts include activated carbon, fiber optic cables, fiberglass, glass rings, glassbeads, wool, thin films, membranes, quartz sand, zeolites, silica, stainless, and polymers (Tompkins et al., 2005a; de Lasa et al., 2005). Obuchi et al. (1999) used porous silica support to adsorb intermediates formed during the reaction and prevent release of harmful substances out of the system during a PCO process.

Various photo-reactor designs and configurations such as packed bed, monoliths, fluidized beds and thin films are described in Tompkins et al. (2005a). Thin-film photoreactors have been described for oxidation of a variety of gaseous pollutants as well as bioaerosols. In this form, immobilization of the catalyst is possible to prevent dispersion of the catalytic nanoparticles into the air. Ushijima et al. (1999) used  $\text{TiO}_2$  film in the decomposition of acetic



acid and acetaldehyde. Sopyan (2007) studied the photocatalytic degradation of gaseous acetaldehyde, ammonia and hydrogen sulfide using nanosized porous anatase and rutile TiO<sub>2</sub> films. Results of the study showed that the anatase film has higher photocatalytic power than rutile. Xu et al. (2006b) reported 95% and 75% photocatalytic efficiency in the destruction of bacteria - *pseudomonas aeruginosa* and *bacillus subtilis* respectively, using nanostructured N-TiO<sub>2</sub> films. The result showed that the photocatalytic power increases with decreasing thickness of the film. Skubal et al. (2008) developed an advanced surface made up of TiO<sub>2</sub> films that have the capability of self-detecting, characterizing, quantifying contaminants and decontamination by a photocatalytic process. The device initiates the decontamination process once the set concentration limit based on regulatory and safety standards, is exceeded. It utilizes the principle of a feed back system to monitor itself. This technology is said to have potential application in combating chemical and biological incidents and contamination. The support substrate was created by depositing fine platinum electrodes on thin aluminum oxide substrate.

The search for new types of light sources other than UV lamps was also explored by other researchers in the field of photocatalysis. Chen et al. (2005) first demonstrated the use of UV Light Emitting Diodes (LEDs) in the PCO of perchloroethylene (PCE) in air. UV LED is said to be an energy-efficient solid state light source that would replace traditional UV light sources (i.e. incandescent and gas-discharge lamps). Unlike fluorescent lamps, it does not contain mercury vapor that can be harmful to people's health. It is said to be long-lasting, robust, small in size and highly efficient. A commercial UV LED has a typical output of 12 mW and a peak wavelength of 395 nm. With these recent developments, it was confirmed that there is great potential for the UV LED to be used as light source for photocatalysis.

Hybrid systems that combine PCO process and other air cleaning devices were studied. Hodgson et al. (2007a) developed a combined UVPCO-chemisorbent system to control the formation of unwanted intermediates and by products of PCO process.

TiO<sub>2</sub>, the standard photocatalyst is active only under UV light with a wavelength of < 384 nm. UV light accounts for only 5% of solar energy while 45% is visible light (Yang et al., 2007). To make PCO technology more energy efficient in the destruction of pollutants in indoor air, photocatalysts that are highly reactive under visible light (i.e. solar light and fluorescent lamps) regime are necessary. The limitation on the use of UV light ( $\lambda < 384$  nm) of TiO<sub>2</sub> due to its wide band gap has been overcome. Several researchers have found a way to extend its activity

under visible light regime. Transition metals (V, Cr, Mn, Fe and Ni) and nonmetal atoms (C, N, S) can be used as dopants to extend the photocatalytic activity of TiO<sub>2</sub> into the visible light region (Qi et al., 2007; Yang et al., 2007). This is one of the most important developments in photocatalysis research - the energy-efficient utilization of the solar or visible light in PCO of indoor air pollutants. Asahi et al. (2001) doped TiO<sub>2</sub> with nitrogen. It resulted in a photocatalytic activity under a light source with 500 nm wavelength. This means that it can cover the main peak of solar irradiation energy beyond earth's atmosphere of about 460 nm and a light source peaking at 390 – 420 nm such as the light-emitting indium gallium nitride. Wang et al. (2007) demonstrated that transition metal incorporated titania-silica aerogels have similar or higher photocatalytic activity under visible light (>420 nm) than the UV-active commercial Degussa P25 TiO<sub>2</sub>. Anpo and Takeuchi (2003) envisaged the potential of ion-implantation method in the development of visible light highly reactive TiO<sub>2</sub> photocatalysts and thin films that are incorporated within zeolite frameworks. Wang et al. (2007) developed multi-type carbon-doped TiO<sub>2</sub> particles via controlled nonhydrolytic sol-gel method that exhibited significant photo response from UV to near infrared region (>950 nm). Tang et al. (2004) claimed that their newly developed CaBi<sub>2</sub>O<sub>4</sub> is efficient in decomposing organic contaminants (i.e. acetaldehyde) under visible light regime ( $\lambda > 400$  nm). Even visible light has some biocidal effects (Futter and Richardson, 1967; Griego and Spence, 1978; Kowalski, 2003). Qi et al. (2007) showed that a carbon-synthesized nitrogen-doped TiO<sub>2</sub> nanoparticle photocatalysts developed by sol-gel process exhibited high photocatalytic activity under visible light illumination in deactivating *E. coli*.

One of the major breakthroughs in the field of photocatalyst development is the 2% C- and V-doped TiO<sub>2</sub> by Yang et al. (2007) which contain some carbon and 2% vanadium. The catalyst has comparable activity both in the dark and under visible light illumination. This development overcomes the limitation of PCO technology in decontaminating the air during night time.

More advances in the PCO technology in the coming years are underway. Researchers are continuously developing materials and other ways to improve the technology for commercialization purposes.

### ***2.3.3 Operational issues of PCO for indoor air applications***

Despite numerous developments in the field of PCO, there are still issues that need to be considered in new PCO systems and photocatalysts. Tompkins et al. (2005a) presented several challenges that must be overcome before commercialization of PCO for gas phase cleaning. Among these challenges were the design of photocatalytic treatment devices with low pressure drop and development of catalysts that use light effectively and can be easily regenerated. Cost studies of PCO in Tompkins et al. (2005b) addressed the potential development of improved catalysts that can give high reaction rates and quantum yields in order to beat granular activated charcoal as a cost effective means of treating VOCs.

There are also technical issues that still need to be resolved. Harmful and unwanted intermediates can be produced along the PCO process. Vorontsov and Dubovitskaya (2004) observed the production of acetaldehyde in the photocatalytic oxidation of gaseous ethanol. The selective nature of PCO in dealing with gaseous mixtures can result in the formation of unwanted products (Hodgson et al., 2005b). Understanding the selectivity and performance of a particular PCO process is important to control the formation of unwanted intermediates. These intermediates can occupy active sites of the catalyst and can contribute to deactivation (Zhao and Yang, 2003). Hodgson et al. (2006) suggested the combination of PCO with other air cleaning systems to remove unwanted by-products. The regeneration and lifetime of the photocatalyst must be also fully understood.

The optimum relative humidity for utilizing PCO process in indoor air cleaning must be determined. Peral et al. (1997) reported the decrease in photocatalytic activity for organic compounds in the absence of water vapor. Though humidity can enhance the production of •OH radicals in a PCO process (Yu et al., 2006), it can promote competitive adsorption between water and the contaminant. (Obee and Brown, 1995).

The performance of PCO in a typical indoor air environment is not fully understood. Typically, pollutant concentrations found in an indoor environment range from ppb to sub-ppm levels (Wang et al., 2007; Hodgson et al., 2006; Hodgson et al., 2005a; Hodgson et al., 2005b; Tompkins et al., 2005a). Most studies were conducted on laboratory settings under relatively high concentrations of pollutants. Because there have been very limited studies on the

performance of catalysts at low pollutant levels, Wang et al. (2007) point out the need for more investigative studies at low concentrations. Also, indoor and ambient air pollutants do not involve just a single pollutant but mixtures of compounds (Zhang et al., 2007; Hodgson et al., 2005b; Hodgson et al., 2006; Hodgson et al., 2007b). Like any other indoor air cleaning method, PCO's efficiency on treating types of pollutant can differ because chemical and physical properties vary from one compound to another.

Nano-sized  $\text{TiO}_2$  can cause respiratory problems in animals and humans. Metal ion dopants can be harmful as well. Safe containment of these materials on a PCO system is necessary to protect the public once it is commercialized.

Due to limited studies, the efficacy of PCO that utilizes visible light in the destruction of most species and type of bioaerosols must be established.

Most of these issues need to be resolved before commercialization of a PCO device intended for indoor air applications commences.

## CHAPTER 3 - Modeling and Simulation Studies

### 3.1 Introduction

Recently, Yang (2008) reported the development of photocatalysts that are active both under visible light and dark conditions. The photocatalyst was made from TiO<sub>2</sub> doped with carbon and vanadium in varying amounts. The activity of the photocatalysts was tested for gaseous acetaldehyde. Results showed that the C- and V-doped TiO<sub>2</sub> containing 2% vanadium had comparable activity under visible light and dark conditions (Yang et al., 2007; Yang, 2008). This characteristic makes the 2% C- and V- doped TiO<sub>2</sub> potentially a great component of an energy-efficient PCO device that can clean the air both during the day and at night. Moreover, the light spectra of the fluorescent lights in homes and offices as well as the visible light component of the solar irradiation can be utilized to initiate the photocatalytic process.

With this major breakthrough in the field of photocatalysis, the use of effective and energy-efficient PCO air cleaning devices in combating indoor air pollution may be within our reach. However, initial evaluation of the photocatalyst's activity was conducted under laboratory setting using a concentration of about  $2.57 \times 10^5$  mg/m<sup>3</sup> (143,000 ppm) acetaldehyde (Yang, 2008; Yang et al, 2007). This very high concentration is much larger than the typical indoor air concentrations of most VOCs, which are only in the ppb to sub-ppm range. This study was the first attempt to explore and evaluate the use of the 2% C- and V-doped TiO<sub>2</sub> as photocatalysts in some PCO systems under ideal indoor air environment. Using this catalyst, IAQ modeling techniques based on mass balances were applied to simulate the fate of acetaldehyde in a typical room size with ideal indoor air conditions. Typical indoor air concentrations of acetaldehyde which are found in available literature were used. Two PCO systems are considered in the study, packed bed and thin films. Tompkins et al. (2005a) noted them as the most common designs that are being adapted by companies commercializing PCO technology. For effective and efficient operation of PCO systems, it is necessary to know the governing factors in their operation as they vary from one type of system to another. For example, the effects of mass transfer and reaction rate limitations and the pressure drop affect performance in packed beds. Results of the

modeling and simulation studies are expected to aid in the design of a PCO system in a room or chamber that might be used in the future. Simulation allows several alternatives to be evaluated based on predicted performance and estimated cost of operation.

At low concentrations mass transfer to the catalyst and diffusion within the catalyst pellets may limit the rate of oxidation. In this work, the values of the kinetic constants are based on a zero order kinetic model and the data of Yang et al. (2007) and Yang (2008). With this assumption, the emphasis of the study is on contaminant oxidation with the rate limited by transport processes.

### 3.2 Indoor air quality modeling

The main source for the presentation in this section is U.S. EPA (1991). Indoor air quality models are considered useful tools in describing the transport and dispersion of air contaminants throughout a structure and the change in indoor air contaminant concentrations as a function of source strengths, air-exchange rates, removal mechanisms, and other parameters. These models are mostly based on the principle of conservation of mass in a compartment or zone. A compartment or zone is an area in which the spatial variations in contaminant concentration can be ignored over the time period of interest. For example, a single room, floor, or house that is well-mixed is regarded to be a single zone. Houses with central forced-air heating systems and circulation fan in operation and where a sufficiently long period of time is allowed for mixing are considered well-mixed. Empirical models are also available that can better describe specific situations, but they do not have wide applicability that the models based from the first principles possess. Equations (3-1) or (3-2) describe the generation and removal of contaminants in a room space based on the principle of conservation of mass.

$$\text{rate of accumulation} = \text{rate of [input + generation - output - sinks]} \quad (3-1)$$

$$\frac{VdC_i}{dt} = \text{rate of change in mass due to} \left[ \left( \text{infiltration of outdoor air} \right) + \left( \text{generation indoors} \right) - \left( \text{exfiltration of indoor air} \right) - \left( \text{indoor removal of contaminants} \right) \right] \quad (3-2)$$

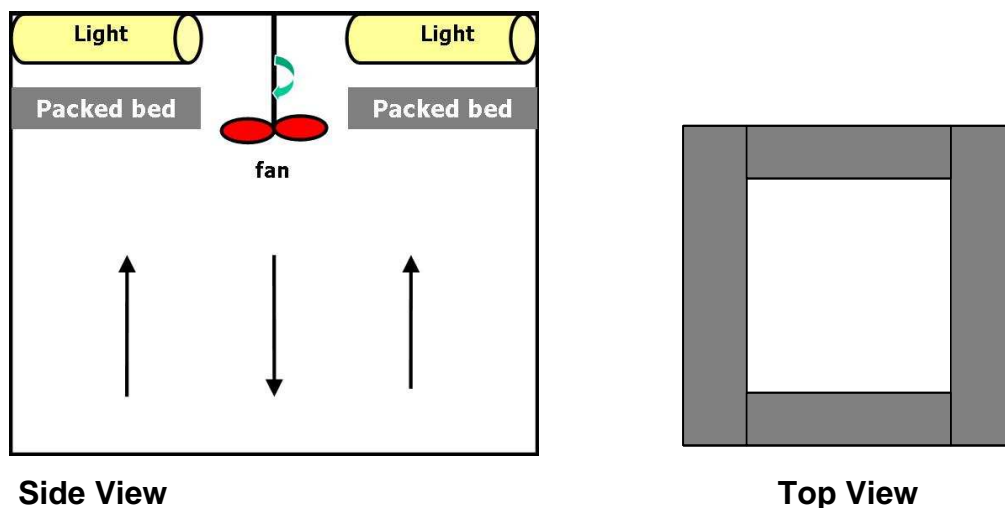
where  $V$  is the indoor volume,  $C_i$  is the indoor concentration and  $t$  is the time. Figures illustrating this balance are presented in the sections which follow.

### 3.3 Packed bed PCO system

#### 3.3.1 Background

One important use of packed bed systems in chemical and other process engineering fields is its use as a fixed-bed catalytic reactor (Geankoplis, 2003). The packing materials may be spheres, cylinders, or other kinds of commercial products. In photocatalysis, a bed of photocatalytic material can be configured to clean the air indoors. Kowalski (2006) noted that this is one of the more recent designs in PCO. Arabatzis et al. (2005) and Ibadon et al. (2007) used packed bed photoreactors incorporating porous foaming titania photocatalysts in their study of the photocatalytic degradation of VOCs.

Figure 3-1 depicts a possible configuration of a packed bed in the upper part of the room that can utilize an effective surface area for photocatalytic oxidation of organic air contaminants.



**Figure 3-1 Packed bed in the upper part of the room.**

The increased surface area resulting from the use of nanosized photocatalysts increases the reaction rate (Zhang et al., 2003). However, the use of nanoparticles in a packed bed system can increase the pressure drop. Pelletization of the photocatalysts can reduce the problem associated with the pressure drop as well as prevent fine particles from becoming entrained in the air. An optimum pellet size is necessary in order to achieve good performance with minimal pressure drop. Along with this, the effect of reaction rate and mass-transport limitations in the

overall PCO process will be considered in modeling and simulation studies for a packed bed photocatalytic reactor.

### 3.3.1.1 Pressure drop in packed beds

Pressure drop ( $\Delta P$ ) is the decrease in pressure from one point in a packed bed to another downstream. In fixed-bed adsorption systems, the energy usage resulting from pressure drop is a significant portion of the overall operating cost (Cooper and Alley, 2002). Bird et al. (2002) presented two theoretical approaches for estimating pressure drops through packed beds. In one method the packed bed is regarded as a bundle of tangled tubes of cross section; the theory is then developed by applying single straight tubes to the collection of crooked tubes. Furthermore, this method assumes that packing is uniform and that there is no channeling. The diameter of the packing is also assumed to be small compared to the diameter of the column in which the packing is contained and the column diameter is constant. In the second method, the packed tower is assumed to be a collection of submerged objects. The pressure drop is calculated by summing up the resistances of the submerged particles. The first approach known as the “tube bundle theory” is regarded to have been somewhat more successful than the second approach; it is where the famous Ergun equation was derived (Bird et al., 2002).

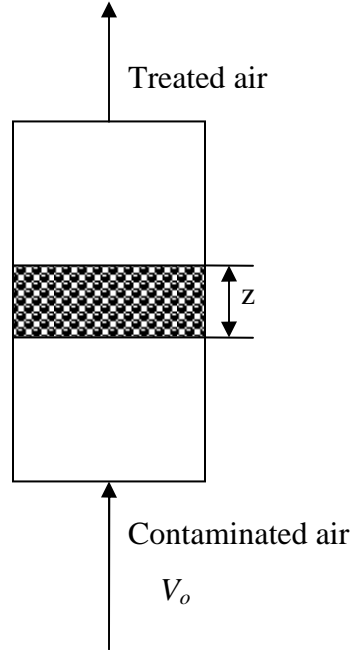
Equation (3-3) is a form of Ergun equation for spherical particles adapted from Bird et al. (2002). The Ergun equation relates the pressure drop with depth of the bed, fluid flow (i.e. velocity), packing size, bed porosity, and viscosity and density of the fluid (Bird et al., 2002; Geankoplis, 2003; McCabe et al., 1993; Copper and Alley, 2002; Fogler, 1999). It is a result of superimposing the Blake-Kozeny equation (Bird et al., 2002) and Geankoplis (2003) or what is known as the Kozeny-Carman equation in McCabe et al. (1993) for laminar flow ( $N_{Re,p} < 10$ ) and the Burke-Plummer equation ( $N_{Re,p} > 1000$ ) for turbulent flow in packed beds.

$$\left(\frac{\Delta P}{z}\right)\left(\frac{\rho_g D_p}{G_o^2}\right)\left(\frac{\varepsilon^3}{1-\varepsilon}\right) = 150\left(\frac{1-\varepsilon}{D_p G_o / \mu}\right) + \frac{7}{4} \quad (3-3)$$

In equation (3-3),  $\Delta P$  is the pressure drop across the bed,  $z$  is the depth of the bed,  $D_p$  is the particle diameter,  $\varepsilon$  is the void fraction or porosity of the bed,  $G_o$  is the superficial mass velocity,



and  $\rho_g$  and  $\mu$  are the gas density and viscosity, respectively. Figure 3-2 describes a typical packed bed PCO system for cleaning indoor air.



**Figure 3-2 Packed bed system for indoor air cleaning applications.**

For packed beds, the Reynolds number ( $N_{Re,p}$ ) is affected by the porosity or void fraction,  $\epsilon$ , in the bed (Geankoplis, 2003; Bird et al., 2002) as shown in equation (3-4).

$$N_{Re,p} = \frac{D_p V_o \rho_g}{(1 - \epsilon) \mu} = \frac{D_p G_o}{(1 - \epsilon) \mu} \quad (3-4)$$

Equation (3-3) may be written as

$$\frac{\Delta P}{z} = \frac{150 V_o \mu (1 - \epsilon)^2}{g_c \Phi_s^2 D_p^2 \epsilon^3} + \frac{1.75 \rho_g V_o^2 (1 - \epsilon)}{g_c \Phi_s D_p \epsilon^3} \quad (3-5)$$

To compensate for the irregular shape of particles, McCabe et al. (1993) incorporated a sphericity shape factor ( $\Phi_s$ ) as shown in equation (3-6). The shape factor is defined by Geankoplis (2003) as the ratio of the surface area of a sphere having the same volume as the particle to the actual surface area of the particle, that is,

$$\Phi_s = \frac{\pi D_e^2}{A_p} \quad (3-6)$$

In equation (3-6),  $D_e$  is the equivalent diameter, defined as the diameter of the sphere having the same volume as the particle and  $A_p$  is the actual surface area of the particle. Therefore, for a sphere,  $\Phi_s = 1.0$ . Sphericity factor values of other shapes are readily available elsewhere (McCabe et al., 1993; Geankoplis, 2003) or can be calculated using equation (3-6).

Equation (3-5) also includes the proportionality constant ( $g_c$ ), an important conversion factor when use of English units is desired. The value of this constant in English system is  $32.174 \text{ lb}_m \cdot \text{ft}/\text{s}^2 \cdot \text{lb}_f$ ; it is  $1.0 \text{ kg} \cdot \text{m}/\text{s}^2 \cdot \text{N}$  in the SI system and  $1.0 \text{ g} \cdot \text{cm}/\text{s}^2 \cdot \text{dyne}$  in the cgs system. Equation (3-7) is a variation of equation (3-5), in which  $G_o = \rho_g V_o$ . In equations (3-5) and (3-7),  $D_p$  can either be the equivalent diameter,  $D_e$  (Geankoplis, 2003) or the nominal size (McCabe et al., 1993; Geankoplis, 2003) for that particle.  $\Phi_s$  is treated to be equal to 1.0 when nominal size is used for  $D_p$  (Geankoplis, 2003; McCabe et al., 1993).

$$\frac{\Delta P}{z} = \frac{150 \mu G_o}{g_c \Phi_s^2 D_p^2 \rho_g} \frac{(1-\epsilon)^2}{\epsilon^3} + \frac{1.75 G_o^2}{g_c \Phi_s \rho_g D_p} \frac{(1-\epsilon)}{\epsilon^3} \quad (3-7)$$

The diameters of the pelletized particles are assumed to be small compared to the dimensions of the column in which the pellets are contained.

### 3.3.1.2 Rate limitations

Most gas-solid catalytic reactions, including heterogeneous photocatalysis, obey the Langmuir-Hinshelwood rate form (Ollis, 2005; Xu and Shiraiishi, 1999):

$$\text{Rate} = r = -\frac{dC}{dt} = \frac{kK_A C}{(1 + K_A C)} \quad (3-8)$$

where  $r$  is the reaction rate,  $C$  is the reactant concentration,  $t$  is the time,  $k$  is the kinetic constant and  $K_A$  is the adsorption equilibrium constant. Equation (3-8) turns into an apparent or pseudo-first order reaction at low concentrations and zero order at high concentrations. Rate equations can be combined with appropriate balance equations to predict performance of various reactor configurations. The importance of mass transfer and other influences on the overall efficiency of PCO in the removal and destruction of pollutants can be investigated (Ollis, 1996). Rate equations due to mass transfer can be incorporated into IAQ models based on mass balances to predict the performance of PCO systems. The influence of diffusion into the particles on the overall reaction process is usually represented by the effectiveness factor,  $\eta$  (Bailey and Ollis, 1986) as shown in equation (3-9).

$$\eta = \frac{\text{observed reaction rate}}{\text{rate which would be obtained with no diffusion resistance}} \quad (3-9)$$

The effectiveness factor indicates the relative importance of diffusion and reaction limitations. It is a measure of how far the reactant diffuses into the pellet before reacting (Fogler, 1999). This dimensionless parameter cannot be easily derived analytically in some cases. The use of a new dimensionless parameter called observable modulus,  $\Phi$ , would eliminate this constraint. Once  $\Phi$  is known, Table 4.21 in Bailey and Ollis (1986) can be used to determine the  $\eta$  for a particular order of reaction.

When the rate of removal of acetaldehyde in a packed bed is limited by the external mass transfer of the pollutant to the surface of the catalyst, the rate of reaction in the catalyst pellets is limited by the mass transfer through a film surrounding each pellet. The removal rate in mass

balances both in the room and in the packed bed will therefore be assumed to be due to the rate of mass transfer. Use of mass transfer coefficients ( $k_m'$ ) will be appropriate to define this process. A suitable correlation of the Sherwood number ( $N_{Sh,p}$ ) to the mass transfer coefficient for this particular system can be found in several sources (Bailey and Ollis, 1986; Bird et al., 2002).

### ***3.3.2 Modeling and simulation methods***

The study of packed beds is divided into three parts. The first part is the estimation of pressure drop given certain operating conditions. The second part is the determination of the effectiveness factor to assess the influence of internal mass transfer limitations on the overall reaction on a catalyst pellet. And lastly, the indoor air modeling and simulation studies of a packed bed system in a room. Under the study, two cases were looked at. First is when the process is reaction rate limited and internal diffusion through the pores of the pellets is limiting the reaction and second is when the external mass transfer is limiting the rate. To simplify calculations, metric units were used throughout.

#### ***3.3.2.1 Pressure drop calculations***

Pressure drop ( $\Delta P$ ) is estimated using the Ergun equation (equations 3-3, 3-5, and 3-7) using the CGS units. Separate pressure drop and modeling calculations were made for beds with spherical and cylindrical shape pellets. The packed bed was assumed to consist of pelletized 2% C-and V-doped  $TiO_2$  photocatalyst that is active both under visible light and dark conditions (Yang et al., 2007). Both spherical and cylindrical pellets have a diameter ( $D_p$ ) of 0.2 cm. Cylindrical pellets have a length ( $L_p$ ) twice the diameter ( $D_p$ ). The bed has a depth ( $z$ ) of 1 cm and a porosity ( $\epsilon$ ) or void fraction of 0.4 which is typical for most packed beds (McCabe et al., 1993). The porosity or void fraction ( $\epsilon$ ) is considered to be the external void fraction of the bed not the total porosity for the reason that the pores are usually too small to allow any considerable flow through them (McCabe et al., 1993).

In accord with the PCO experimental studies in Yang et al. (2007), acetaldehyde was selected to be the representative VOC in the room. As most PCO processes for indoor applications occur at nearly ambient conditions, calculations were made at room temperature ( $T$ ) of 20 °C and a pressure ( $P$ ) of 1 atm. Normally, in estimating the pressure drop in packed beds using the Ergun equation, the gas density ( $\rho_g$ ) varies with pressure and temperature (Fogler,

1999). However in this study, the effect of temperature and pressure in the gas density is considered unimportant since the photocatalytic process is assumed to occur nearly at constant ambient conditions. Moreover, the fans that draw the gas through the packed bed do not generate significant pressure drop. Since typical concentrations of pollutants in indoor environment are in the ppb to sub-ppm range, the feed gas stream to the packed bed can assume properties of air at the PCO operating conditions. Using the ideal gas law, the density of air at 20 °C and 1 atm was determined to be  $1.206 \times 10^{-3} \text{ g/cm}^3$ . Likewise, viscosity of air ( $\mu$ ) at this condition is  $1.81 \times 10^{-4} \text{ g/cm-s}$  (Bird et al., 2002). The study was carried out using a range of gas flow rates corresponding to superficial gas velocity ( $V_o$ ) of 5 to 25 cm/s. This is to cover the range of typical air movement in office buildings of 13 cm/s (25 ft/min) to 25 cm/s (45 ft/min) (ASHRAE, 2007a; ASHRAE, 2004).

### 3.3.2.2 Estimation of the effectiveness factor

The focus of the study is on the diffusion of the contaminant within the particles. Using the effectiveness factor ( $\eta$ ), the magnitude of diffusion effects on overall kinetics of catalyst pellets were evaluated for the range of pore radius ( $r_{\text{pore}}$ ) of 2 – 10 nm. To obtain  $\eta$ , the observable modulus ( $\Phi$ ) must be estimated first using the following equation (Bailey and Ollis, 1986):

$$\Phi = \frac{v_o}{D_{\text{eff}} C_i} \left( \frac{V_p}{A_p} \right)^2 \quad (3-10)$$

where  $v_o$  is the observed rate in  $\text{gmol}/\text{cm}^3\text{-s}$ ,  $V_p$  is the pellet volume in  $\text{cm}^3$ ,  $A_p$  is the external surface area of the pellet,  $C_i$  is the concentration of the contaminant gas (i.e. acetaldehyde) in indoor air and  $D_{\text{eff}}$  is the effective diffusion coefficient defined by equation (3-11) in Bailey and Ollis (1986). In Yang et al. (2007), the rate of  $\text{CO}_2$  production was used as a measure of the rate of acetaldehyde decomposition and in this study we will treat it the same way. Kim et al. (2002) indicated that in practice, the use of initial rate (at  $t = 0$ ) in the kinetic study is sufficient since it is difficult to develop a model for dependence of photocatalytic degradation rate on the experimental parameters for the whole treatment time. This also prevents the possible

interference from by-products. Thus, the initial rate of CO<sub>2</sub> production ( $1.4 \times 10^{-8}$  gmoles/cm<sup>3</sup>-s) provided in Yang et al. (2007) was used as the observed rate ( $v_o$ ) in equation (3-10).

$$D_{eff} = D \frac{\varepsilon_p}{\tau} \frac{K_p}{K_r} \quad (3-11)$$

In equation (3-11) (Bailey and Ollis, 1986),  $D$  is the diffusivity or diffusion coefficient of the contaminant (i.e. acetaldehyde) in air in cm<sup>2</sup>/s,  $\varepsilon_p$  is the porosity parameter;  $\tau$  is the tortuosity factor, and  $\frac{K_p}{K_r}$  is a parameter that accounts for restricted diffusion within the pellets.

Several resources are available to estimate the diffusivity or diffusion coefficient ( $D$ ) of acetaldehyde in air for the temperature and pressure of interest. A result of the combination of the kinetic theory and the corresponding-states arguments, equation (17.2-1) in Bird et al. (2002) can be used to estimate diffusion coefficients at low pressures. Two versions of online calculators are also available in U.S. EPA (2006) that can estimate diffusion coefficients of most compounds in air at certain conditions. The first version contains preset inputs for some compounds while the second version requires generation of input parameters for the chemicals of interest. Several literature sources also provide diffusivity values for certain compounds in air at a specific temperature and pressure. For instance, the diffusivity of acetaldehyde in air at 25 °C (0.124 cm<sup>2</sup>/s) was found in Rafson (1998), U.S. DOE (2006) and U.S. EPA (1994). To convert this parameter to the temperature ( $T$ ) of interest, which in this case is 20 °C, the direct relationship of diffusion coefficient with  $T^{1.823}$  in equation (17.2-1) in Bird et al. (2002) was utilized. The diffusion coefficient was estimated to be 0.1202 cm<sup>2</sup>/s at 20 °C.

Some literature sources give a range of internal void fraction or porosity ( $\varepsilon_p$ ) of 0.3 to 0.8 (Froment and Bischoff, 1990; Fogler, 1999; McCabe et al., 1993; Geankoplis, 2003). Although 0.4 is a typical pellet porosity, a pellet porosity parameter ( $\varepsilon_p$ ) of 0.5, which was used in this study, can account for some macropores that can be present in the C- and V-doped TiO<sub>2</sub> pellets. These macropores can be attributed to the spaces between individual crystallites and aggregates.

In actual diffusion in porous solid, the pores are not straight and cylindrical but irregular. The tortuosity factor ( $\tau$ ) compensates for this effect. Typical measured values of  $\tau$  factors given in Bailey and Ollis (1986) are in the range of 1.4 to 7 while other literatures indicate 1.5 to

greater than 10 (Froment and Bischoff, 1990; Geankoplis, 2003). For commercial porous solids  $\tau$  values range from 2 to 6 (Geankoplis, 2003). In this study, a  $\tau$  of 2 was assigned that was consistent also with the value inherent in laminar regime part of the Ergun equation (McCabe et al., 1993).

Small pores associated with the crystallites in consideration are very small but larger than the molecular dimensions of both the contaminant and air, which suggest the occurrence of restricted diffusion. Equation (3-12) gives a rough estimate of the parameter  $\frac{K_p}{K_r}$  which compensates for this phenomenon.

$$\frac{K_p}{K_r} \cong \left( 1 - \frac{r_{cont}}{r_{pore}} \right)^{0.4} \quad (3-12)$$

In equation (3-12),  $r_{cont}$  is the molecular (equivalent) radius of acetaldehyde, the contaminant gas, and  $r_{pore}$  is the characteristic pore radius of the catalyst pellet. The equivalent radius of acetaldehyde is estimated by obtaining the volume of one molecule (in  $\text{cm}^3/\text{molecule}$ ) through the Avogadro's number ( $6.023 \times 10^{23}$  molecules/gmole) and the density of liquid acetaldehyde ( $0.785 \text{ g/cm}^3$ ). Assuming that the acetaldehyde molecule is spherical in shape, the corresponding equivalent radius can then be obtained with a value of about 0.28 nm. This is not very much different from the diameter of a typical molecule of air of about 0.4 nm (Practical Physics, 2008). Although in the system in consideration for determining the effectiveness factor, the concentration of acetaldehyde in air is only 1 ppm, the pore radius of acetaldehyde molecules is more appropriate to use than just the air molecular size. This is advantageous in the sense that it will over estimate the effect of mass transfer limitations on the photocatalytic process. The range of pore radius ( $r_{pore}$ ) of the pellet considered in the study is from 2 to 10 nm. The average pore radius of NanoActive®  $\text{TiO}_2$  with mean aggregate size of 5  $\mu\text{m}$  is about 1.6 nm (Nanoscale, 2008). Yang et al. (2007) obtained a particle size of 9.2 nm in the characterization of the 2% C- and V-doped  $\text{TiO}_2$ . Chorkendorff and Niemantsverdriet (2003) discussed the many length scales of catalyst: Subnanometer in the molecular level, 1 to 10 nm for small catalytically active particles that go into the pores of support particles in the micrometer dimensions, mm to cm for shaped catalysts in the form of extrudates, spheres and monoliths, and cm to m length scales for

the macroscopic level (i.e. catalytic reactor beds in industrial plants). Transport phenomena such as diffusion of molecules inside pores are very important as they may affect the rate of product formation. The pore system of supports such as silica, alumina and carbon is usually irregular in shape and contains macropores, with dimensions of about 100 nm and micropores with characteristic dimensions of 5 to 10 nm. C- and V-doped TiO<sub>2</sub> individual particles are very small about 9.2 nm in size (Yang et al., 2007) and when pelletized, the number of micropores will be more significant than the macropores. This suggests that the use of a range of pore radius from 2 to 10 nm chosen for this study is appropriate.

Figure 4.21 of Bailey and Ollis (1986) can be used to determine  $\eta$  for a particular order of reaction using calculated values of  $\Phi$  using equations (3-10), (3-11), and (3-12). Table 3-3 shows both the  $\eta$  and  $\Phi$  for zero and first order reactions as a function of  $r_{\text{pore}}$  in spherical pellets. The observable modulus for cylindrical shape pellets was also calculated in similar manner with spherical pellets. However, difficulty arises in determining the  $\eta$  since Figure 4.21 in Bailey and Ollis (1986) does not have a plot for this particular geometry. The use of a generalized modulus, allows all geometries to be the same. The use of the Figure 3.6.1-2 in Froment and Bischoff (1990) can be used to estimate  $\Phi$  values for cylindrical geometry. It is a plot of  $\eta$  versus thiele modulus ( $\phi$ ), in which the cylindrical geometry is in between slab and spherical geometry. For first-order kinetics, the observable modulus ( $\Phi$ ) is related to thiele modulus ( $\phi$ ) by equation (3-13):

$$\Phi = \eta\phi^2 \quad (3-13)$$

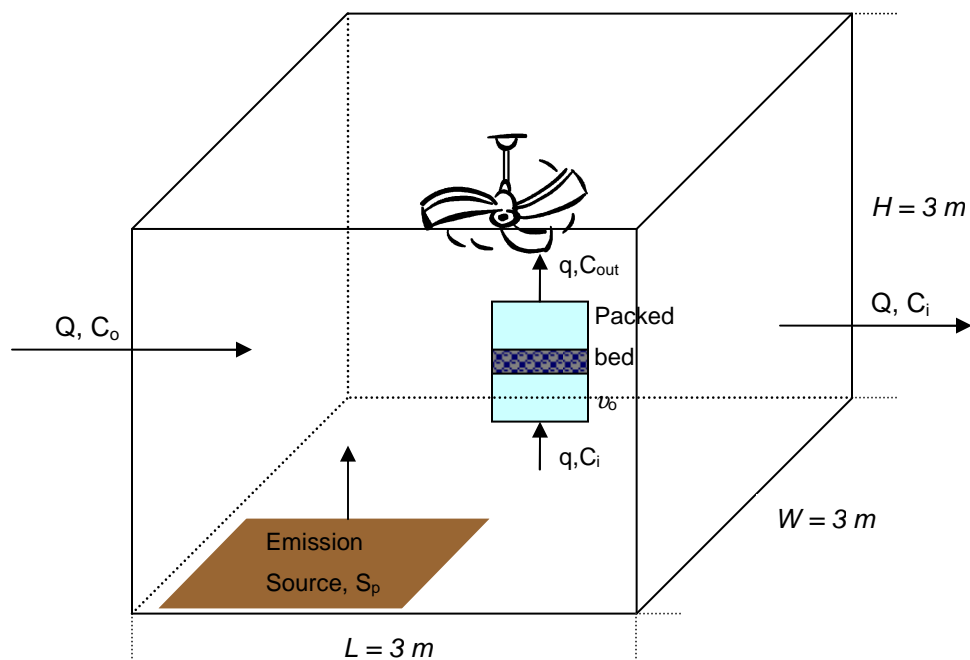
In Figure 4.21 in Bailey and Ollis (1986), the curves for slab and spherical geometry merge for  $\Phi \geq 15$ . Since the values of observable modulus for cylindrical geometry obtained in this study is greater than this ceiling value, we can use the same curve to obtain the effectiveness factor. Furthermore, Figure 12-5b in Fogler (1999) shows the merging of the curves of  $\eta$  versus  $\phi$  for sphere, cylinder and slab geometries for different reaction orders at  $\phi \geq 2$ .



### 3.3.2.3 Indoor air quality modeling (Reaction rate limited with internal diffusion)

This section studies the effects on the air quality of a typical indoor air environment upon installing a packed bed loaded with 2% C-and V-doped TiO<sub>2</sub> (Yang et al., 2007) . Given an acceptable value for the air movement in the room, depth of the bed and certain bed characteristics (i.e. density), a feasible area of the bed can be also determined.

For the purpose of this study, a small office room with typical dimensions of 3 m x 3 m x 3 m was considered to be the zone or compartment area (Figure 3-3).



**Figure 3-3 Well-mixed room with a packed bed in the room;**

The design in Figure 3-1 is an example arrangement (not drawn to scale)

In conformity with the standard ventilation rate ( $V_R$ ) for office buildings in ASHRAE (2007b), the room in Figure 3-3 is ventilated at a rate of  $0.48\text{ m}^3/\text{min}$  per person. For one person ( $p=1$ ) in the room (which is considered in this study), the ventilation rate ( $Q$ ) is  $0.48\text{ m}^3/\text{min}$  or 1.07 air changes per hour (ACH).

The acetaldehyde outdoor concentration ( $C_o$ ) was set to the typical value of  $20.12\text{ }\mu\text{g}/\text{m}^3$  (11 ppb) that is indicated in ASHRAE (2005) and ASHRAE (2007a). ASHRAE (2007a) also

provides an emission rate ( $S_p$ ) of 35  $\mu\text{g/h}$ -person of acetaldehyde which will be adopted herein. The room is equipped with a packed bed reactor that contains pellets of 2% C- and V-doped  $\text{TiO}_2$  of spherical geometry. With the packed bed in operation, the concentration inside the room is being maintained at a certain level ( $C_i$ ). The concentration of the contaminant inside the room is assumed to be uniform. This completely mixed model assumption allows  $C_i$  to be equal to the concentration of air leaving the room and the concentration of acetaldehyde entering the packed bed ( $C_i$ ). Two mass balances were made in order to solve for  $C_i$ . First is the mass balance within the room as shown in equation 3-14.

$$\frac{VdC_i}{dt} = QC_o + S_p p - QC_i - v_o \eta W_{cat} M_p \quad (3-14)$$

In the above equation  $V$  is the volume of the room,  $t$  is time,  $Q$  is the ventilation rate in  $\text{m}^3/\text{min}$ ,  $C_o$  is the concentration of acetaldehyde entering the room,  $S_p$  is the source emission rate per person,  $p$  is the number of people in the room,  $C_i$  is the concentration of acetaldehyde in the room,  $v_o$  is the reaction rate,  $\eta$  is the effectiveness factor,  $W_{cat}$  is the weight of the catalyst and  $M_p$  is the molecular weight of the acetaldehyde.

A steady state assumption was made in equation (3-14), wherein  $V \frac{dC_i}{dt} = 0$ . This means that generation of contaminants is equal to removal. It was also assumed that the rate of removal due to the packed bed is mainly influenced by the rate of destruction of acetaldehyde, a diffusion rate limited case. The experimental studies in Yang et al. (2007) involved the treatment of very high concentrations of acetaldehyde and in this study, small amounts of the photocatalyst particles were used to make pellets. In these regard, we can say that the observed reaction rate ( $v_o$ ) of  $2.283 \times 10^{-8}$  gmol/gcat-s obtained from Yang et al. (2007) can be an estimate of the reaction rate with no mass transfer resistance. For the effectiveness factor ( $\eta$ ) in equation (3-14), a value of about 0.15 was used, which is the estimated value for pore sizes of 5 to 9 nm assuming zero order reaction and using equations (3-10), (3-11), and (3-12).

The second mass balance is performed within the packed bed reactor (equation 3-15)

$$qC_i - qC_{out} = v_o\eta W_{cat}M_p \quad (3-15)$$

where  $q$  is the flow rate in the packed bed,  $C_i$  is the concentration of acetaldehyde entering the packed bed and  $C_{out}$  is the concentration of acetaldehyde coming out of the packed bed. Under steady state conditions, equation (3-14) can be written as

$$C_i = \frac{QC_o + S_pP - v_o\eta W_{cat}M_p}{Q} \quad (3-16)$$

As  $C_{out}$  approaches zero,

$$C_i = \frac{C_oQ + S_pP}{Q + q} \quad (3-17)$$

which gives the lower limit of  $C_i$  when all of the acetaldehyde that enters the packed bed is oxidized.

The indoor air concentration of acetaldehyde ( $C_i$ ) was evaluated using different values of flow rates ( $q$ ) in the packed bed. The flow rates in the packed bed were set as multiples of 0.48 m<sup>3</sup>/min, the ventilation rate in the room ( $Q$ ) for one person (say  $1Q$ ,  $2Q$ ,  $3Q$  etc...). The area of the bed was estimated for superficial velocity ( $V_o$ ) values from 13 cm/s (25 fpm) to 25 cm/s (45 fpm) (ASHRAE, 2004; ASHRAE, 2007a). A zero order reaction rate assumption (where  $k = v_o$ ) resulted in equation (3-18) which can be used to estimate the weight of catalyst needed to bring a particular indoor air concentration to zero ( $C_{out} = 0$ ).

$$W_{cat} = \frac{qC_i}{\eta k M_p} \quad (3-18)$$

Table 3-5 shows the calculated indoor air concentration ( $C_i$ ), area of the bed and weight of catalyst required for a 100% efficient packed bed. However, a finite length of bed is necessary that will not compromise a large surface area for reaction. A bed depth ( $z$ ) of 1 cm will serve for this purpose. The weight of the catalyst needed to maintain low levels of acetaldehyde in the room are presented in Table 3-6.

#### 3.3.2.4 Indoor air quality modeling (External mass transfer limited)

Considering a packed bed design in the room as shown in Figure 3-2, the rate of removal of the acetaldehyde due to reaction is  $61.6 \times 10^{-8} \text{ g/cm}^3\text{-s}$  and approximately equal to  $1.34 \times 10^{-9} \text{ g/cm}^3\text{-s}$  if its due to mass transfer of the acetaldehyde to the surface of the pellets for  $V_o = 15 \text{ cm/s}$ . The lower value of the rate due to mass transfer than the rate due to reaction suggests that for a packed bed system, external mass transfer is limiting.

Similar indoor air environment in section 3.3.2.3 was assumed. However in this case, the effect of external mass transfer limitations to the pellets in the bed was evaluated. Due to its closeness to a packed bed system, a plug flow model shown in equation (3-19) was used to describe the change of concentration through the packed bed over time due to mass transfer of the pollutant to the surface of the pellets.

$$\frac{dC}{dt} = -k'_m CA_m \quad (3-19)$$

where  $C$  is the pollutant concentration at any residence time,  $t$ .  $k'_m$  is the mass transfer coefficient in cm/s and  $A_m$  is the area of mass transfer. The acetaldehyde concentration at the pellet surface is assumed to be zero. Integration of equation (3-19) and applying the following boundary conditions in the packed bed yields equation (3-20): At  $t = 0$ ,  $C = C_i$  and at  $t = t_R$ ,  $C = C_{out}$ , where  $C_i$  is the concentration of the gas at the inlet of the packed bed,  $C_{out}$  is the concentration of the pollutant coming out of the packed bed and  $t_R$  is the residence time in the bed.

$$C_{out} = C_i e^{-k'_m A_m t_R} \quad (3-20)$$

The area of mass transfer ( $A_m$ ) can be estimated by finding the total external surface area of the pellets over a differential volume of the bed. First, a  $1 \text{ cm}^2$  differential area is assumed with a depth,  $z$  of 1 cm. The volume of each spherical pellet with a diameter,  $D_p$  of 0.2 cm is  $0.004187 \text{ cm}^3$ . A bed porosity,  $\varepsilon$  of 0.4 gives  $0.6 \text{ cm}^3$  of solid volume in the bed. This results in an  $N_p$  value of 143 pellets/ $\text{cm}^3$ . For the given diameter of the spherical pellet, we also have a surface area,  $A_p$  of  $0.1256 \text{ cm}^2$ . Thus, the area of mass transfer ( $A_m$ ) as a result of using equation (3-21) is approximately  $18 \text{ cm}^2/\text{cm}^3$ .

$$A_m = N_p A_p \quad (3-21)$$

The mass transfer coefficient values for the range of velocities of 5 to 25 cm/s are estimated using the correlation of the Sherwood number ( $N_{Sh,p}$ ) for flow around a spherical particle shown in equation (3-22). This equation is appropriate for Reynolds numbers greater than 20 for flow in packed beds (Bird et al., 2002).

$$N_{Sh,p} = \frac{k'_m D_p}{D} = 2.0 + 0.60(N_{Re,p})^{1/2} (N_{Sc})^{1/3} \quad (3-22)$$

$N_{Re,p}$  and  $N_{Sc}$  are the Reynolds number for pellets in packed beds and the Schmidt number, respectively. For a steady state balance around the packed bed and with equation (3-22), equation (3-15) becomes

$$qC_i - qC_{out} = qC_i(1 - e^{-k'_m A_m t_R}) \quad (3-23)$$

A mass balance around the room similar to equation (3-14) was performed, however equation (3-23) is used to replace the removal term in the packed bed in equation (3-14) to yield equation (3-24).

$$V \frac{dC_i}{dt} = QC_o + S_p p - QC_i - qC_i(1 - e^{-k'_m A_m t_R}) \quad (3-24)$$

where  $q = V_o S$  and  $S$  is the area of the bed normal to the flow. At steady state conditions, equation (3-24) was rearranged to solve for  $C_i$  at various velocities in the bed.

$$C_i = \frac{QC_o + S_p p}{Q + V_o S(1 - e^{-k_m A_m t_R})} \quad (3-25)$$

The residence time ( $t_R$ ) in a 1 cm length of the bed ( $z$ ) for velocities of 5 to 25 cm/s is calculated as follows:

$$t_R = \frac{z\mathcal{E}}{V_o} \quad (3-26)$$

The indoor air concentrations for 1000, 5000 and 10,000 cm<sup>2</sup> area of the bed ( $S$ ) are determined as shown later in Table 3-7.

### 3.3.3 Results and discussion

#### 3.3.3.1 Pressure drop

The pressure drop ( $\Delta P$ ) across a packed bed with 0.2 cm-diameter spherical pellets of 2% C-and V-doped TiO<sub>2</sub> and a bed depth of 1 cm was estimated using the Ergun equation described in equations (3-5) and (3-7). The equivalent superficial mass velocities ( $G_o$ ) are for flow velocities from 5 cm/s to 25 cm/s using the relation  $G_o = \rho_g V_o$ . The Reynolds number in the bed ( $N_{Re,p}$ ) obtained using equation (3-4) for 5 to 25 cm/s ranges from 11 to 55 (Table 3-1). This means that operating the air circulation in the room and the packed bed under acceptable air movement for office buildings indicated in ASHRAE (2007a) and ASHRAE (2004) favors a process occurring in the transition between the Kozeny-Carman ( $N_{Re,p} < 10$ ) and Burke-Plummer ( $N_{Re,p} > 1000$ ) regime. The use of the Ergun equation therefore is appropriate to estimate the pressure drop for this range of velocities. The pressure drops within the given velocity range are low and range from 22 dynes/cm<sup>2</sup> (2.2 Pa) to 159 dynes/cm<sup>2</sup> (15.9 Pa) as shown in Table 3-1. The low values of pressure drop obtained from the modeling studies suggest that this system has the potential for commercialization.

**Table 3-1 Calculated pressure drops across a packed bed with spherical pellets ( $D_p = 0.2$  cm).**

$V_o$ (cm/s)	$G_o$ (g/cm <sup>2</sup> -s)	$N_{Re,p}$	$\Delta P$ (dynes/cm <sup>2</sup> )
5	0.0060	11	22
10	0.0121	22	49
15	0.0181	33	80
20	0.0241	44	117
25	0.0301	55	159

Results for cylindrical pellets with diameter of 0.2 cm and a length twice the diameter are presented in Table 3-2. This size proportion chosen for this study is common for cylindrical pellets of activated carbon. Results for the superficial mass velocity, Reynold's number and pressure drop are shown in Table 3-2.

**Table 3-2 Calculated pressure drops across a packed bed with cylindrical pellets ( $D_p = 0.2$  cm,  $L_p = 2D_p = 0.4$  cm).**

$V_o$ (cm/s)	$G_o$ (g/cm <sup>2</sup> -s)	$N_{Re,p}$	$\Delta P$ (dynes/cm <sup>2</sup> )
5	0.0060	13	16
10	0.0121	26	35
15	0.0181	39	59
20	0.0241	53	87
25	0.0301	66	119

A cylindrical pellet with a length ( $L_p$ ) twice the diameter ( $D_p$ ) resulted in a reduced pressure drop across the bed. As previously discussed in section 3.3.1.1, the relationship of the pressure drop ( $\Delta P$ ) with both properties of the particle and the fluid being treated in a packed bed system can be referred to the Ergun equation (equations 3-5 and 3-7). For cylindrical particles, the equivalent diameter ( $D_e$ ) was calculated as follows:

$$D_e = \left( \frac{3}{2} D_p^2 L_p \right)^{\frac{1}{3}} \quad (3-27)$$

Using equation (3-19), the size and proportion of the cylindrical pellet resulted in an equivalent diameter ( $D_e$ ) of 0.29 cm, a size larger relative to the spherical shape pellet. Using equation (3-6), the value of the sphericity factor ( $\Phi_s$ ) is 0.832. The shape of the cylindrical pellets also affects their orientation in the bed, which can create more void space between the pellets resulting in an increased available area for flow in the bed.

### 3.3.3.2 Effectiveness factor

As described in equation (3-9), the effectiveness factor,  $\eta$  is the ratio of the observed rate with the rate which would be obtained with no mass-transfer resistance. Figure 4.2 of Bailey and Ollis (1986) describes the effectiveness factor as a function of the observable modulus ( $\Phi$ ). The values obtained from the experimental work can be used to estimate the observable modulus for acetaldehyde decomposition. The corresponding value of  $\eta$  from Bailey and Ollis, (1986) is used in section 3.3.2.3 in the removal term in the IAQ model in equations (3-14), (3-15) and (3-16). The mass balance is used to explore the effect of this reaction process on the concentration of acetaldehyde in the room.

Values of the observable modulus and effectiveness factor for spherical pellets and cylindrical pellets are obtained using equation (3-10) and are shown in Tables 3-3 and 3-4.

**Table 3-3 Observable modulus ( $\Phi$ ) and effectiveness factor ( $\eta$ ) as a function of pore radius in spherical pellets.**

$r_{\text{pore}}$ (nm)	$\Phi$	$\eta$	
		Zero Order	First Order
2	23	0.09	0.05
4	17	0.13	0.06
6	15	0.15	0.07
8	14	0.15	0.08
10	14	0.17	0.08



**Table 3-4. Observable modulus ( $\Phi$ ) and effectiveness factor ( $\eta$ ) as a function of pore radius in cylindrical pellets.**

$r_{\text{pore}}$ (nm)	$\Phi$	$\eta$	
		Zero Order	First Order
2	33	0.06	0.03
4	24	0.09	0.05
6	22	0.09	0.05
8	21	0.10	0.05
10	20	0.10	0.05

When  $\Phi$  is sufficiently large (say  $>3$ ), internal diffusion of acetaldehyde is limiting reaction or consumption (Bailey and Ollis, 1986).  $\Phi$  values in Tables 3-3 and 3-4 are much larger than 3. This means that the extent of diffusion limitation is large for both spherical and cylindrical pellets and that the diffusion of acetaldehyde is controlling and the observed rate is limited by diffusion. With cylindrical pellets with  $L_p = 2D_p$ , higher  $\Phi$  and lower  $\eta$  values were obtained as compared with the spherical pellets described in Table 3-3, which implies more diffusion limitations.

### 3.3.3.3 Indoor air pollutant concentration and amount of catalyst

Table 3-5 presents the results of the IAQ modeling studies for a reaction rate-limited case with internal diffusional effects on spherical pellets. The concentration of acetaldehyde ( $C_i$ ) is highest when there is no packed bed or it is not in operation ( $q = 0$ ). The value of  $C_i$  decreases from  $21.33 \mu\text{g}/\text{m}^3$  to  $1.93 \mu\text{g}/\text{m}^3$  with increasing flow rate in the packed bed from zero to  $4.8 \text{ m}^3/\text{min}$ . Flow rate has dual effects on the photocatalysis process (Yu et al., 2007). It can affect the rate of decomposition in certain ways by increasing diffusion and convective mass transfer between VOC molecule and  $\text{TiO}_2$ , thereby increasing the rate of decomposition. However, too high flow rates can shorten the residence time and decrease the time for photocatalytic activity.

**Table 3-5 Calculated indoor air concentration,  $C_i$ , area of the packed bed and weight of catalyst needed for  $C_{out} = 0$  for various flow rates in the packed bed.**

Flow rate in the packed bed, $q^a$ ( $m^3/min$ )		$C_i$ ( $\mu g/m^3$ )	Area of the bed <sup>b</sup> , $S$ ( $cm^2$ )				Weight of catalyst <sup>c</sup> needed for $C_{out} = 0$ (g)
			$V_o = 13$ cm/s	$V_o = 15$ cm/s	$V_o = 20$ cm/s	$V_o = 25$ cm/s	
0	0	21.33	0	0	0	0	0
$Q$	0.48	10.67	617	535	401	321	0.57
$2Q$	0.96	7.11	1234	1070	802	642	0.75
$5Q$	2.4	3.56	3085	2674	2005	1604	0.94
$10Q$	4.8	1.94	6171	5348	4011	3209	1.02

<sup>a</sup>The flow rates in the packed bed are multiples of the ventilation rate for one person in the room,  $Q$ .

<sup>b</sup>The area,  $S$ , was calculated using the volumetric flow rate,  $q$  and the superficial velocity,  $V_o$  in the bed.

<sup>c</sup>The weight of catalyst to maintain the concentration of acetaldehyde in the second column of Table 3-5 was estimated using equation (3-18).

For the various flow rates in consideration, about 0.5 to 1 gram of catalyst is needed to make  $C_{out} = 0$ . The amount of the catalyst required increases with increasing flow rate. However, we need a finite length of the bed, say 1 cm, so we need to increase the amount of catalyst. Table 3-6 shows the amount of catalyst needed if we have a bed depth ( $z$ ) of 1 cm. The amount of catalyst required for a 1 cm depth of catalyst bed increases significantly. This amount would be sufficient to provide the room with a packed bed similar to that shown in Figure 3-1. Moreover, it will facilitate the degradation of the contaminant and maintain good air quality in the room due to increased area for photocatalysis. The largest area 6171  $cm^2$  is less than 10% of the 90,000  $cm^2$  of area for a 3 m x 3 m room.

**Table 3-6 Calculated weight of catalyst using a bed depth of 1 cm for maintaining low levels of acetaldehyde in the room.**

Flow rate in the packed bed, $q$ ( $\text{m}^3/\text{min}$ )		Weight of catalyst if bed depth is 1 cm (g)			
		$V_o = 13$	$V_o = 15$	$V_o = 20$	$V_o = 25$
		cm/s	cm/s	cm/s	cm/s
0	0	0	0	0	0
Q	0.48	370	321	241	193
2Q	0.96	740	642	481	385
5Q	2.4	1851	1604	1203	962
10Q	4.8	3703	3209	2407	1925

For the packed bed photocatalytic reactor in a room, optimum characteristics of the bed (i.e. bed depth, area) are necessary in order to have an appropriate flow rate and pressure drop through the device, and at the same time maintain an acceptable air quality.

Table 3-7 shows the estimated mass transfer coefficients, residence time for a bed depth of 1 cm and indoor air acetaldehyde concentrations obtained by using equation (3-25) assuming that the rate is limited by the mass transfer exterior to the pellet.

**Table 3-7 Calculated indoor air concentrations ( $C_i$ ) of acetaldehyde for external mass transfer control in a packed bed.**

$V_o$ (cm/s)	$k'_m$ (cm/s)	$t_R$ (s)	Indoor air concentration, $C_i$ ( $\mu\text{g}/\text{m}^3$ )		
			1000 $\text{cm}^2$	5000 $\text{cm}^2$	10000 $\text{cm}^2$
5	2.496	0.080	13.28	5.29	3.02
10	3.031	0.040	10.13	3.27	1.77
15	3.443	0.027	8.49	2.49	1.32
20	3.789	0.020	7.47	2.08	1.09
25	4.095	0.016	6.76	1.81	0.95

The weight of the catalyst for the 1000, 5000 and 10000 cm<sup>2</sup> of area and bed depth (z) of 1 cm is 600, 3000 and 6000 g, respectively for a bulk density of 0.6 g/cm<sup>3</sup>. Results are for one person in the room. The implication of the above results in relation to Table 3-5 and 3-6 is that to obtain even lower indoor pollutant concentration for a particular flow rate, more area for external mass transfer should be provided. This suggests that lower overall indoor air pollutant concentration can be achieved with greater area for mass transfer even though the outgoing air from the packed bed still contains some acetaldehyde. The largest area, 10000 cm<sup>2</sup> is 1/9 of the available area for a 3 m x 3 m room.

## 3.4 Thin films on walls and ceilings

### 3.4.1 Background

PCO systems that incorporate thin films of photocatalytic materials have gained attention in recent years as an approach to treat gaseous pollutants (Yu et al., 2007; Xu et al., 2006b). Thin film PCO designs have good commercialization potential (Tompkins et al., 2005a). Materials coated with photocatalysts in the form of thin films can generate self-cleaning surfaces (Noguchi and Fujishima, 1998). Walls and ceilings can be made catalytically-active to treat and maintain low levels of air contaminant indoors. This configuration offers some advantages over other PCO configurations. Immobilizing the catalytic particles in building construction materials will enable them to be contained well, thus preventing the unintentional release of the particles in the air. Most important, this configuration offers large surface area for photocatalytic reaction. Sopyan et al. (1996) compared the photocatalytic activity of Degussa P-25 powder with TiO<sub>2</sub> film in the degradation of acetaldehyde. The study revealed that the TiO<sub>2</sub> film is superior to the Degussa P-25 powder owing to former's higher number of adsorption sites per unit mass. Using a Langmuir-Hinshelwood model in studying the kinetics of acetaldehyde degradation, Sopyan et al. (1996) found that the first order rate constant was larger with the film than with the powder. Moreover, one of the common problems of photocatalysts in powder form is they tend to agglomerate.

Surface area is one of the most important factors affecting photocatalytic activity (Jung, 2008). The use of nanoparticles in thin films to increase surface area for reaction is often favorable. Maness et al. (1999) indicated that photocatalytic activity can be enhanced by decreasing nanoparticle diameter and increasing contact area between the photocatalyst and target material. Xu et al. (2006b) demonstrated that the use of smaller nanoparticle sizes in thin films exhibited higher photocatalytic activity and that the photocatalytic chemical reaction mainly occurred on the film surface.

Chemical vapor deposition (Jung et al., 2005; Jung, 2008) and sol gel solution with dip coating (Xu et al., 2006b; Jung, 2008; Sopyan, 2007; Maeda and Yamada, 2007; Kim et al., 2002) are the most common methods of fabricating thin films. Noguchi et al. (1998) developed TiO<sub>2</sub> thin films using spin coating method. Film thickness is usually in the micron range (Yu et

al., 2007; Sopyan et al., 1996). Maeda and Yamada (2007) developed metal-doped TiO<sub>2</sub> thin films that are active in the visible region via sol gel process. The activity depended on the type of metal dopants used. The 2% C-and V-doped TiO<sub>2</sub> in Yang et al. (2007) may be potentially incorporated into thin films, also.

### **3.4.1.1 Mass transfer to a wall in a room for oxidation of organic contaminants**

Mass transfer is important in processes which involve diffusion. Mass transfer and diffusion along with adsorption and photochemistry were determined as mechanisms that may control the photocatalytic degradation of VOCs using nano-TiO<sub>2</sub> catalyst (Yu et al., 2007). In thin films on walls, the overall rate of reaction may be limited by the rate of mass transfer of reactants (air contaminants) between the bulk gas and the catalytic surface. For instance, Noguchi et al. (1998) studied the decomposition of formaldehyde and acetaldehyde using thin films and found that the rate was mass transfer-limited for acetaldehyde. Molecular diffusion in the catalyst is not fully understood in this type of system (Yu et al., 2007):

The diffusion of air containing VOCs in TiO<sub>2</sub> film can be described by the film model theory and the diffusion equation from Fick's law as shown below (Bird et al., 2002)

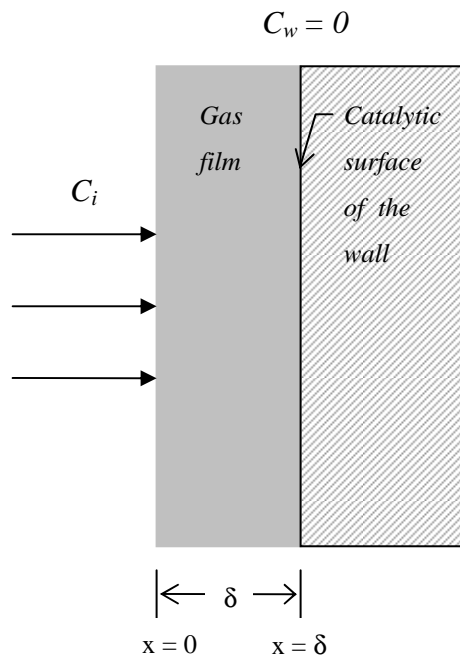
$$N_{Ax} = y_A (N_{Ax} + N_{Bx}) - cD \frac{\partial y_A}{\partial x} \quad (3-28)$$

where  $c$  is the total concentration,  $D$  is the binary diffusion coefficient,  $N_{Ax}$  is the molar flux of A (in this case the contaminant) in the  $x$  direction,  $N_{Bx}$  is the molar flux of any other substance B in the  $x$  direction, and  $y_A$  is the mole fraction of the pollutant. In equation (3-28), the first term in the right accounts for the transport due convective or bulk flow of species A and B and the second term accounts for the mass transfer due to molecular diffusion.

For cases wherein boundary parameters (i.e. gas film thickness) are difficult to determine, the rate of mass transfer can be best correlated in terms of mass transfer coefficients. This is valid for systems wherein the external resistance is limiting and the bulk or convective flow is neglected (Hines and Maddox, 1985; Fogler, 1998).

### 3.4.1.2 Mass transfer limitations

There are two types of diffusion resistance involved in heterogeneous reactions: external resistance and internal resistance. As described by Fogler (1998), the first is the diffusion of the reactants or products between the bulk fluid and the external surface of the catalyst while the latter is the diffusion occurring in the interior of the catalyst. The first will be the main focus of this study. In a system shown in Figure 3-4, the pollutant has to diffuse to reach the catalytic surface. Mass transfer limitations in gas-solid catalysis occur when the rate of reaction is rapid and the rate is controlled by the diffusion of the contaminant in the hypothetical gas film near the catalytic surface with thickness,  $\delta$ . Mass transfer resistance can affect the overall reaction rate for the photocatalytic process. This occurs when the rate of disappearance of the contaminant in the indoor environment is controlled by the rate of mass transfer of the pollutant to the catalytic surface.



**Figure 3-4 Diffusion process occurring on a catalytic surface.**

### ***3.4.2 Modeling and simulation methods***

The modeling studies conducted here on systems involving catalytic surfaces such as thin films involve two parts. The first is the estimation of the mass transfer coefficients ( $k'_m$ ) to obtain the rate of mass transfer. The second is the mass balance for IAQ modeling to determine the effect of mass transfer limitations on the overall contaminant removal process in a typical indoor environment.

#### ***3.4.2.1 Estimation of mass transfer coefficient***

When the pollutant reaches the photocatalytic surface, it disappears and is converted instantaneously and irreversibly to another substance (i.e. CO<sub>2</sub>, H<sub>2</sub>O and other byproducts). Although there is not much information about how the hydroxyl radicals and superoxides attack the pollutant (in this case acetaldehyde) they can be assumed to be dispersed in the film very near the catalytic solid. It is assumed that they never diffuse much beyond the surface of the wall because they are very reactive. One dimensional degradation process is assumed. The reaction products diffuse out through the gas film. However, in a typical indoor air environment, the concentration of the contaminant is low (within the ppb to sub-ppm) range. It follows that a very small amount of products are formed during the photocatalytic process, thus resulting in very dilute concentrations of products. This allows us to neglect the bulk or convective flow term in equation (3-28) and to use the mass transfer coefficient ( $k'_m$ ) in estimating the rate of mass transfer in this particular case. The substance in a surrounding stream is lost on the catalytic solid surface according to the relation

$$N_{Ax} = k'_m (C_i - C_w) \quad (3-29)$$

where  $N_{Ax}$  is the molar flux of A,  $C_i$  is the concentration of the contaminant in the stream flowing over the surface,  $C_w$  is the concentration of the contaminant at the wall or catalytic surface (where  $x = \delta$ ) and  $k'_m$  is the mass transfer coefficient. In this model, we assume that the gas film is isothermal and the effect of products on the model can be neglected.



Fogler (1998) modified equation (3-28) in terms of concentrations for a case with negligible bulk or convective flux as

$$N_{Ax} = \frac{D}{\delta}(C_i - C_w) \quad (3-30)$$

where  $\delta$  is the thickness of hypothetical stagnant film described in Figure (3-4) or the length of the diffusion path (Hines and Maddox, 1985). Comparing equations (3-28) and (3-29) suggests that in a case where the flux is due to diffusion only,  $k'_m = \frac{D}{\delta}$ . However,  $\delta$  is difficult to determine as compared to  $k'_m$  which can be derived from correlations such as the Sherwood number ( $N_{Sh,L}$ ). Thus, the use of equation (3-28) is a convenient means of describing the mass transfer process. Equation (3-28) is limited to low mass transfer rates in which the bulk flow is negligible and the concentration profile is not distorted (Hines and Maddox, 1985).

Mass transfer coefficients can be obtained through empirical expressions relating the Sherwood number ( $N_{Sh,L}$ ) to the Reynolds and Schmidt numbers. For instance, Perry and Green (1997) noted the following expression for a flat plate:

$$N_{Sh,L} = \frac{k'_m L}{D} = 0.646(N_{Re,L})^{1/2}(N_{Sc})^{1/3} \quad (3-31)$$

Reynolds number ( $N_{Re,L}$ ) and Schmidt number ( $N_{Sc}$ ) in equation (3-31) are defined by

$$N_{Re,L} = \frac{\rho_g V_o L}{\mu} \quad (3-32)$$

$$N_{Sc} = \frac{\mu}{\rho_g D} \quad (3-33)$$

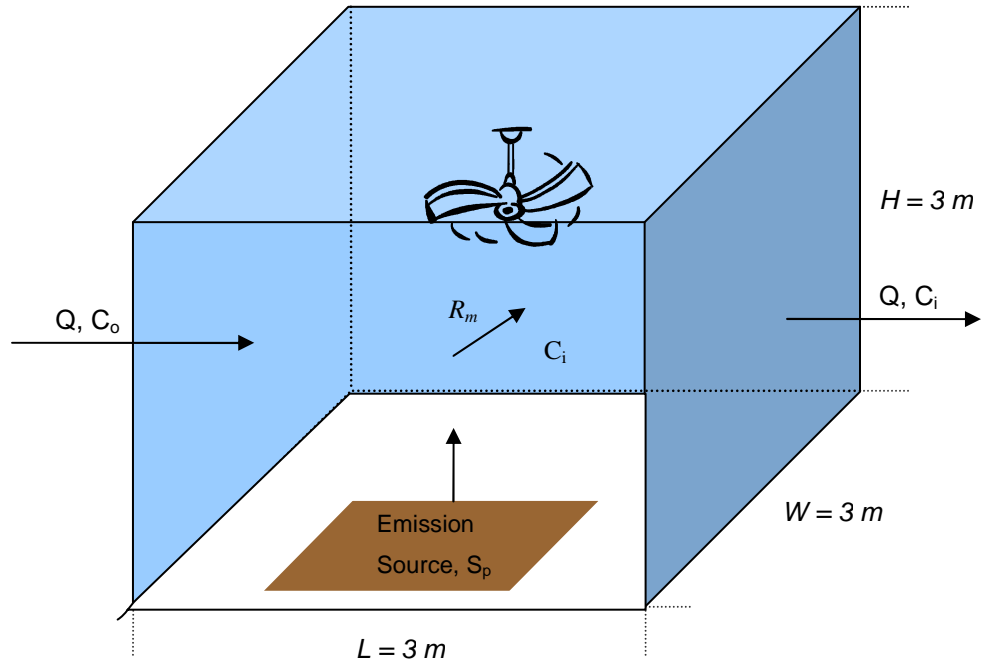
where  $\rho_g$  and  $\mu$  are the density and viscosity of the contaminated gas,  $V_o$  is the superficial velocity parallel to the catalytic surface and  $L$  is the characteristic length of the wall.

With the catalytic films immobilized on the walls and ceiling of an office room with dimensions of 3 m x 3m x 3 m, the characteristic length,  $L$  is set to be 300 cm. The mass transfer coefficients for the range of superficial velocities from 5 to 25 cm/s were obtained using equation (3-31). Results are shown on Table (3-8).

#### **3.4.2.2 Indoor air quality modeling (Mass transfer limited case)**

As previously mentioned, in a mass transfer limited model, the chemical reaction is fast relative to diffusion. Thus, mass transfer controls the overall rate of removal of the contaminant. The focus of the study is diffusion of the pollutant in a hypothetical film located between the bulk fluid and the surface of the catalytic solid film. At the surface of the catalyst or wall ( $x = \delta$ ), a finite pollutant concentration is required. It is assumed that when the pollutant touches the catalytic surface, it disappears and is converted to products instantaneously, thus  $C_w = 0$ .

The system in consideration (Figure 3-5) in this study is similar with the one used in the IAQ modeling studies of a room equipped with a packed bed system in section 3.3.2. The only difference is that the in-room device is composed of catalytically-active walls and ceiling (instead of a packed bed) and that the rate of pollutant removal in the film is assumed to be mass transfer-controlled. Thin films of 2% C- and V-doped TiO<sub>2</sub> described in Yang et al. (2007) and Yang (2008) were assumed to be incorporated into the four walls and ceiling of the room. Any molecules of the contaminant gas (acetaldehyde) that are present in the room are expected to be oxidized when they come into contact with the reactive surfaces. The study was conducted at normal ambient conditions ( $T = 20$  °C,  $P = 1$  atm). A well mixed office room described in Figure 3-5 was considered in this study. The fan located at the center of the ceiling circulates the air inside the room.



**Figure 3-5 Well-mixed room with catalytically-active walls and ceiling.**

(not drawn to scale)

A mass balance inside the room for this system was made (equation 3-34). The rate of removal ( $R_m$ ) is due to the rate of mass transfer of the pollutant defined by equations (3-29) and (3-34) in which  $C_w$  is assumed equal to zero.

$$\frac{VdC_i}{dt} = QC_0 + S_p p - QC_i - k'_m A_m (C_i - C_w) \quad (3-34)$$

$$R_m = k'_m A_m (C_i - C_w) \quad (3-35)$$

At steady state conditions,  $V \frac{dC_i}{dt} = 0$  and with  $C_w = 0$ , equation (3-34) becomes

$$C_i = \frac{QC_o + S_p P}{Q + k'_m A_m} \quad (3-36)$$

Given certain conditions, equation (3-36) can be used to estimate the indoor air concentration,  $C_i$  (in  $\mu\text{g}/\text{m}^3$ ). The area of mass transfer,  $A_m$  includes the four walls and ceiling of the room, thus, with a value of  $4.5 \times 10^5 \text{ cm}^2$ . The emission rate,  $S_p$ , inside the room is steady at  $35 \mu\text{g}/\text{h}$ -person (ASHRAE, 2007a). The influence of the following factors on the indoor air concentration ( $C_i$ ) for the range of superficial velocities of 5 to 25 cm/s was studied: the mass transfer-limited rate of pollutant removal ( $R_m$ ), ventilation rate ( $Q$ ), magnitude of emission source ( $p$ ), and outdoor air concentration ( $C_o$ ). The variation of the levels of acetaldehyde inside the zone was studied for cases when there was no in-room device and with the device (thin film) installed inside the room. The contrasting effect on  $C_i$  of having a clean ventilation air versus outdoor air with a typical acetaldehyde concentration ( $C_o$ ) of  $20.12 \mu\text{g}/\text{m}^3$  (ASHRAE, 2005; ASHRAE, 2007a) was also explored. Levels of acetaldehyde indoors were determined for conditions where there is no ventilation and with the ASHRAE standard ventilation rate ( $V_R$ ) of  $0.48 \text{ m}^3/\text{min}$  per person (ASHRAE, 2007b). The ventilation rate guidelines provided by ASHRAE (2007b) and the emission rate ( $S_p$ ) are both dependent on the number of people ( $p$ ) inside the room.

### ***3.4.3 Results and discussion***

#### ***3.4.3.1 Mass transfer coefficient***

The corresponding values of the mass transfer coefficient ( $k'_m$ ) for air velocities of 5, 10, 15, 20 and 25 cm/s were calculated using equations (3-31), (3-32) and (3-33). Reynolds number ( $N_{Re,L}$ ) was estimated based on a length of 3 m of length using equation (3-32). The  $k'_m$  values (in cm/s) and Reynolds number for each flow velocity are tabulated in Table (3-8). As expected, both the Reynolds number and mass transfer coefficient increased as the air velocity to the wall

increased. This is due to the favorable effect of the superficial velocity ( $V_o$ ) on the inertial and convective forces.

**Table 3-8 Calculated mass transfer coefficients as a function of superficial velocity.**

$V_o$ (cm/s)	$N_{Re,L}$	$k'_m$ (cm/s)
5	9845	0.028
10	19691	0.039
15	29536	0.048
20	39381	0.056
25	49227	0.062

### 3.4.3.2 Indoor air pollutant concentration

The mass transfer coefficients above were used to estimate the rate of removal term in equation (3-35). The concentration of the contaminant ( $C_i$ ) in the room for various operating conditions was evaluated by utilizing the steady state mass balance in equation (3-36), wherein the rate of contaminant removal (described by equation 3-35) is mass transfer-controlled. Results are summarized in Tables 3-9 to 3-14. The indoor air concentration for a room with no in room device, one person as a source of emission and a standard ventilation rate ( $V_R$ ) of 0.48 m<sup>3</sup>/min-person (ASHRAE, 2007b) is shown in Table 3-9. When the outside air is clean ( $C_o = 0$ ), the concentration of the acetaldehyde ( $C_i$ ) in the room is steady at 1.21 µg/m<sup>3</sup> (0.66 ppb) as air velocity along the wall increases from 5 to 25 cm/s. It is also constant at 21.33 µg/m<sup>3</sup> (12 ppb) when the air coming into the room is assumed to have the typical outdoor acetaldehyde concentration of 20.12 µg/m<sup>3</sup> (11 ppb) (ASHRAE, 2005; ASHRAE, 2007a). The typical emission rate ( $S_p$ ) of 35 µg/h-person (ASHRAE, 2007a) is used throughout the study. This parameter and the suggested ventilation rate ( $V_R$ ) for an office room in ASHRAE (2007b) are both dependent on the number of people inside the room. When  $C_o$  is zero, the occupants are the only contributors to the pollution load inside the room in contrast to a case in which the ventilation air is contaminated. In both cases at steady state condition and when there is no in room air cleaning device, the velocity does not have an effect on  $C_i$ . This is because the

contaminated air in the room is only being flushed out of the room at a rate that is equal to the ventilation rate. The effect of one person in the room on the quality of air inside the room is minimal compared to the impact of contaminated ventilation.

**Table 3-9 Indoor air concentration without in room device, air ventilation rate = 0.48 m<sup>3</sup>/min-person, and 1 person.**

$V_o$ (cm/s)	Indoor Air Concentration, $C_i$ ( $\mu\text{g}/\text{m}^3$ )	
	$C_o = 0$	$C_o = 20.12 \mu\text{g}/\text{m}^3$
5	1.21	21.33
10	1.21	21.33
15	1.21	21.33
20	1.21	21.33
25	1.21	21.33

Table 3-10 describes the effect on the indoor air concentration ( $C_i$ ) of having catalytic walls and ceiling as an air cleaning device in a non-ventilated room with one person as the only source of emission. The in room device alone is effective in cleaning the air as can be seen by lower values of  $C_i$  in Table 3-10 compared to those in Table 3-9. Since there is no ventilation, the outdoor air concentration ( $C_o$ ) does not contribute to the levels of contaminant for this particular case. In Table 3-10,  $C_i$  decreases with increasing flow of the air to the wall. The influence of the flow of the air is on the rate of mass transfer as described in equations (3-31) to (3-28).

A significant reduction in  $C_i$  values is achieved when an air cleaning device is used in a non-ventilated room as compared to a room that is ventilated with clean air but without a device as described in Table 3-9. The  $C_i$  values in Table 3-10 can also be compared to a system without an in room device but ventilated with outside air containing  $20.12 \mu\text{g}/\text{m}^3$  (11 ppb) of the pollutant. The removal of the contaminated outside air ventilation coupled with the use of an air cleaning device lowered the indoor air concentration values significantly (Table 3-10).

**Table 3-10 Indoor air concentration with in room device, 1 person and ventilation rate = 0.**

$V_o$ (cm/s)	Indoor Air Concentration, $C_i$ ( $\mu\text{g}/\text{m}^3$ )
5	0.78
10	0.55
15	0.45
20	0.39
25	0.35

The combined effect of outside air ventilation and having catalytically-active walls and ceiling in a room with one person was evaluated using the mass transfer-controlled mass balance at steady state conditions (equation 3-36). The predicted values of  $C_i$  for velocities of 5 cm/s to 25 cm/s are shown in Table 3-11. The systems in Table 3-9 and 3-11 are similar except the addition of the air cleaning device in the latter. The  $C_i$  values of  $0.47 \mu\text{g}/\text{m}^3$  to  $0.27 \mu\text{g}/\text{m}^3$  (for  $C_o = 0$ ) and  $8.34 \mu\text{g}/\text{m}^3$  to  $4.76 \mu\text{g}/\text{m}^3$  (for  $C_o = 20.12 \mu\text{g}/\text{m}^3$ ) are much smaller than those for the system described in Table 3-9. These observations reveal that the addition of an air cleaning device reduces the concentration indoors regardless of how contaminated the ventilation air is. The use of outside ventilation air in Table 3-11 is the only dissimilarity with the system in Table 3-10. In the case where the outdoor air contains  $20.12 \mu\text{g}/\text{m}^3$ , the level of contaminants in the room as shown in Table 3-11 is much greater than the values in Table 3-10. This suggests that use of clean ventilation air is also important in lowering the levels of the pollutant indoors.

**Table 3-11 Indoor air concentration with in room device, ventilation rate 0.48 m<sup>3</sup>/min-person, and 1 person.**

$V_o$ (cm/s)	Indoor Air Concentration, $C_i$ ( $\mu\text{g}/\text{m}^3$ )	
	$C_o = 0$	$C_o = 20.12 \mu\text{g}/\text{m}^3$
5	0.47	8.34
10	0.38	6.66
15	0.33	5.76
20	0.29	5.18
25	0.27	4.76

Different organizations and agencies dealing with occupational health and environment have different standards and guidelines for acetaldehyde (Spengler et al., 2001). For instance, OSHA prescribes the lowest permissible exposure limit (PEL) of 100 ppm for TWA and 150 ppm for STEL/C. ACGIH's recommended exposure limit (REL) is 25 ppm (probably the lowest value). NIOSH's recommended exposure limit is the lowest possible level. In Table 3-11, the maximum indoor concentration obtained using an outdoor concentration of 20.12  $\mu\text{g}/\text{m}^3$  is 8.34  $\mu\text{g}/\text{m}^3$  which is equivalent to 4.56 ppb, a value much below the ACGIH's limit. Even with no in-room device, the indoor pollutant concentration is also very small and much less than any numerical health-based standards, the use of an air cleaning device together with ventilation air will undoubtedly help in maintaining the air quality in indoor environments especially those that involves odorous compounds.

In Table 3-12, 3 people are assumed to be contributing to the acetaldehyde load inside the room. With no in room device, the ventilation air is the only means of diluting or expelling the pollutant out of the room. However, the ventilation air can be the source of the pollutant indoors as in the case where it contains 20.12  $\mu\text{g}/\text{m}^3$  of acetaldehyde as shown on Table 3-12.



**Table 3-12 Indoor air concentration without an in room device, 3 people and ventilation rate = 0.48 m<sup>3</sup>/min-person.**

$V_o$ (cm/s)	Indoor Air Concentration, $C_i$ ( $\mu\text{g}/\text{m}^3$ )	
	$C_o = 0$	$C_o = 20.12 \mu\text{g}/\text{m}^3$
5	1.21	21.33
10	1.21	21.33
15	1.21	21.33
20	1.21	21.33
25	1.21	21.33

The results above are exactly the same with the values presented in Table 3-9. The explanation for this exact similarity is that the emission rate ( $S_p$ ) and the outside air rate from ASHRAE are both dependent on the magnitude of the source, which in this case the number of people ( $p$ ) inside the room. Without the rate of removal due to mass transfer term, equation (3-36) reduces to  $C_i = C_o + \frac{S_p}{V_R}$ , an expression that is independent of the number of people in the room.

With an increased number of emission sources in the room from one person to 3 people, it is expected that the results in Table 3-13 will be a factor of the results in Table 3-10. This is because equation (3-36) reduces to  $C_i = \frac{S_p P}{k_m A_m}$ . The  $C_i$  values range from 1.04  $\mu\text{g}/\text{m}^3$  to 2.33  $\mu\text{g}/\text{m}^3$  and vary inversely with velocity. The velocity influences the mass transfer rate.

**Table 3-13 Indoor air concentration with in room device, 3 people and ventilation rate = 0.**

$V_o$ (cm/s)	Indoor Air Concentration, $C_i$ ( $\mu\text{g}/\text{m}^3$ )
5	2.33
10	1.65
15	1.35
20	1.17
25	1.04

Table 3-14 shows the indoor air concentrations ( $C_i$ ) which are derived through the use of equation (3-36) for a room with 3 occupants, equipped with catalytically active walls and ceiling and is being ventilated at a rate of  $0.48 \text{ m}^3/\text{min}$ -person. The values of indoor air concentration increase from  $0.56$  to  $0.80 \mu\text{g}/\text{m}^3$  for  $C_o = 0$  and  $9.87 \mu\text{g}/\text{m}^3$  to  $14.04 \mu\text{g}/\text{m}^3$  for  $C_o = 20.12 \mu\text{g}/\text{m}^3$  (11 ppb). These numbers vary in inverse relation with the air velocity. Higher velocities tend to reduce the levels of the pollutant in the room. It has a direct relation with the mass transfer coefficient values portrayed by equations (3-31 and 3-32). Increased velocity in the room improves the removal rate due to improved mass transfer of the pollutant to the catalytically active surfaces and makes the indoor air cleaning more effective.

**Table 3-14 Indoor air concentration with an in room device, 3 people and ventilation rate =  $0.48 \text{ m}^3/\text{min}$ -person, 3 people.**

$V_o$ (cm/s)	Indoor Air Concentration, $C_i$ ( $\mu\text{g}/\text{m}^3$ )	
	$C_o = 0$	$C_o = 20.12 \mu\text{g}/\text{m}^3$
5	0.80	14.04
10	0.70	12.30
15	0.64	11.22
20	0.59	10.46
25	0.56	9.87

To evaluate the effect of the addition of the in room device, the indoor air concentration results from Table 3-12 and Table 3-14 were compared. Table 3-14 showed significant reduction on the concentrations in Table 3-12 both for  $C_o = 0$  and  $C_o = 20.12 \mu\text{g}/\text{m}^3$  because of the active walls. To assess the effect of ventilation in the system, results in Table 3-13 and 3-14 were compared. For  $C_o = 0$ ,  $C_i$  values in Table 3-14 are smaller than those in Table 3-13 because of ventilation. However, with  $C_o = 20.12 \mu\text{g}/\text{m}^3$ , the values in Table 3-14 are larger than those in Table 3-13. The values of  $C_i$  in Table 3-10 and 3-11 where there is only one person are lower. For 3 people in the room the ventilation rate is increased in accordance with ASHRAE (2007b) to compensate for the number of emission sources inside the room. A comparison of Tables 3-11 and 3-14 shows that the increased ventilation contributes to the increased values of  $C_i$  in Table 3-14 when  $C_o = 20.12 \mu\text{g}/\text{m}^3$ . Comparable studies done between Table 3-10 and 3-11; and between Tables 3-13 and 3-14 for the condition with  $C_o = 20.12 \mu\text{g}/\text{m}^3$ , show that high pollutant concentration of outdoor ventilation air greatly affects the concentration of the indoor air, and so it is always favorable to use a relatively clean ventilation air. The maximum value of  $C_i$  in Table 3-14 is  $14.04 \mu\text{g}/\text{m}^3$  (7.68 ppb) which was obtained when the acetaldehyde outdoor level is  $20.12 \mu\text{g}/\text{m}^3$  is much smaller than the ACGIH occupational limit of 25 ppm for acetaldehyde. The presence of an indoor air cleaning device is attractive to maintain IAQ especially when the quality of outdoor air ventilation is always compromised and uncertain.

The mass of catalyst associated with the thin film depends on the thickness of the layer of catalyst in the film. For a  $10 \mu\text{m}$  film thickness, the volume of the film for a  $3 \text{ m} \times 3 \text{ m} \times 3 \text{ m}$  room would be  $450 \text{ cm}^3$ . For a bulk density of the catalyst ( $\rho_{\text{bulk}}$ ) of  $0.6 \text{ g}/\text{cm}^3$ , the mass of catalyst is 270 g. The mass of the catalyst is similar in magnitude to that used in the packed bed design with 1 cm bed depth.

### 3.5 Summary of parameters used in the modeling and simulations studies

Table 3-15 lists the values of the parameters that were selected for the simulations for a packed bed system and catalytically active walls in chapter 3.

**Table 3-15 Values of parameters used in the modeling and simulation studies.**

Parameter	Value and Units
<b><u>Assumptions and general considerations</u></b>	
Room Dimensions ( $L \times W \times H$ )	3 m x 3m x 3m
Temperature, $T$	20 °C
Pressure, $P$	1 atm
Feed gas to the packed bed or catalytic walls and ceiling	
Air contaminant	Acetaldehyde (very dilute concentration)
Equivalent radius of the acetaldehyde molecule, $r_{cont}$	0.28 nm
Density, $\rho_g$	$1.206 \times 10^{-3} \text{ g/cm}^3$ (air)
Diffusion coefficient of acetaldehyde in air, $D$	$0.1202 \text{ cm}^2/\text{s}$
Viscosity, $\mu$	$1.81 \times 10^{-4} \text{ g/cm-s}$ (air) (Bird et al., 2002)
Range of superficial velocity, $V_o$	5 to 25 cm/s (13 to 25 cm/s in ASHRAE, 2007a; ASHRAE, 2004)
Emission rate, $S_p$ in the room	35 $\mu\text{g/h-person}$
Ventilation rate, $V_R$	0.48 $\text{m}^3/\text{min-person}$ (ASHRAE, 2007b) and equivalent to $Q/p$
<b><u>Packed bed</u></b>	
Porosity, $\varepsilon$	0.4
Depth, $z$	1 cm

**Table 3.15. Cont...**

Parameter	Value and Units
Pellets of 2% C-and V-doped TiO <sub>2</sub>	
Rate, $v_o$	1.4 x 10 <sup>-8</sup> gmol/cm <sup>3</sup> -s = 2.283 x 10 <sup>-8</sup> gmol/gcat-s
Shapes of pellet	
a) Spherical	
Diameter, $D_p$	0.2 cm
Shape factor, $\Phi_s$	1.0
b) Cylindrical	
Diameter, $D_p$	0.2 cm
Length, $L_p$	0.4 cm
Shape factor, $\Phi_s$	0.832
Range of pore radius ( $r_{pore}$ )	2 – 10 nm
Pellet porosity parameter, $\epsilon_p$	0.5
Bulk density of the catalyst, $\rho_{bulk}$	0.6 g/cm <sup>3</sup>
Tortuosity factor, $\tau$	2.0
<b>IAQ modeling (<i>Reaction with internal mass transfer limited case</i>)</b>	
Outdoor acetaldehyde concentration, $C_o$	20.12 µg/m <sup>3</sup>
Number of people in the room, $p$	One (1)
<b>IAQ modeling (<i>External mass transfer limited rate</i>)</b>	
Pollutant concentration in the gas stream coming out of the packed bed, $C_{out}$	$C_{out} = C_i e^{-k'_m A_m t_R}$ (see equation 3-20)
Area of mass transfer, $A_m$	18 cm <sup>2</sup> /cm <sup>3</sup> (see equation 3-21)
<hr/>	
<b><u>Catalytically active walls and ceiling</u></b>	
<b>IAQ modeling (<i>External mass transfer limited rate</i>)</b>	
Number of people in the room, $p$	One (1) or three (3)
Area of mass transfer, $A_m$	4.5 x 10 <sup>5</sup> cm <sup>2</sup> (four walls and ceiling)

## CHAPTER 4 - Conclusions and Recommendations

### 4.1 Summary and conclusions

Indoor air quality models help in understanding the effect of different air cleaning processes on the air quality of a simulated indoor environment. They are useful tools in understanding how the factors that influence air quality relate to one another and in predicting concentrations for places and conditions that are potential design options.

Two processes for cleaning indoor air utilizing 2% C-and V-doped TiO<sub>2</sub>, a newly developed photocatalyst described in Yang et al. (2007), have been evaluated with the use of modeling and simulation techniques. They are the packed bed design and thin films on the walls and ceiling of a room. Both are studied in a typical size room under typical indoor air environmental conditions, with acetaldehyde as the test pollutant and where the emission rates,  $S_p$  are small.

The packed bed reactor is assumed to be made up of pellets of the photocatalytic material. The assumed parameters and the given range of superficial velocities in accordance with ASHRAE Standards of 25 fpm (13 cm/s) to 45 fpm (25 cm/s) gave low values of pressure drop in the bed (Tables 3-1 and 3-2). Values of effectiveness factor and observable modulus showed significant internal diffusion limitations on the photocatalyst. External mass transfer to the surface of the pellet limits the rate of oxidation in the packed bed reactor.

Low values of  $C_i$  were obtained from indoor air quality modeling studies at steady state conditions in a packed bed where the rate of acetaldehyde removal is mass transfer limited. The weight of the catalyst to clean the air that passes through the packed bed ranges from 600 to 6000 g for air flow rates that are in accord with the ASHRAE standard air movement rates for a finite length of the bed of 1 cm.

For thin films on the walls and ceiling, an external mass transfer controlled model was used in a small room at steady state in order to evaluate the influence of combined effects of the magnitude of the source, ventilation rate, and outdoor contaminant concentration. The model resulted in indoor air concentrations of acetaldehyde that are significantly smaller than those without the film. It can be deduced from this study that if sufficient amount of nanoparticles are

put on the wall to make the process mass transfer controlled, there is no incentive to further increase the amount of the catalyst.

The results that are presented are for transport limited processes. It is assumed that the reaction rate is sufficiently fast to have transport limited conditions. This assumption is based on the kinetic data of Yang et al. (2007) and Yang (2008) and a zero order kinetic model.

Both systems (packed bed and catalytically active walls and ceiling) reduce indoor contaminant concentrations significantly and have the potential to be commercialized for use in appropriate applications based on the parameters used in the modeling studies.

## **4.2 Suggestions for further studies**

The use of 2% C- and V-doped TiO<sub>2</sub> as a photocatalyst in PCO systems is relatively new. It has potential for indoor air applications due to its comparable activity under both visible light and dark conditions. However, the first experimental studies (Yang, 2008; Yang et al., 2007) were done on a laboratory scale which lacks the true representation of a typical indoor environment. The modeling and simulation studies in this research are an attempt to study the potential of the photocatalytic material to be incorporated on systems that have the potential for commercialization such as packed bed and thin film designs. Considering that the above ideas are still under development, there is still a lot of room for research. The following are recommended for future studies.

- Measure actual performance of the proposed air cleaning devices or systems. Predicted values of contaminant concentrations should be evaluated and compared with actual measured data.
- Extend both modeling and experimental studies to other VOCs or pollutants of concern (i.e. biological airborne particulate matter), emission rate and indoor environments such as buildings; nursing homes.
- Conduct PCO studies on systems that involve combination and mixtures of contaminants that are more representative of typical indoor air environments.
- Study experimentally the formation of intermediates or undesired by-products during PCO process. The common indoor air pollutant concentrations are within the ppb to sub-ppm range. The concentrations of any undesired products may be below the detection

limits of most analytical methods. These issues and other aspects that limit modeling studies from addressing them should be resolved by suitable experimental designs.

- Establish optimum operating parameters to achieve better designs and performance. These include mean residence time needed for the photocatalytic process to oxidize the intermediates or by-products into final products.
- Conduct economic studies to determine the cost of these devices. Like any other PCO air cleaning devices, the two systems explored in this study have the potential to lower energy costs significantly through effective and efficient decomposition of air pollutants, thereby lowering the need for more ventilation air.
- Develop the best combination of in room devices and ventilation for various applications.
- Determine operational life of the catalyst before regeneration.



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