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A REACTIVE INDOOR AIR PURIFICATION DEVICE AND ITS ESCHERICHIA COLI INACTIVATION EFFECT

(Spine title: An Indoor Air Purification Device and its E. Coli Inactivation)
(Thesis format: Monograph)

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Engineering Science

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E. coli bioaerosol was disinfected using an indoor air purification device that is composed of an annular photocatalytic reactor with a baffle system inside and a gas buffer tank. Activated carbon supported photocatalyst $10\%TiO_2$-$10\%SiO_2/AC$ prepared by dip coating method, using 10 wt% colloidal silica and 10 %(w/v) TiO_2, has the highest photocatalytic oxidation activity and was used for the E. coli bioaerosol disinfection tests in terms of air flow rate, UV intensity, TiO_2 loading, and photocatalyst preparation methods. The results showed that it took longer time to completely disinfect E. coli if the flow rate is higher. Higher UV intensity significantly reduced the E. coli disinfection time. E. coli disinfection rate increased when the TiO_2 loading going up from 1 to 10 %(w/v). E. coli disinfection efficiency can also be improved by adding colloidal silica into the impregnation suspension when the activated carbon supported photocatalysts were prepared.

Keywords: Indoor air purification, E. coli, Photocatalytic oxidation, Photocatalysis, Titanium dioxide, TiO_2, Photocatalytic reactor, Annular reactor, Photocatalyst, Activated carbon

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List of Abbreviations, Symbols, and Nomenclature

AOTs	Advanced Oxidation Technologies
BANG	Bioaerosol Nebulizing Generator
CB	Conduction band
CFU	Colony Forming Unit
E. Coli K-12	Escherichia coli K-12
HEPA Filter	High Efficiency Particle Air Filter
HVAC	Heating, Ventilating, and Air Conditioning
LPM	Liter per Minute
PCO	Photocatalytic Oxidation
VB	Valance Band
UVGI	Ultraviolet Germicidal Irradiation
VOCs	Volatile Organic Compounds
UV-A	Ultraviolet A

Chapter 1

Introduction

1.1 Indoor Air Pollution and the Related Pollutants

Clean air is essential for good health, and this is especially true when it comes to indoor air. Studies have shown that people spend up to 90% of their time indoor. Indoor air contains many contaminants and it is becoming an increasingly more concerning health hazard than outdoor air. The physical symptoms commonly attributed to indoor air quality problems include headache, fatigue, shortness of breath, sinus congestion, cough, sneezing, dizziness, nausea, and irritation. Indoor air pollution is ranked as one of the top five environmental risks. It has become an important health issue for both workplace and home. The indoor air pollution, caused by outdoor vehicular exhaust (Li et al., 2001), building materials (Hines et al., 1993) and the use of HVAC and cooking utensils (Lee et al., 2001; Lee et al., 2002), is usually inevitable for quality personal life. Concerns over the quality of indoor air have increased because nowadays buildings are more tightly sealed for energy conservation. A lack of ventilation in air-tight buildings leads to the buildup of contaminants and it is a key factor that impacts the quality of indoor air. The growing use of synthetic building materials, modern office equipment (photocopiers, laser printers, and computers), furnishings, cleaning products, numerous personal care products as well as outdoor air pollution can also contribute to a considerable amount of indoor air contaminants. It has also been found that public places such as schools and hospitals tend to have poor indoor air quality mainly because of high occupant density. Thus, control of indoor air quality is particularly important.

Indoor air pollution is the presence of one or more contaminants indoors that carry a certain degree of human health risk. Indoor air pollutants mainly include particulates, chemical pollutants, and microbial pollutants. Particulates consist of dust, pollen, and animal dander etc. Chemical pollutants are mainly gases such as volatile organic compounds (VOCs) and odors that come from combustion appliances, tobacco smoke, household and personal care products, various building materials and outdoor air. Microbial pollutants usually appear as bioaerosols which are airborne particles of living microorganisms such as bacteria, viruses and fungi. Bioaerosols are ubiquitous, highly variable, complex, natural or man-made in origin. The indoor air pollution caused by airborne microorganisms has received more attention in recent years due to concerns with its associated health effects, including infectious diseases, acute toxic effects, allergies and cancer (Douwes, J. et al., 2003; O'Riordan, T.G. et al. 2004; Stetzenbach, L. D. et al. 2004). Indoor air containing significant number of microorganisms can act as a medium for disease transmission or dispersal. It has been reported that bioaerosols contribute to about 5% to 34% of indoor air pollution (http://www.airqualitydirect.com/bio-aerosols.html; http://www.pollutionissues.com/Ho-Li/Indoor-Air-Pollution.html). The particle size of bioaerosol is generally in the range of 0.3 to 100 μm in diameter. Although larger particles of bioaerosol can deposit on surfaces, the much tiny particles ranging from 1.0 to 5.0 μm usually exist stably as part of the indoor air and may cause serious problem to human health (Cox, C. S. et al., 1995; Mohr, A. J., 2002). Incidences of nosocomial and occupational diseases due to exposure to low quality indoor air contaminated by bioaerosols have been increasingly reported, indicating the need for a thorough knowledge and solution in this respect (Ayliffe, G. A., 1991; Beggs. C. B., 2003; Eickhoff, T. C., 1994; Schaal, K. P., 1991).

1.2 Methods for Indoor Air Purification

Methods used for indoor air purification are generally grouped in three categories, namely source control, ventilation and air cleaning. Source control is often ungovernable and not all indoor air pollution sources can be identified or practically eliminated or reduced. Ventilation or purging with outside air just dilutes the concentrations of indoor air contaminants in the air stream instead of completely eliminates or destroys them. Using ventilation to dilute contaminants might even transport more pollutants from outdoor environment (Jones, 1999) because the outdoor air itself may contain undesirable levels of contaminants. In addition, using ventilation to dilute the indoor pollutants usually causes significant costs for heating or cooling. Thus, air cleaning remains to be the most feasible option to improve indoor air quality.

Technologies used for indoor air cleaning or purification include filtration, adsorption, ultraviolet germicidal irradiation (UVGI), ozonation, electrostatic precipitation, negative ion generation, and photocatalytic oxidation. Some of these technologies have already been used in commercial indoor air cleaners. However, none of these methods can completely remove all types of pollutants in the indoor air and each method has its own limitations. Filtration is only effective to remove airborne particles and can not eliminate gaseous chemicals such as VOCs and odors. Although VOCs and odors can be eliminated by adsorption, this process only transfers the pollutants from air to the solid adsorbent. The pollutants are only concentrated in the adsorbent and they are still there without decomposition. UVGI can disinfect bioaerosols in indoor air and it has no effect on removal of particles and gaseous pollutants. If UV-C is used as light source, ozone will be generated at trace level, which is another source of indoor air pollution. Ozonation is an extremely reactive process to oxide airborne pollutants, but it has been proven that even a trace amount of ozone is hazardous to humans. Electrostatic precipitation and negative ion processes also produce trace ozone. Due to the negative effect of ozone to human health, these ozone-producing processes have limited use in indoor air purification.

Among these methods, photocatalytic oxidation (PCO) is believed to be effective on indoor air purification. Previous studies have shown that PCO is a promising and effective technology for pollution control (Fujishima et al., 2000; Hoffmann et al., 1995; Obuchi et al., 1999; Peral et al., 1997; Yu et al., 2002), and it can be used as an effective indoor air purification technology (Tompkins et al., 2005; Zhao and Yang, 2003). Unlike traditional pollution control method such as adsorption which merely transfers pollutant from gaseous phase to solid phase, PCO can completely oxidize pollutants present in indoor air to CO_2, H_2O and other small inorganic molecules. This process is commonly called mineralization.

1.3 Photocatalyst and Photocatalytic Oxidation Process

Titanium dioxide or titania (TiO_2) has been commonly accepted as the most effective photocatalyst and it is widely used in photocatalytic oxidation processes. The TiO_2-based photocatalysts need to be activated by the ultraviolet radiant source to produce reactive radicals in the system. When irradiated by light with the wavelength less than 380 nm, electrons can be promoted from the valence band to the conduction band of TiO_2, leading to the formation of electron-hole pairs. These photo-generated holes and electrons can transfer to the surface of TiO_2 and react with water and oxygen adsorbed on the surface, forming highly oxidative hydroxyl radicals (•OH) and other reactive oxygen species, such as $O_2\bullet^-$, $HO_2\bullet$ and H_2O_2. It is these radicals that can completely oxidize organic pollutants or disinfect microorganisms present in indoor air.

A photocatalyst with high activity and long life time is the most important part of the photocatalytic oxidation process in organic degradation or microbial inactivation. TiO_2 can be used in either slurry or immobilization state. Although many previous studies for the photocatalytic degradation of organic pollutants in water employed TiO_2 in the slurry state as the photocatalyst, immobilized photocatalysts with TiO_2 loaded on appropriate support have attracted more attention for the application in indoor air purification.

For an immobilized photocatalyst, the photocatalytically active component, which is TiO_2 in most cases, is fixed on the support surface using an immobilization method. Materials which can be employed as supports for TiO_2 immobilization include glass (Kim et al., 1996; Sirisuk, 2003; Trivedik, 1994; Zorn et al., 2000), quartz (Mune et al., 1996; Sauer and Ollis, 1996; Takeda et al., 1995), ceramics, metals, polymers (Fabiyi et al., 2000; Takeuchi, 1996) as well as porous materials such as activated carbon (Takeda et al., 1995; Ishihara and Furutsuka, 1996), zeolite and alumina (Takeda et al., 1995). Using porous materials as the support of photocatalyst can increase the surface area of the photocatalyst and thus improve the photocatalytic oxidation activity because the surface area of TiO_2 is relatively lower. (The surface area of the commercial product Degussa P25 TiO_2 is 35 to 65 m^2/g.) The porosity of the support material can also improve the adsorption capability of the photoacatalyst. This property is especially useful when photocatalytic oxidation process is used for indoor air purification.

Sol-gel and dip-coating are two common methods for photocatalyst immobilization, or preparation of a TiO_2 film on a support surface. For the sol-gel method, the first step is to make the TiO_2 sol by hydrolysis of its organic precursor — titanium alkoxide. Stable solid film is formed (gel process) on the surface of support by immersion or dip-coating followed by drying and calcination (Keshmiri et al., 2004). The sol can sometimes be mixed with binding materials such as silica sol. Or the TiO_2 powder may be added into the sol to make a thicker mixture. Methods with the modified sol generated by the above steps are called "modified sol-gel method" in this thesis. Preparation of photocatalysts by dip-coating methods is relatively easier compared to the sol-gel method. This method involves the immersion of support material in TiO_2 slurry, a mixture of TiO_2 powder with water. A TiO_2 coating is subsequently obtained by drying and calcination. To improve the coating properties, dispersants or binders can be added into the TiO_2 slurry.

1.4 Objective of the Study

The objective of the research work in this thesis is to develop a reactive indoor air cleaning unit and apply it for the disinfection of bioaerosols in indoor air.

Design of a high-performance photocatalytic reactor is the most important issue for the indoor air purification. A continuous-flow annular reactor is to be employed with higher photocatalytic activity. A baffle system is to be used inside the reactor to improve the mass transfer of the air pollutants on the surface of photocatalyst. The photocatalyst is conveniently located around the baffles for the better elimination of indoor air pollutants.

A highly active photocatalyst is to be prepared and applied in the photocatalytic reactor to remove indoor air pollutants simultaneously. Various methods will be used to prepare the photocatalysts with different support materials. The photocatalyst with the highest photocatalytic activity will be loaded in the photocatalytic reactor to evaluate its indoor air purification effect.

The performance of the indoor air cleaning unit will be characterized on its bioaerosol disinfection capability with respect to air flow rate, UV light intensity, TiO_2 loading and photocatalyst preparation methods, using E. coli as the model bacterium.

Coupled with various types of airborne particulate filtration technologies that are generally employed in commercial indoor air purifiers, this novel air cleaning module would lead to a complete solution to indoor air contamination caused by microbiological pollutants, VOCs and odors, as well as airborne particles. The indoor air cleaning unit could be used in central heating and air-conditioning systems or as a portable unit.

Chapter 2

Literature Review

Indoor air pollution has negative effect on human health. Airborne particulates, chemical pollutants, and microbial pollutants are three main contamination types of indoor air pollution. Particulates present in indoor air, such as dust, pollen, and animal dander, can be removed by filtration technologies which have been well employed in commercial air purifiers. Chemical pollutants in indoor air, most commonly being found as volatile organic compounds (VOCs) and odors, can be generated from combustion appliances, tobacco smoke, household and personal care products, various building materials or introduced from outdoor air. The methods that have been proven to be effective on the elimination of VOCs and odors are adsorption and photocatalytic oxidation. Microbial pollutants usually appear as bioaerosols which are airborne particles of living microorganisms such as bacteria, viruses and fungi. They are very common as contaminants in polluted indoor air. Ultraviolet germicidal irradiation and photocatalytic oxidation are both efficient in bioaerosol disinfection.

The literature review first introduces the traditional and new indoor air purification technologies and compares their advantages and disadvantages. Then some commercial indoor air purifiers and the technologies used in these products are summarized. Finally, photocatalysis, which is the main technology used in our research, is discussed in detail from its theory to applications.

2.1 Technologies for Indoor Air Purification

There are several different indoor air purification technologies available in the market today. Currently the technologies used in the commercial indoor air purifiers include: activated carbon adsorption, HEPA filtration, ultraviolet germicidal irradiation, electrostatic precipitation, negative ion generation, ozonation, and photocatalytic oxidation.

2.1.1 Activated Carbon Adsorption

Activated carbon adsorption is widely used as an indoor air purification technology. Activated carbon includes a wide range of amorphous carbon-based materials that exhibit a high degree of porosity and an extended surface area. The surface area of one gram of activated carbon can be thousands of square meters. As chemicals pass over the activated carbon, they are “adsorbed” though a process in which chemicals bond to the surface of the carbon. Once the chemicals are bonded to the carbon, they have been filtered and removed from the air.

The activated carbon used in air purifiers can be derived from many different sources such as peat moss, anthracite coal or coconut shells. Different carbon sources have slightly different chemical properties, making specific blends of activated carbon more effective for individual chemicals.

The activated carbon is most effective to remove volatile organic compounds (VOCs) and odors. The removal efficiency is related to the amount and type of gases present in air, the quantity, type and depth of the adsorbent material and the velocity of the air traveling through the media. Many indoor purifiers truthfully claim to use activated carbon, but they only use it in a very small amount and it quickly loses its effectiveness. Also, the residence time, the time that the air spends passing through the carbon, influences the effectiveness of the filtration process. The depth of the carbon filter and the speed of the motor are the main factors that affect the dwell time (deeper filters or slower motor speeds add dwell time).

Carbon filters must be replaced occasionally. For the average home it is about once every two years, though in highly chemical industrial environments it may be more frequent. Overall, activated carbon adsorption is the only mainstream and safe method for gas removal, and it is highly effective. An activated carbon filter does not remove particles though it is generally coupled with a HEPA or other particle filters in most air purifiers.

The advantages of activated carbon adsorption are:

- It is highly effective on capturing chemical fumes, gases, cigarette smoke, and odors.
- It does not release captured contaminates back into the indoor air.

Its disadvantages include:

- It does not effectively capture airborne particles and microorganisms.
- It needs to be changed periodically.

2.1.2 HEPA Filtration

Filtration using the HEPA filter (high efficiency particle air filter) is one of the most common particle filtration technologies used in the commercial air purification products. A hospital-grade HEPA filter, with a filtration rate of 99.97% for removing particles greater than or equal to 0.3 μm in diameter, can capture dust particles, dust mites, microorganisms, bacteria, mold and viruses.

To be fully effective, a HEPA filtration system must be leak-proof. The true effectiveness of the HEPA filter is dependent on how it is installed. This is the reason that some air purifiers claim different effectiveness ratings despite the fact that they are using the exact same filtration material. The biggest factor influencing the effectiveness of a HEPA filter is the seal around it. If air can bypass the filter by seeping around it, it is not going to get filtered properly and the 99.97% effectiveness rating can decrease considerably. Also, the way the HEPA filter is rolled and pleated, influences its effectiveness. HEPA filter should be rolled when it is warm to eliminate cracks (it is a glass-based material) and should be evenly pleated to make sure that the air does not go through a single part of the filter more than any others.

HEPA Filters work well in indoor air purification by trapping particulates. Overall, a HEPA filter is extremely effective on removing all airborne particles with diameter less than 0.3 μm. The downside of HEPA filtration is that the filters must be changed every 6 months to 5 years depending on the manufacturer. Another disadvantage is that HEPA air purifiers do not remove chemical pollutants such as VOCs and odors. Therefore, some HEPA air purifiers actually used the combination of HEPA and activated carbon filters to remove both particulates and gaseous chemicals present in the indoor air.

The review of any HEPA unit depends on the efficiency (how much air by-passes the filter), fan noise, filter life and price. Maintenance costs associated with HEPA filters are higher compared with those for other types of filters, but the use of in-line disposable prefilters can increase the life of the HEPA filter.

The advantages of HEPA filtration are:

- HEPA filters remove most airborne particles from the air such as dust, pollens, mold spores, dust mites, and other allergens.
- They also remove airborne bacteria.
- Solid particles captured are not released into the indoor air again.

It disadvantages include:

- HEPA filters do not remove gaseous pollutants or odors from the air.
- They do not capture ultra-fine particles, viruses or germs.
- Microorganisms captured in HEPA filter can breed and/or reproduce, resulting in increased microorganism populations.
- Replacement filters may be costly.
- The fan in HEPA units may be noisy

2.1.3 Ultraviolet Germicidal Irradiation (UVGI)

Ultraviolet (UV) light can be used as an anti-microbial technique. UV germicidal sterilization in air purifiers works by breaking down microorganisms and disrupting their DNA, making them unable to reproduce.

UVGI is a form of radiation encompassing wavelengths from 100 to 400 nm of the electromagnetic spectrum. UV light has been classified into 3 wavelength bands: UV-A (long wavelengths, range: 315 to 400 nm); UV-B (midrang
315 nm); and UV-C (short wavelengths, range: 100 to 2
available UV lights used for germicidal purposes are low-p
that emit radiant energy at the UV-C wavelength of 253.7 nm

Ultraviolet irradiation is a proven indoor air purification technology used for medical, food and residential sterilization. It is widely used in air purifiers to neutralize airborne tuberculosis, cold and flu viruses, smallpox, anthrax, and other airborne diseases and bacteria. UV used in indoor air purifiers has also proven effective against airborne mold mycotoxins, animal dander, cat saliva, dust mites, and pollen.

The ability for UVGI to kill pathogens such as bacteria, molds, and viruses depends on the intensity of the light, the duration of exposure of the pathogen to the UVGI, and the relative humidity of the environment. Different pathogens require different light intensities and durations of exposure. Importantly, the airflow rate through the in-room air cleaner will affect the duration of exposure of the pathogen to the UVGI light and therefore the effectiveness of the UVGI to disinfect. The effectiveness of UVGI to kill or inactivate microorganisms has been shown to decline when the relative humidity in a room exceeds 60%.

UV is not sufficient by itself because it removes few gasses and no particles. Therefore it needs to be combined with other air purification technologies. While UV technology is excellent at destroying viruses and bacteria it should not be employed without a particulate filter system ahead of the UV lamps. Without a particulate filter system too many microorganisms may be shaded from the light by particulates. Therefore, most air purifiers that employ UV start by filtering the air with HEPA and activated carbon filters and use the UV as a final stage of indoor air purification.

The advantage of ultraviolet germicidal irradiation (UVGI) is:

- It has the ability to destroy microorganisms, such as bacteria, viruses and fungi (including mold).

Its disadvantages include:

- It has no effect on particulates, including most allergens.
- It has little effect on gaseous chemicals such as VOCs and odors.
- This technology may produce a small amount of ozone when UV-C is used as irradiation source.

2.1.4 Electric Air Cleaning Technologies

Electric air cleaning technologies include electrostatic precipitation and negative ion generation.

Electrostatic precipitation is an electric air purification technology using an electric field to help trap particles in indoor air. As the air particles pass into the air cleaner, an electronic charge is given to them through a high voltage (also called ionization). The statically charged particles are then attracted and trapped to a series of flat plates or low efficiency filter media with an opposite electrical charge. These units can operate with or without a fan.

An electrostatic purifier is quite effective for particle removal. The downsides of this type of purifier are the lack of chemical filtration, the need of regular maintenance, ozone generation, and the noise generated. An electrostatic filter does nothing to eliminate gases or odors, and the charged plates must be cleaned frequently. After used for a period of time, the surfaces of the particulate colleting plates become covered with contaminants.

This reduces the ability of the air cleaner to capture more particles. Plates need to be constantly cleaned to remove particle build-up to maintain efficiency.

Negative ion generation uses chemical injection technology to clean the air. A negative ion is a molecule that has an extra electron charged with it. A high voltage needle is used to negatively charge the molecule. These negative ions attach themselves to airborne particles, which are positively-charged. The newly-formed larger particles are then able to fall to the nearby wall, ground or other items in the room and get out of the air we breathe.

However, these particles which stick to the nearby surface in the room could easily become loose and circulate in the indoor air again. The particles that the negative ion attract and charge are not cleanly taken out of the air or absorbed into the air purifier. Many ion generators also release a small amount of toxic ozone. Air purifiers using negative ion generation technology do not remove gases or odors at all.

Advantages of the electric air cleaning technologies are:

- It can remove particles from the air, including ultra-fine particles as small as 0.01 microns.
- There is no need to replace filters.
- Electronic air cleaners without fans are nearly silent while in use.

Its disadvantages include:

- It is not as effective as HEPA filtration in removing particles from the indoor air.
- It does not remove gaseous chemicals and odors.
- Models without fans may not effectively clean all of the air in a room.

- All ionic air cleaners produce some amount of ozone, which are harmful to human health.

2.1.5 Ozonation

Ozone (O_3) is a highly-reactive oxidizer which is extremely effective in destroying strong odors, airborne bacteria, and certain chemical pollutants. Ozone, however, has no effect at all on airborne allergens and other particulate pollutants. By and large, air purifiers using ozone are used for very specific applications, such as smoke removal and restoration work, and they are not suitable for use in occupied areas. Even the manufacturers recommend avoiding their use when people or pets are present.

Ozonation as an indoor air purification technology has serious problems. According to the EPA, available scientific evidence shows that at concentrations that do not exceed public health standards, ozone has little potential to remove indoor air contaminants. This means that to be effective at removing chemicals or preventing bacterial or mold growth (two uses of ozone) the amount of ozone that needs to be used would be dangerous to humans. Thus, ozone purification is either dangerous or ineffective. Also, ozone does not remove airborne particles such as dust or pollen. It has also proven that ozone emitted indoors can lead to significant increase in indoor levels of other pollutants such as formaldehyde (a suspected carcinogen), other aldehydes, VOCs and ultrafine particulate matter.

Exposure to even small amount of ozone can cause bad effects on human health. If a person inhales a small amount of ozone, it can cause side effects such as coughing, shortness of breath, chest pains and irritation of the throat. Since ozone is proven to a toxic dangerous gas if inhaled, there are strict limits on how much ozone can be used in a work place, which make the ozone technology unfavorable for the indoor air purification (ACGIH, 2004; EPA, 2006; FDA, 1989; OSHA, 2006).

Advantages of ozonation are:

- Ozone is highly effective in removing odors, including cigarette smoke odors from the indoor air.
- It helps destroy certain chemicals and bacteria (Foarde et al., 1997; Li and Wang, 2003).

Its disadvantages include:

- Ozone generators intentionally produce toxic levels of ozone.
- It has no effect on removal of solid particles.

2.1.6 Photocatalytic Oxidation (PCO)

As a promising new environmental protection technology, photocatalytic oxidation (PCO) has been studied extensively in both scientific and engineering areas over last decade (Demeestere et al., 2007). It has been reported that annually about 400 papers, reports, and conference proceedings and a similar number of patents were published in this field (Blake, 2001). By far, most attention has been paid to photocatalytic degradation of both inorganic and organic compounds in wastewaters (Bhatkhande et al., 2001; Blake, 2001). However, there is a rapidly increased interest in new fields of applications such as photocatalytic purification, decontamination, and deodorization of waste gases and indoor air (Fu et al., 1996; Peral et al., 1997; Zhao and Yang, 2003) and photocatalytic destruction of bacteria, viruses, and cancer cells (Blake et al., 1999; Mills and Le Hunte, 1997; Wolfrum et al., 2002).

Used primarily for the removal of gaseous contaminants such as volatile organic compounds (VOCs), the PCO is a process of shining ultraviolet light (UV) onto a catalytic surface composed of a titanium oxide (TiO_2), to create a chemical reaction that converts gases that pass through the device into less harmful substances such as carbon dioxide and water. The PCO process is also very effective for odor removal and microbiological pollutant disinfection.

PCO is not a filtering technology, as it does not trap or remove airborne particles. It is very promising indoor air cleaning technology when coupled with other air purification technologies such as filtration and adsorption. Efforts need to be made for this technology becoming a commercial working device under real living conditions. Because photocatalytic oxidation is the main technology used in our study, its background and applications in indoor air purification were further discussed in section 2.3 of this chapter.

2.2 Commercial Indoor Air Purifiers

The technologies listed in Table 2.1 were used for manufacturing commercial air purifiers. Each indoor air purification system designed by the companies has its own special features that assist the model in removing a certain toxin or contaminant from the air. Some commercial indoor air purifiers are showed in Table 2.2.

The IQAir HealthPro series consists of air purifiers that specialize in removing basic contaminants. The air purifiers emphasize their ability to seal the air that is entered into the system and run it through all filters before it is released. The GC series by IQAir is a line of air purifiers that are designed with special media to remove harmful gases and odors from the air.

BlueAir has developed air purifiers dedicated to make indoor air safer for allergy and asthma sufferers to breathe in. The models use HEPA filters and other media to eliminate harmful contaminants and particles from the air. Each system has its own design with certain media that specialize in removing a certain contaminant. Some air purifiers by BlueAir also include the option to add another filter that is able to remove tobacco smoke from the air.

By using different filters but keeping the design and system the same, Allerair has developed innovative air purifiers that are efficient at cleaning indoor air. The air purifiers contain an efficient HEPA filter and also can contain a certain medium or extra filter to eliminate a certain contaminant that may be present in indoor air. The consumer can choose from an Allerair system that specializes in removing bacteria or gaseous materials from the air. The company has also developed a general purpose model that is perfect for allergy and asthma sufferers.

Austin Air has developed the Healthmate indoor air purifiers for consumers who are concerned with possessing chemical-free and contaminant-free indoor air. The air purifiers use a HEPA filter to remove toxins and release clean and safe air. The company also has designed the Allergy Machine, which specializes in destroying allergens and allergy triggers from the indoor air. Upgraded air purifiers were offered for consumers who may be concerned with the presence of organic chemicals.

The Friedrich C90B system is the efficient and effective air purification products on the market for allergy and asthma sufferers. Unlike many other air purifiers, this model uses electrostatic technology to attract particles from the air and eliminate them before releasing the clean air. The system requires little maintenance and specializes in removing mold, dust and pollen from the indoor air.

Lifebreath turbulent flow precipitator (TFP) in-home air cleaner is the indoor air purifier manufactured by Nutech. It can remove close to 99.97% of particles such as pollen, fungus spores, dust, animal dander and dirt as well as some bacteria. TFP and HEPA filtration technologies are used in this commercial air purifier. The LifeBreath TRP In-home Air Cleaner is available in whole house and portable models.

Table 2.1 Technologies for indoor air purification

Air purifier Technology	**Particulate Matter**	**Allergens**	**Bacteria, Viruses**	**Odors**	**Smoke**	**Chemical Pollutants**
Activated Carbon Adsorption	No	No	No	Excellent	Excellent	Good
HEPA Filtration	Excellent	Excellent	Fair	No	No	No
UV Irradiation	No	No	Excellent	No	No	No
Electrostatic Precipitation	Good	Good	Good	Poor	Good	Fair
Negative Ion Generation	Good	Good	Good	Poor	Good	Fair
Ozonation	No	No	Good	Excellent	Excellent	Fair
Photocatalytic Oxidation	No	No	Good	Excellent	Good	Excellent

Table 2.2 Commercial indoor air purifiers

Manufacturer	Product	Technology	Room Size (ft^2)	Max Flow Rate (CFM)	Dimensions H x W x D (in)
IQAir	HealthPro Compact	HEPA Pre-filter	1000	240	24x15x16
	HealthPro		1100	260	28x15x16
	HealthPro Plus	HEPA Activated Carbon $KMnO_4/Al_2O_3$	1000	240	28x15x16
	GC VOC	HEPA Activated Carbon, $KMnO_4/Al_2O_3$ Post filter	900	260	28x15x16
	GC MultiGas		900	260	28x15x16
	GC AM		900	260	28x15x16
	GC Chemisorber		900	260	28x15x16
Blueair	Airpod	HEPA Electrostatic Activated Carbon	45	N.A.	N.A.
	201		200	141	21x17x9.5
	250E		200	141	21x17x9.5
	402		365	240	23x20x11
	501		500	450	26x20x13
	601		679	490	26x20x13
Allerair	4000 Exec	HEPA, Activated Carbon	1200	400	17.5 x15 (HxD)
	4000 Exec UV	UV, HEPA Activated Carbon	1200	400	17.5 x15 (HxD)
	4000 Vocarb	HEPA Ultra Activated Carbon	1200	400	17.5 x15 (HxD)
	5000 Exec	HEPA Activated Carbon	1500	400	20.5 x15 (HxD)
	5000 Exec UV	UV, HEPA Activated Carbon	1500	400	20.5 x15 (HxD)
	5000 Vocarb	HEPA Ultra Activated Carbon	1500	400	20.5 x15 (HxD)
	6000 Exec	HEPA Activated Carbon	1800	400	23.5 x15 (HxD)
	6000 Exec UV	UV, HEPA, Activated Carbon	1800	400	23.5 x15 (HxD)
	6000 Vocarb	HEPA Activated Carbon	1800	400	23.5 x15 (HxD)
Austin Air	HealthMate Jr	HEPA Activated Carbon	700	200	16.5x11x11
	HealthMate Plus Jr		700	200	16.5x11x11
	HealthMate		1500	400	23x14.5x14.5
	HealthMate Plus		1500	400	23x14.5x14.5
	Allergy Machine		1500	400	23x14.5x14.5
	The Pet Machine	HEPA Activated Carbon Special Media	1500	400	23x14.5x14.5
Friedrich	C90B	Electrostatic Activated Carbon	506	390	19x15x21.5
Nutech	Lifebreath TFP Air Cleaner	TFP* HEPA	N.A.	150	34.25x14.50x14.75

- TFP: Turbulent Flow Precipitation

2.3. Photocatalysis for Indoor Air Purification

2.3.1 Background of Environmental Photocatalysis

The word photocatalysis is composed of two parts. The prefix “photo-” means light and the catalysis is a process where a catalyst increases the rate of a reaction by reducing the activation energy. Photocatalysis is a still a catalysis process. What is special in a photocatalysis process is that the catalyst involved needs to be activated by light (usually UV). Commonly the catalyst used in a photocatalysis reaction is called photocatalyst.

In 1972 a famous study on photoelectrochemical solar energy conversion was published in the journal of Nature by the Japanese scientists A. Fujishima and K. Honda (Fujishima et al., 1972). The results of their electrochemical studies showed that water can be decomposed into oxygen and hydrogen using UV–visible light, without the application of external voltage.

Their experimental setup is shown in Figure 2.1. They used an electrochemical photocell consisting of two electrodes, one being titanium dioxide (TiO_2) which is a single crystal in the rutile form, and another being platinum black (Pt). A complete electrochemical circuit was connected with these two electrodes, as illustrated in Figure 2.1. When the light with wavelength less than 415 nm irradiated the surface of the TiO_2, photocurrent was formed and it flowed from the platinum counter electrode to the TiO_2 electrode through the external circuit. At the same time, oxygen and hydrogen gases were evolved at the TiO_2 electrode and Pt electrode, respectively, which means the oxidation and reduction reactions occurred.

This study showed the possibility of generating hydrogen by water splitting using the irradiated semiconductor TiO_2. The study on water photo-splitting was then extended to heterogeneous photocatalytic approach. The main purpose of this kind of studies is to try to find a way to produced hydrogen, which is a clean energy source, by splitting the water using the solar energy. Although the photocatalytic water splitting is still an attractive research area, the low efficiency of the hydrogen production is a limitation. Therefore, the focus of the heterogeneous photocatalysis was changed.

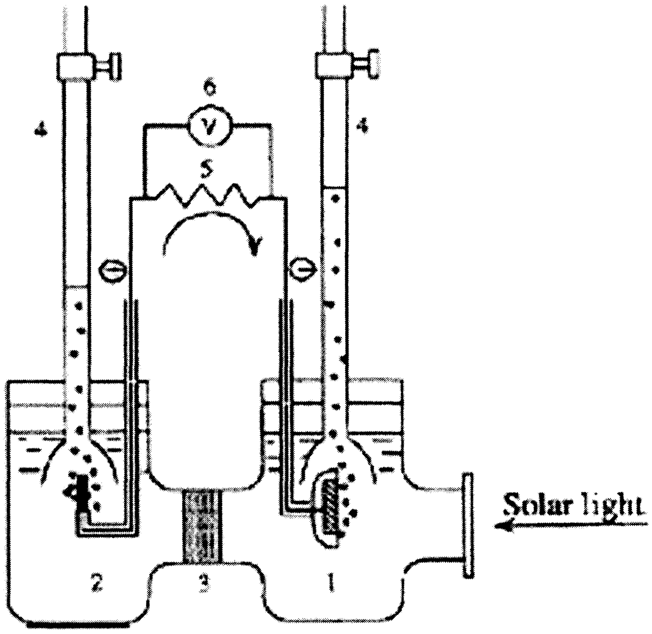


Figure 2.1 Schematic diagram of an electrochemical photocell. (Fujishima et al., 2006) (1) n-type TiO_2 electrode; (2) platinum black counter electrode; (3) ionically conducting separator; (4) gas burette; (5) load resistance and (6) voltmeter.

Since 1977, when Frank and Bard first found that it is possible to decompose cyanide in water using TiO_2 under irradiation (Frank et al., 1977), the focus of photocatalysis studies has shifted into the area of its environmental applications, called environmental photocatalysis. Nowadays the application of photocatalysis to environmental cleanup is still one of the most active areas. The main categories of environmental photocatalysis are drinking water purification and wastewater treatment, air purification, self-cleaning materials, and disinfection or bacterial killing. In recent years, some new applications of photocatalysis attract the attention of researchers, which include the photo-induced super hydrophilicity and the cancer cell killing by photocatalysis.

2.3.2 Mechanism of Photocatalysis

Semiconductors are usually used as photocatalysts. That is why in many cases the photocatalysis is also called semiconductor photocatalysis. The basic mechanism of heterogeneous photocatalysis can be described by the semiconductor band gap model (Bhatkhande et al., 2001; Fox and Dulay, 1993; Fu et al., 1996; Hoffmann et al., 1995; Pelizzetti and Minero, 1993; Peral et al., 1997; Prousek et al., 1996; Zhao and Yang, 2003) as shown in the Figure 2.2. A semiconductor is characterized by a valance band (VB) filled with electrons and a vacant conduction band (CB). Unlike metals which have a continuum of electronic states, semiconductors possess a void energy region extending from the top of the VB to the bottom of the CB, which is called the band-gap. When a semiconductor photocatalyst is illuminated with light whose photons have energy equal to or greater than the bandgap ($hv \geq E_g$), electrons in the filled VC are promoted to the vacant CB due to the light adsorption, simultaneously leaving the electron vacancies or positive charges called holes in the valence band. In this way, electron-hole (e^--h^+) pairs are created within the bulk of semiconductor. The photo-generated electron-hole pairs can migrate to the surface of semiconductor photocatalyst particles where it can be captured by the species adsorbed on the photocatalyst surface through redox reactions. In competition with the charge transfer to the adsorbed species is the electron and hole recombination in the bulk or on the surface of the semiconductor with the release of thermal energy. This charge recombination can reduce the efficiency of the photocatalytic process.

The lifetime of an electron-hole pair is commonly a few nanoseconds which is long enough for their migration and being captured (Kabra et al., 2004). Generally, the holes oxidize water molecules or hydroxyl groups on the surface of a semiconductor photocatalyst to hydroxyl radicals (•OH), while the electrons can be trapped by the electron acceptors such as surface-adsorbed molecular oxygen leading to the formation of superoxide anion radicals ($\bullet O_2^-$), which can subsequently be transformed into hydrogen peroxide or hydroxyl radicals.

The mechanism of photocatalysis using TiO_2 as the photocatalyst can be expressed as follows:

(1) Excitation of the photocatalyst:

$TiO_2 + hv \rightarrow e^- + h^+$

(Recombination: $e^- + h^+ \rightarrow$ heat)

(2) Trapping of the holes:

$h^+ + OH^- \rightarrow \bullet OH$

$h^+ + H_2O \rightarrow \bullet OH + H^+$

$h^+ + R \rightarrow R^+$

(3) Trapping of the electrons:

$e^- + O_2 \rightarrow O_2^-\bullet$

$O_2^- + H^+ \rightarrow HO_2\bullet$

$HO_2\bullet + H^+ + O_2^-\bullet \rightarrow H_2O_2 + O_2$

$H_2O_2 + hv \rightarrow 2OH\bullet$

(4) Mineralization of organic contaminants by hydroxyl radicals

$OH\bullet + R \rightarrow CO_2 + H_2O$

The redox potential for photogenerated holes is +2.53 V versus the standard hydrogen electrode (SHE) in pH 7 solution (Fujishima et al., 2006). The redox potential of hydroxyl radicals produced by holes reacted with adsorbed water or hydroxyl group is only slightly decreased. The redox potential for conduction band electrons is – 0.52 V, which is negative enough to reduce molecular oxygen to superoxide anion radicals. The potentials of photogenerated holes and electrons together with other redox processes occurring on the TiO_2 surface at pH 7 are shown in Figure 2.3.

The hydroxyl radical possesses very high redox potential of + 2.53 V, which is the second strongest known oxidant after fluorine. It can completely oxidize a wide range of organic contaminants into carbon dioxide, water and small inorganic molecules (mineralization). This is why the photocatalysis process is frequently referred as photocatalytic oxidation.

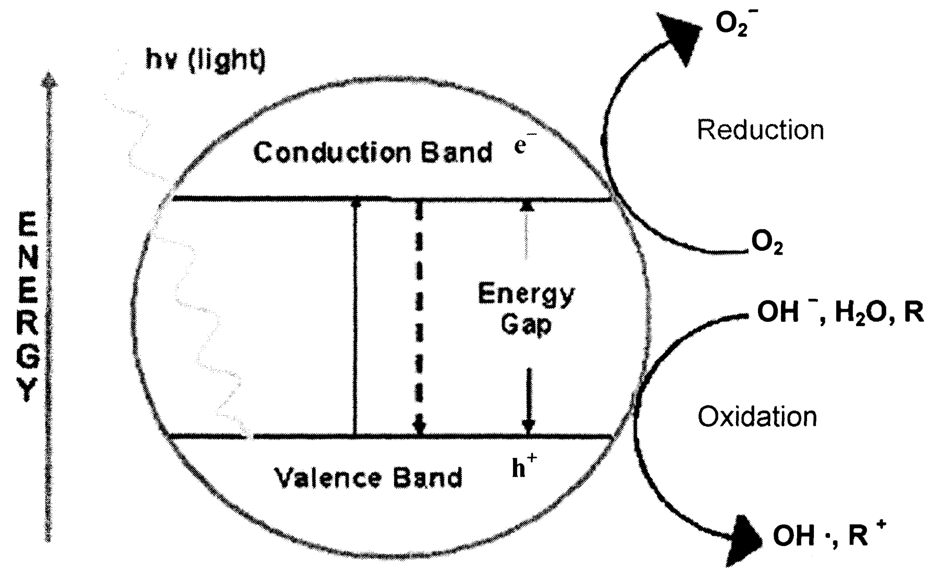


Figure 2.2 Mechanism of the semiconductor photocatalysis

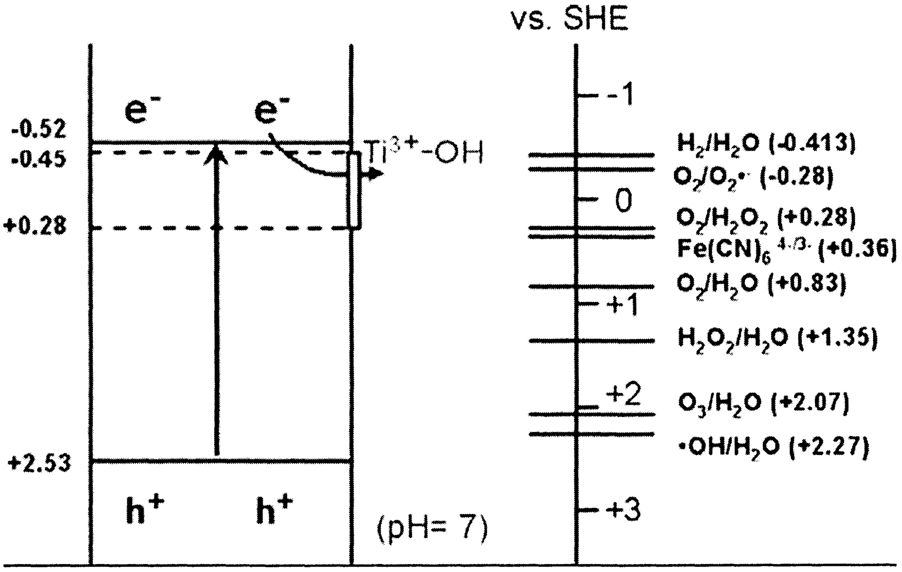


Figure 2.3 Schematic diagram showing the potentials for various redox processes occurring on the TiO_2 surface at pH 7 (Fujishima et al., 2006).

2.3.3 Applications of Environmental Photocatalysis

As a quickly developing technique, heterogeneous photocatalysis find its applications in many areas including drinking water purification and waste water treatment, air purification, anti-bacteria materials and self-cleaning materials.

Compared to the conventional water treatment techniques such as activated sludge biodegradation, activated carbon adsorption, and chemical oxidation, photocatalysis or photocatalytic oxidation has the following advantages: (a) It can oxidize a wide range of organic contaminants, leading to their complete oxidation or mineralization to water, CO_2 and small inorganic compounds. (b) It has powerful oxidizing capacity due to the generation of highly oxidative •OH radical. Most organic contaminants and microbiological pollutants can be photocatalytically degraded or eliminated. (c) The reaction conditions of photocatalysis are mild and the reaction time is modest. (d) There is no need to add chemicals in the treated fluid for the photocatalytic reaction.

Photocatalysis is very suitable for the treatment of wastewater consisting of very complicated organic components with lower concentration. Some organic compound, such as dyes in textile industry wastewater and herbicides and pesticides in agriculture wastewater, which are very difficult to be treated by biological, physical or chemical methods, can be well degraded by the photocatalytic reaction.

However, much effort is needed to make the photocatalysis a competing technique to the conventional wastewater treatment techniques, especially in the engineering area. The development of inexpensive and highly active photocatalysts and effective photoreactors are the focus of the engineering studies.

Another important application of photocatalysis is the purification of indoor air. Indoor air pollution can cause serious problems to human health. The concentrations of the indoor air pollutants are usually low, and this makes the photocatalysis a very suitable technology for the indoor air cleaning.

A photocatalytic oxidation-type air cleaner is typically composed of TiO_2-based filters, UV lamps, and a fan for air circulation. TiO_2 particles as photocatalyst are coated on or dispersed in the body of filters with active carbon, zeolite, etc., as co-adsorbents.

Photocatalysis also finds its applications in antibacterial materials, self-cleaning materials, and cancer cell killing.

2.3.4 Photocatalysts for Indoor Air Purification

The basis of the photocatalysis is the photocatalyst. It has been found that some semiconductors can act as photocatalysts, which are usually metal oxides or sulfides such as TiO_2, ZnO, CeO_2, ZrO_2, SnO, CdS, ZnS.

Among these semiconductors, titanium dioxide (TiO_2) is the most commonly used material as the photocatalyst. It is almost close to the ideal photocatalyst because it is highly active, commercially available, inexpensive, chemically and biologically inert, thermally stable, and non-toxic.

There are three types of crystal structures for natural titanium dioxide which are rutile, anatase and brookite. But only the anatase and rutile types can be used as photocatalysts. Figures 2.4.and 2.5 show the crystal structures of anatase and rutile TiO_2, both of which belong to the tetragonal crystal system. Of both TiO_2 crystalline phases, anatase is widely reported to be the most active one in photocatalysis (Fox and Dulay, 1993; Huang et al., 2000; Jung and Park, 1999; Sclafani and Herrmann, 1996; Zhao and Yang, 2003). The anatase is thermodynamically less stable than rutile, but its formation is kinetically favored at lower temperature (<600 °C). This lower temperature could result in higher surface area, and a higher surface density of active sites for adsorption and catalysis reactions.

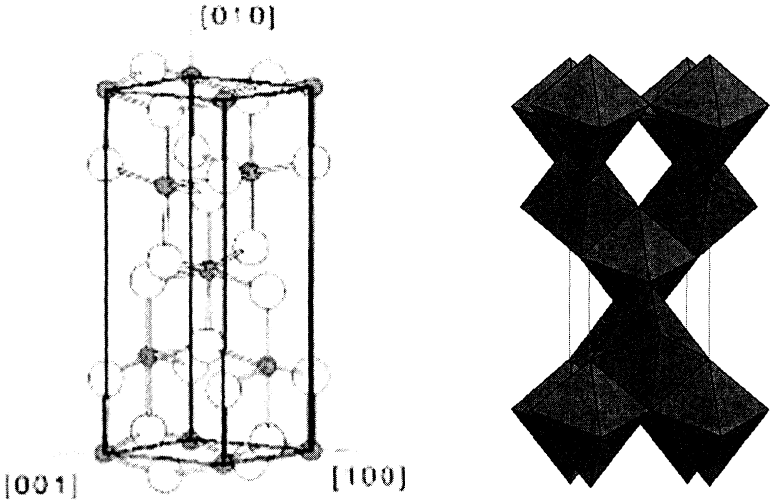


Figure 2.4 The crystal structure of anatase TiO_2

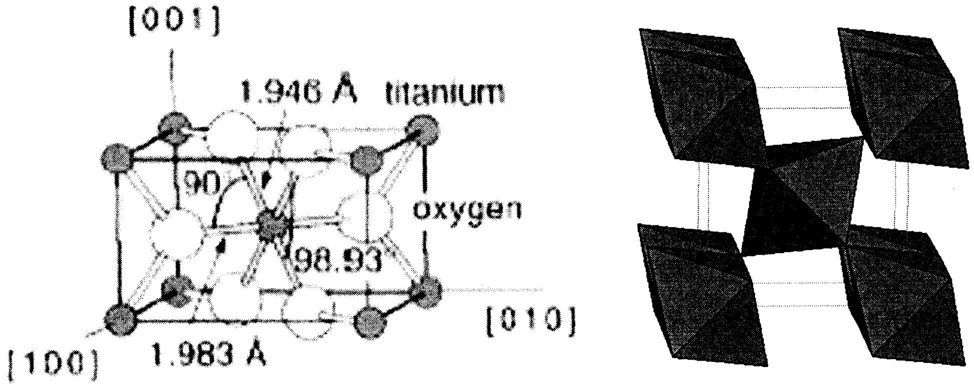


Figure 2.5 The crystal structure of rutile TiO_2

Many studies showed that mixed anatase/rutile TiO_2 photocatalysts exhibited higher activity than pure anatase (Fotou and Pratsinis, 1996; Sattler and Liljestrand, 2003). Thus the Degussa P25 TiO_2 (product of Degussa Corporation in Germany), a mixture of anatase and rutile, has been widely applied and become a research standard for environmental applications of photocatalytic oxidation (Bhatkhande et al., 2001; Sattler and Liljestrand, 2003). The characteristic specifications of Degussa P25 TiO_2 are: non-porous particles; 70:30 anatase: rutile; specific surface area 35 to 65 m^2/g; crystalline size 30 nm; aggregate with 0.1 μm diameter; purity 99.5% TiO_2. There are also commercial products of anatase TiO_2. Hombikat UV-100 is the product of Sachtleben Chemie GmbH (manufacturer and supplier, Duisburg, Germany). It is porous TiO_2 with only anatase crystal phase (purity > 99 wt%). It has the specific surface area of 300 m^2/g. Its particles are small with diameter less than 10 nm (Ibrahim, 2001).

Although TiO_2 has many advantages as the most popular and promising photocatalyst, it can only absorb ultraviolet radiation due to its relatively large band-gap (band-gaps of anatase and rutile TiO_2 are 3.2 and 3.0 eV, respectively).

TiO_2 is sometimes modified either by ion doping or by deposition of a metal (Pt, Rh, Ni etc) in order to improve the properties of TiO_2, especially enhancing its photocatalytic activity. Ion doping includes the transition metal cation doping and anion doping (such as N doping in the TiO_2 crystalline phase). The former can improve the photocatalytic activity by preventing the electron-hole recombination, while the latter is one of the ways to develop photocatalysts which are sensitive to visible light. For the metal deposition modification, the metal is deposited by impregnation of TiO_2 with a metal salt followed by drying and reduction under hydrogen flow at high temperature. In addition, there are some studies using composite semiconductors as photocatalyst, the main purpose of which is to find visible light sensitive photocatalysts.

The TiO_2 photocatalyst can be used either in the slurry state or in the immobilized state. The slurry is the suspension of contaminated water and fine TiO_2 particles, and it is very easy to make. The immobilized TiO_2 is a photocatalyst anchored or coated to a fixed substrate or support.

Many studies on photocatalytic degradation of aqueous organic contaminants were carried out using slurry TiO_2. Although the TiO_2 in slurry state has relatively higher photocatalytic efficiency, it needs to be separated from the solution after reaction. This will greatly affect the economic efficiency of TiO_2 photocatalysis as an applied environmental technology.

One of the methods to overcome the TiO_2 separation problem is to immobilize TiO_2 on a support. In recent years, TiO_2 immobilization has become a hot research area due to its promising application on environmental photocatalysis.

Materials can be employed as the substrate or support for TiO_2 immobilization include glass (Kim et al., 1996; Sirisuk, 2003; Trivedik, 1994; Zorn et al., 2000), quartz and silica (Mune et al., 1996; Sauer and Ollis, 1996; Takeda et al., 1995), ceramics, metals (such as stainless steel), activated carbon (Ishihara and Furutsuka, 1996; Takeda et al., 1995), zeolite and alumina (Takeda et al., 1995), and polymers (Fabiyi et al., 2000; Takeuchi, 1996). Among these materials, glass is mostly studied in the forms of glass plate, glass fiber, glass beads, and glass wool. Considering the UV light transmitting, borosilicate glass is commonly used in the studies of TiO_2 photocatalysis. Quartz is a very good material as the TiO_2 substrate because UV light can transmit it without adsorption. Nevertheless, its high cost limits it as a photocatalyst support for common use. Metals can also be used as support for TiO_2 immobilization. Some studies also used stainless steel. Before fixing TiO_2 on it, the metal substrate has to be well cleaned to get rid of grease and other contaminants on the surface so that a firm attachment of TiO_2 can be obtained. Still there are two problems with metal substrates. One is that it is not easy to shape it unless it is used as the very thin film; the other is metal corrosion while it is immerged in the acidic or basic solutions.

Sol-gel (Cao et al., 2000; Yamazaki, 1999) and dip-coating (Obee and Hay, 1997; Sauer and Ollis, 1994) are two common methods used for TiO_2 immobilization. The sol-gel process is a very popular method to prepare immobilized TiO_2, especially the TiO_2 film. The procedure of the sol-gel method includes three steps: the sol preparation by the hydrolysis of titanium alkoxide solution (precursor); sol film formation on the substrate or support by immersion; formation of stable gel film by drying and calcination (Keshmiri et al., 2004). Sometimes, the sol can be mixed with binding materials such as silica sol. TiO_2 powder may also be added into the sol to make a thick mixture. For example, the TiO_2 film coated on the ceramic beads is prepared by the following steps: First, titanium isopropoxide $Ti\ [OCH(CH_3)_2]_4$ is added in the mixture of water and iso-propanol. This is a hydrolysis process to form TiO_2 sol. Then SiO_2 sol is added to the resulting solution as the binder. Finally the resulting sol mixture is coated on the ceramic beads by immersion followed by the treatment of drying and calcination.

Relative to sol-gel method, dip-coating is a simple method to prepare immobilized TiO_2. First, TiO_2 slurry is made by mixing TiO_2 powder well in water. Then the support material is dipped into the slurry to get the coating. Finally, the coated support is dried and then calcined. Sometimes the dispersant or binder is added into the slurry to improve the coating properties.

2.3.5 Photocatalytic Reactors

Types of Photocatalytic Reactors

Despite intensive research that has been carried out on heterogeneous photocatalysis as a air cleaning technology, little progress has been made so far toward reactor optimization and scale-up (Mohseni and Taghipour, 2004). There are different types of photocatalytic reactors. Photocatalytic reactors can be classified based on the state of photocatalyst, the geometry of the reactor and the illumination arrangement of the light source.

Based on the state of photocatalyst used in photocatalytic reactions, photocatalytic reactors are divided into two groups – slurry photoreactors and immobilized photoreactors. The slurry reactor, which uses the suspension of photocatalyst, requires the separation and recycling of the ultrafine photocatalyst particles from the treated effluent by filtration, centrifugation or coagulation, and flocculation (Mukherjee et al., 1999). The extra separation step makes the overall treatment process more complex and clearly decreases the economical viability of the slurry reactor. Also, the penetration depth of light into the slurry is limited. These problems can be avoided by immobilization of photocatalyst on a support. The advantage of the immobilized photocatalytic photoreactor is that separation of photocatalyst fine particles after purification is not necessary. In addition, by combining the photocatalyst and substrate together, some positive properties from substrates, such as the porosity, light reflection or conduction, may be utilized by the photocatalyst. The main problem of the immobilized photocatalytic reactors is that the mass transfer limitation can easily occur. Better photoreactor design and proper selection of support can reduce these drawbacks. Immobilized photoreactors can be further divided into two reactor types, which are the fixed bed reactors and the fluidized reactors. The TiO_2 film photoreactors belong to the former. For a fluidized bed immobilized photoreactor, the photocatalyst needs to be immobilized on the fine substrate particles in order to be fluidized.

For the photocatalytic reactors with immobilized photocatalyst TiO_2, there are two problems to which much effort needs to be made. One is the strength of the immobilized TiO_2. The TiO_2 coating fixed on the support should not be easily worn out or washed off by the treated fluid. What we need to do is try to find a way to attach the TiO_2 film firmly on the surface of support. Some TiO_2 immobilization methods result in cracks on the TiO_2 film, especially for the thick film. Thus it is very important to obtain a firmly attached film on the supporting materials with appropriate thickness and crack free texture. Another problem is the reduced efficiency of the immobilized TiO_2 due to the mass transfer limitation. To improve the mass transfer, it is essential to have a good configuration of the photocatalyst, radiation source and the treated fluid in the photoreactor. Some methods such as using baffles within the reactor can be used to enhance the contact of contaminant molecules with photocatalyst as well as the mixing efficiency of contaminated water or air (Fabiyi et al., 1999; Stonestreet et al. 1999).

According to the illumination manner, photocatalytic reactors can be grouped into three categories: (a) immersion-type with lamps immersed within the reactor; (b) external-type with lamps outside the reactor; and (c) distributive-type with the light distributed from the source to the reactor by optical means, such as reflectors and light conductors or optical fibers (Mukherjee et al., 1999).

By the flow state of stock solution, photocatalytic reactors have two groups. One group includes the batch reactors in which the treated fluid is enclosed in the reactor vessel and not in flow state; the other group is continuous flow reactors in which the treated fluid is in flow state at a certain flow rate.

In addition, photocatalytic reactors can be classified by the reactor geometry as plate reactors, tubular reactors, annular reactor (Sahle-Demessie et al., 2003) etc.

Factors Related to the Photoreactor Efficiency

For a photocatalytic reactor, factors affecting its efficiency include not only those in the design of conventional reactors, such as reactant-catalyst contact, flow patterns, mixing, mass transfer, reaction kinetics, catalyst installation, temperature control, etc., but also the illumination factor since the photocatalyst needs to be activated by the light irradiation (Mukherjee et al., 1999). Much attention should be paid to the illumination factor while a photocatalytic reactor is designed since the treatment capacity of the photoreactor is determined by the amount of photocatalyst activated by the light radiation. Thus, one of the major issues for the photocatalytic reactor design is how to distribute light uniformly to a larger surface area of the photocatalyst and what is the better arrangement of the radiation source and reactor system.

A question closely related to the illumination of photocatalytic reactor is how to select an appropriate lamp. Since TiO_2 has the bandgap of 3.2 eV (anatase), it can only be activated by the UV light with wavelength less than 388 nm. Lamps commonly employed in photocatalysis include arc lamps (mercury lamps and xenon lamps), fluorescent lamps, and blacklight lamps. Mercury lamps are divided into low-pressure, medium-pressure and high-pressure mercury lamps. The light produced by low-pressure mercury lamps is mainly in the ultraviolet region with wavelength around 253.7 nm, while medium and high-pressure mercury lamps have radiation in ultraviolet, visible light, and infrared. The Xenon lamps produce continuous radiation spectrum in both ultraviolet and visible light regions which is similar to that of sunlight, and they are often used to simulate the sunlight in the photocatalysis studies. A fluorescent lamp has a tube filled with mercury and inert gas such as argon or neon gas. When the electricity is turned on, a mercury arc is excited, by which UV light is initiated. A phosphor coating exists on the inside of tube. The UV light then causes a phosphor coating to generate visible light. For the fluorescent lamp, most radiation is visible light with very small portion of UV-A. So far, the most common light source in use in TiO_2 photocatalysis is the blacklight-type UV lamp, which emits light in the UV-A range with the wavelengths between 300 nm to 400 nm. Typical blacklight lamp has the emission peak at about 352 nm or 365 nm. A black light lamp has the similar structure to a fluorescent lamp and work in the similar way, except that there is a special "black" phosphor coating on the inside of light envelope. This coating absorbs harmful short-wave UV-B and UV-C light emitted from energized mercury atoms, and emits UV-A light. The black glass tube itself blocks most visible light, so in the end, only long-wave UV-A light and some blue and violet light pass through. The tube-type blacklight lamp is relatively cheap, low power UV source, and most importantly, TiO_2 can utilize its emission very efficiently. Therefore, it has been widely applied as the light source for photocatalytic oxidation.

There are also other UV illumination sources which can be used in photocatalysis. UV-A or UV-C germicidal lamps have been employed for photocatalytic degradation of some organic contaminants. The UV-C germicidal lamp has the peak wavelength of 253.7 nm. Pen-Ray UV lamps, supplied by UVP (Upland, California, USA), are low-pressure lamps made of double quartz tubing with broad UV emission band between 300-400 nm. The most attracting characteristics of Pen-Ray UV lamps are their long life (5000-8000 hours) and small size.

The state of photocatalyst has much effect on the photocatalytic reaction efficiency. This includes the components of photocatalyst, the crystalline structures, the particle properties (such as particle size and size distribution, porosity and surface area), and the manner of photocatalyst immobilization.

The efficiency of photoreactors is also affected by the building materials of the reactor. Quartz, polymer and borosilicate glass are popular materials used to build up photocatalytic reactors. Quartz has excellent light transmission capability in the region from infrared to ultraviolet, especially in the ultraviolet region. Even the 160 nm UV light can transmit it. Polymers containing fluorine can be used to construct photoreactors because of their stability and higher transmissivity to UV light (for UV light with wavelength of 300 nm to 400 nm, the transmittance is $0.735 \leq T \leq 0.846$). Borosilicate glass can cut off light with wavelength below 300 nm.

2.3.6 New Development of Indoor Air Purification Using Photocatalytic Oxidation

One of the major challenges involved in photocatalytic research is to increase the spectral sensitivity of photocatalysts to visible light, which composes the largest part of solar radiation.

To utilize the visible light for photocatalysis, several different approaches have been proposed, one of which is doping of photocatalysts with metal ions (for example Cr^{3+}, Fe^{3+}), which create local energy levels within the bandgap of the photocatalyst, with corresponding absorption bands lying in the visible spectral range. Another is doping of photocatalysts with non-metal atoms, such as N, S and C.

Finding new light sources for highly efficient photocatalyst activation is another new direction for photocatalytic air purification process. Light emitting diodes that can emit ultraviolet light (UVLED) have appeared on the market. They are produced by the Izumi Optical Devices Co., Japan. UVLED devices are almost ideal light sources for miniaturized photocatalytic devices. However, at present their price is much higher than that of the tube-type blacklight lamp.

2.4 Photocatalysis for Bioaerosol Disinfection in Indoor Air

Indoor air quality is an important health issue both for workplaces and homes. Indoor air contamination can cause serious problems to human health because most people spend a substantial amount of time indoors. Studies from the United States and Europe showed that persons in industrialized nations spend up to 90 percent of their time indoors (EPA, 1989). It was concluded that indoor air pollution poses a greater risk than outdoor air pollution by a study conducted by the US Environmental Protection Agency (EPA) in

1987. Indoor air contamination is estimated to cause significant increases in medical costs and a decline in work productivity (EPA, 1987). The potential risks related to indoor air quality have increased because nowadays buildings are, for energy conservation purpose, more tightly sealed to recirculate air inside and reduce the amount of outside air supply.

Sources of indoor air pollution include particles, volatile organic compounds (VOCs) and odors, and microbial contaminants. Most commercial indoor air purifiers can remove particles and much effort has been done to eliminate VOCs and odors from indoor air. But fewer studies have been carried out for the inactivation of microbial contaminants in indoor air. Microbial contaminants are one of the significant sources of indoor air pollution. They consist of particles of biological origin such as bacteria, viruses, fungi. These microbiological contaminants are commonly in the form of bioaerosols, which are microorganisms or fragments of biological origin (alive or released from a living organism) that are uniformly suspended in the air. Many studies have shown association between the indoor bioaerosols and health problems. Indoor bioaerosols can cause serious hypersensitivity diseases and infectious diseases. One of the biggest disease outbreaks due to microbial contamination of indoor air was the Legionnaires' disease outbreak in Philadelphia in 1976 (Dennis, 1990). Microbial contamination in indoor air has been considered a serious health hazard (Block, 1991). In recent years, biological problems in indoor environments have received considerable attention and interest has been increased in developing disinfection technologies for indoor air.

Typical methods used to purify indoor air include filtration, adsorption, ozonation, air ionization, and ultraviolet germicidal irradiation. Although there are commercial indoor air purifiers in the market using one or the combination of these technologies, none of them are completely effective to mitigate the problem of contamination in the indoor environment. Filtration, using either fiber or HEPA filters, can only remove airborne particles. It is totally not effective for removal of gaseous contaminants such as VOCs and odors. HEPA filters can remove particles bigger than 0.3 microns. Thus they are used to capture some microorganisms relatively in bigger size, but they are ineffective in removing VOCs as well as smaller microorganisms such as viruses. Furthermore, the microbial contaminants just stay at the surface of HEPA filters instead of being completely disinfected (Schneider, 1996). Once these organisms grow through the HEPA filter, air released from the downstream side could contain microbial contaminants in much higher concentration than originally captured, causing a bigger indoor air quality threat than the unfiltered air. HEPA filters also produce very large pressure drops and therefore are expensive to operate. Adsorption using porous materials such as activated charcoal is much more effective to remove VOCs and odors from the indoor air, but this method can not remove particles and microorganisms. Although ozonation is effective in destroying strong odors, certain chemical pollutants as well as airborne bacteria, the concentration of ozone that is necessarily to be used could exceed the public health standards and would be dangerous to humans. Ozonation is also not effective for particle removal. Air ionization is mainly used for indoor air particle removal. However, its use in indoor air purification is much limited because some amount of ozone is also produced, which is harmful to health. Ultraviolet germicidal irradiation has the ability to destroy microorganisms, such as bacteria, viruses and fungi, but it has no effect for particle removal and little effect on elimination of gaseous chemicals and odors.

Photocatalytic oxidation as one of the advanced oxidation technologies (AOTs), is the promising method for indoor air purification (Tompkins et al., 2005; Zhao and Yang, 2003). It uses titanium dioxide-based materials as photocatalysts because of their higher photocatalytic activity and better performance. A large variety of organic compounds can be mineralized or totally oxidized to carbon dioxide, water as well as small inorganic molecules by the photocatalytic oxidation process. Because microbial contaminants are composed of organic compounds, they can also be oxidized by photocatalytic oxidation using UV illuminated titanium dioxide as photocatalyst. In such a way, the microbiological contaminants can be disinfected effectively.

Scientific and engineering interest in environmental applications of semiconductor-mediated photocatalysis has grown drastically. Since the antibacterial effect of TiO_2 photocatalytic reaction was first reported in 1985 (Matsunaga et al., 1985), there are many studies that described photokilling of bacteria and viruses using TiO_2 in aqueous media (Cai et al., 1992; Kuhn et al., 2003; Lee et al., 1998; Rincon and Pulgarin, 2004; Sunada et al.,1998; Sunada et al., 2003). By far, most attention has been paid to photocatalytic degradation of both inorganic and organic compounds in water and there is relatively less work on the photocatalytic decontamination of microorganism-containing indoor air. However, there is a rapidly increased interest in the application of photocatalytic oxidation in air purification (Fu et al., 1996; Peral and Ollis, 1997; Zhao and Yang, 2003). Photocatalytic disinfection of microbiological contaminants in indoor air (Blake et al., 1999; Mills and Le Hunte, 1997; Wolfrum et al., 2002) is of great interest for public health reasons and deals with a large spectrum of applications for rooms or vehicles with high infection and contamination risks, such as hospitals, public buildings, domestic households, cars and aircraft. Photocatalytic oxidation technology can provide one of the most viable solutions to the problem of indoor air contaminated by airborne microorganisms or bioaerosols.

There are relatively fewer publications for the studies of photocatalytic disinfection of indoor air, compared to those in the field of microorganism disinfection in water. Goswami et al first studied the indoor air disinfection by photocatalytic oxidation. A recirculating duct facility was used in their study and the bacterium Serratia marcescens was input in the indoor air. The results showed that the model bacterium was completely destroyed (Goswami et al., 1995; Goswami et al., 1997). Photocatalytic oxidation of E. coli in air was studied by Jacoby et al. (Jacoby, 1998). It was found in their study that 54% of E. coli existing in the air can be finally oxidized to carbon dioxide and water. This is the first time for the study of complete photocatalytic oxidation or photomineralization of E. coli. Complete mineralization of E. coli, Micrococcus luteus, Bacillus cereus (bacterial cells and spores), and Aspergillus niger spores was also demonstrated by the study of Wolfrum et al. (Wolfrum, 2002). Masaki and coworkers studied the destruction of bacteria and foul odor in air using stainless steel coated by TiO_2 film (Masaki, 1999). Disinfection effect was also found for E. coli contaminated air when the air stream passed through a metal microfibrous mesh filter coated with TiO_2 (Lopez and Jacoby, 2002). Study conducted by Lin and Li concluded that photocatalytic oxidation was effective for the disinfection of airborne microbes. In their study, nebulized E. coli (gram negative bacteria), B. subtilis (bacterial spores), Candida famata (yeast), and Penicillium cetrinum (fungal spores) were used as bioaersol contaminants. All the airborne microorganisms were destroyed in a laboratory setup using commercial titanium dioxide coated filters (Lin and Li, 2003). Inactivation of airborne E. coli was also reported by Keller et al. when the contaminated air passed through a photoreactor loaded with coated TiO_2 film as photocatalyst (Keller et al., 2005). Pal et al. investigated the inactivation effect of E. coli, Microbacterium sp. and Bacillus subtilis using both batch and continuous reactor (Pal et al., 2005). Different TiO_2 loadings and radiation intensities were used for the disinfection study. The study showed that photocatalytic oxidation using coated TiO_2 as photocatalyst can be used for the treatment of bioaerosol-contaminated indoor air. Their further batch study (Pal et al., 2007) concluded that six different species of bacteria can be inactivated by fluorescent light activated TiO_2. The six bacteria are four ATCC bacteria (Escherichia coli K-12, Pseudomonas fluorescens, Bacillus subtilis and Microbacterium sp.) and two other species of bacteria collected from outdoor air in Singapore (Microbacteriaceae str. W7 and Paenibacillus sp. SAFN-007). Gram-negative bacterium E. coli K-12 was the most effectively inactivated, while Gram-positive B. subtilis exhibited the least response to the photocatalytic treatment. They also studied the disinfection of aerosolized E. coli K-12 in air using a continuous annular reactor by varying UV-A light intensity, relative humidity (RH), and photocatalyst loading at an air flow rate of 1 L/min (Pal et al., 2008). Effective E. coli inactivation was proved.

Chapter 3

Experimental Methods and the Design of a Reactive Indoor Air Purification Device

3.1 Experimental Methods

3.1.1 Steps to Revive Freeze Dried Pellets of E. Coli K-12

E. coli K-12 freeze-dried culture (ATCC 10798), purchased from the American Type Culture Collection (ATCC), was used for bioaerosol generation in the tests. E coli is a facultative anaerobic, Gram negative, rod-shaped bacterium which is often used as model for disinfection studies.

The E coli K-12 purchased from ATCC is preserved as freeze dried pellets and it was revived before use. The following steps were followed for the revival of E. coli K-12:

(1) 6 mL of ATCC 294 broth solution is prepared.

The composition of ATCC 294 broth is Tryptone 8.0 g + NaCl 0.5 g + distilled water 1.0 L.

(2) The ATCC 294 agar solution is autoclaved and prepare 10 plates.

For the preparation ATCC 294 agar plates, 1.5% agar was added to the formula of the ATCC 294 broth.

(3) The above broth and agar plates are incubated at 37 ^{o}C for 16 hours to check for any contamination.

(4) After confirming that there is no contamination in the ATCC 294 broth and the agar plates, the vial containing E. coli K-12 in freeze dried state is carefully cracked open in

an aseptic environment according the product instruction, and 1 mL of ATCC 294 broth from the 6 mL solution was added with the help of a Pasteur pipette.

(5) The contents in the vial is shook gently and followed by being transferred into the 5 mL ATCC 294 broth left. The contents are shook gently.

(6) A sterile loop is dipped into the 6 mL broth for streaking on the ATCC 294 agar plates.

(7) The 6 mL broth and the streaked agar plates are incubated at 37 °C for 24 hours.

(8) After 24 hours of incubation, the 6-mL broth turns into a dirty white suspension of E. coli K-12 colonies and the colonies of E. coli also appear on the surface of ATCC 294 agar plates. These agar plates with E. coli K-12 colonies are served as the source to make the diluted solutions of E. coli.

(9) Finally, the liquid suspension is mixed with 50 % (vol/vol) glycerol and stored at –20 °C to preserve the revival of E. coli K-12 for further use.

3.1.2 Preparation of E. Coli K-12 Diluted Solutions

The E. coli K-12 diluted solutions, used for bioaerosol generation, are prepared by the following procedure:

(1) From the revived stock of E. coli K-12 stored in freezer at –20 °C in the mixture with 50% vol/vol glycerol, fresh cultures are prepared on Tryptone agar plates or LB (Luria Bertani) agar plates every month to guarantee the strain is viable and not contaminated.

(2) 10 mL of LB broth is prepared in a test tube. It is then autoclaved and inoculated with a loop full of the bacteria of E. coli K-12. The bacterial source is the above made agar

plate with E. coli colonies. The inoculation is carried out by using the sterile loop scraping gently on the E. coli colonies on the surface of agar plate.

(3) The inoculated media of LB broth is then incubated for 16 hours at 37 °C. After incubation the LB broth in the test tube becomes cloudy suspension due to the living E. coli.

(4) This cloudy suspension in the test tube is centrifuged at 4000 rpm for 5 minutes. The aliquot, cell mass settled down at the bottom of the tube, is then washed with 0.9% NaCl solution in order to strip off any nutrient media from the cell agglomeration. After washing, 10 mL of 0.9% NaCl solution is added to the E. coli cell mass left at the bottom of the test tube, followed by well mixing by the vortex mixer. This is the mother solution for the series of dilutions made below.

(5) Series of dilutions are prepared as shown by the table below:

Dilutions	10^0	10^1	10^2	10^3	...	10^8
Preparation Method	Mother Solution	1 mL 10^0 + 9 mL 0.9% NaCl	1 mL 10^1 + 9 mL 0.9% NaCl	1 mL 10^2 + 9 mL 0.9% NaCl	...	1 mL 10^7 + 9 mL 0.9% NaCl

(6) 1 mL of each dilution is spread on freshly prepared Tryptone agar plates or LB agar plates using a glass stick shaped as a hockey stick, and incubated at 37 °C for 24 hours. The purpose of this step is to get the concentration of E. coli K-12 colonies in each dilution.

3.1.3 Photocatalyst Preparation

Refer to Chapter 4 for the preparation of photocatalysts 10%TiO_2-10%SiO_2/AC, 10%TiO_2/AC, and PC-30%SiO_2/AC. The photocatalysts 10%TiO_2-10%SiO_2/AC, 4%TiO_2-10%SiO_2/AC and 7%TiO_2-10%SiO_2/AC were prepared by the same procedure as that of 10%TiO_2-10%SiO_2/AC except that the TiO_2 amount in the impregnation suspension is 1, 4 or 7 %(w/v), respectively, instead of 10 %(w/v) for 10%TiO_2-10%SiO_2/AC.

3.1.4 Experimental Setup and Procedure for E. Coli Photocatalytic Inactivation

The experimental set up for E. coli K-12 bioaerosol photocatalytic inactivation is shown in Figure 3.1. Compressed air (1 in Figure 3.1) with purity of 99.99% from air cylinder was used as the air source. The air was split in two flows, one of which went through the bioaerosol nebulizing generator (BANG, 4 in Figure 3.1) filled with 20 mL of diluted E. coli suspension to produce E. coli bioaerosol. This air flow with E. coli bioaerosol was mixed with another air flow in the stainless steel buffer tank (5 in Figure 3.1) in order to generate the aerosolized air with constant E. coli concentration. The flow rates of the two air flows were controlled by two gas flow meters (2 and 3 in Figure 3.1). The air with constant E. coli concentration from the buffer tank was blown through the annular photocatalytic reactor (6 in Figure 3.1) for bacteria disinfection. Air samples with E. coli were collected at the outlet of the reactor every two minutes using a single stage Anderson air sampler (8 in Figure 3.1) with eosin methylene blue (EMB) agar plate inside. The air flow was switched to the Anderson air sampler by turning the gas flow switch (7 in Figure 3.1) when air samples were taken. After sampling, the air flow switch was turned back so that the air can go directly to the air pump without passing through the air sampler. An air pump (9 in Figure 3.1) was used to draw the air through the air sampler. The tail gas passed through an impinger (11 in Figure 3.1) containing 70%

ethanol to kill the remaining E. coli bacterial before its release to the atmosphere. All sampling EMB agar plates containing E. coli bacteria were carefully sealed and placed in an incubator at 37 °C for 24 hours. Fresh photocatalyst was used for every experiment. After each run of the experiment, the reactor was cleaned with 70% ethanol three times followed by drying with pure air for 30 minutes. The concentration of E. coli dilution in the bioaerosol nebulizing generator was carefully selected to make sure the E. coli colony forming unit (CFU) on the EMB agar plate was within the range of 50 to 300.

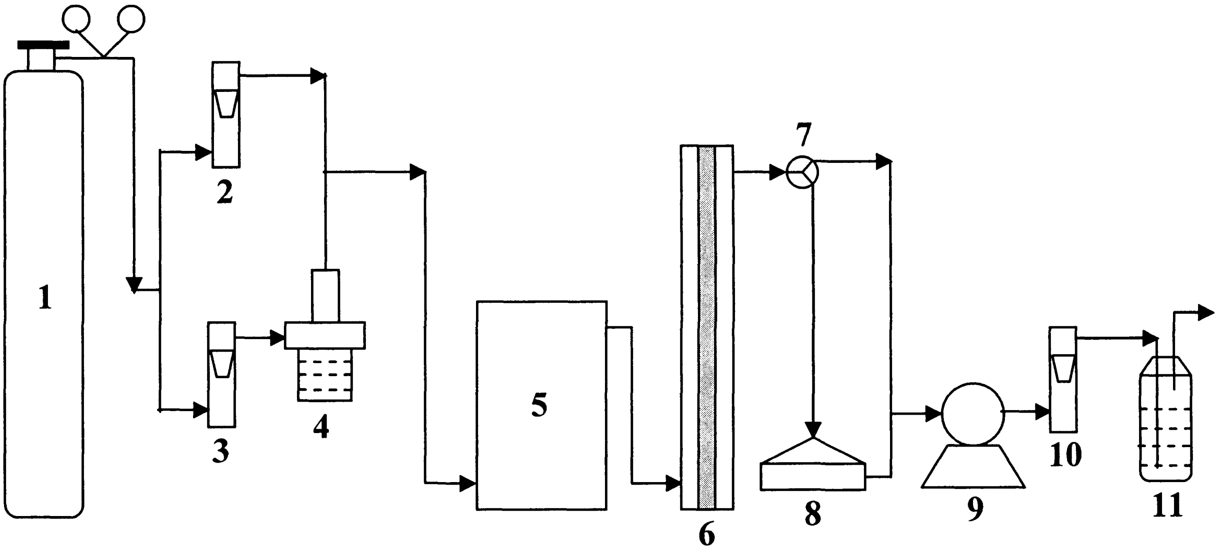


Figure 3.1 The reactive indoor air purification system for E. coli K-12 bioaerosol inactivation (a continuous photocatalytic reaction systerm).

* 1-compressed air; 2 & 3-gas flow meters; 4-bioaerosol nebulizing generator (BANG); 5-stainless steel buffer tank; 6-annular photocatalytic reactor; 7-gas flow switch; 8-single stage Anderson air sampler; 9-air pump; 10-gas flow meter; 11-impinger.

3.2 Design of a Reactive Indoor Air Purification Device

The reactive indoor air purification device mainly consists of three components: the photocatalytic reactor, the baffle system inside the reactor, and the gas buffer tank. The three parts are all made of stainless steel. Among them, the photocatalytic reactor is the core of the device, in which the photocatalytic reaction occurs. The reactor is in annular shape with a baffle system inside. A UV lamp is located in the centre of the reactor with photocatlyst around it. The gas buffer tank is used to obtain the stable flow of indoor air. The whole device was used for the E. coli inactivation present as bioaerosol in indoor air.

3.2.1 The Photocatalytic Reactor

The design parameters of the annular photocatalytic reactor with a baffle system inside were shown in Figure 3.2. The overall length of the reactor (including the thickness of walls) is 263 mm with inside diameter of 73 mm. The effective inside volume of the photocatalytic reactor is 1.0 liter. The annular reactor was made of stainless steel with an inner quartz cylinder located at its center. The quartz tube, which is used to house the UV lamp, has the dimensions of length 263 mm, outer diameter 22 mm, and inner diameter 18 mm. A blacklight blue lamp (F8T5/BLB, BULBTRONICS) with a peak emission at 365 nm (UV-A) and an energy output of 8 W was used as the light source for the photocatalytic reactor. The dimensions of the lamp are: lamp part length 266 mm, overall length 305 mm, diameter 16 mm.

The actual designs of the photocatalytic reactor are separately shown in Figures 3.3, 3.4 and 3.5.

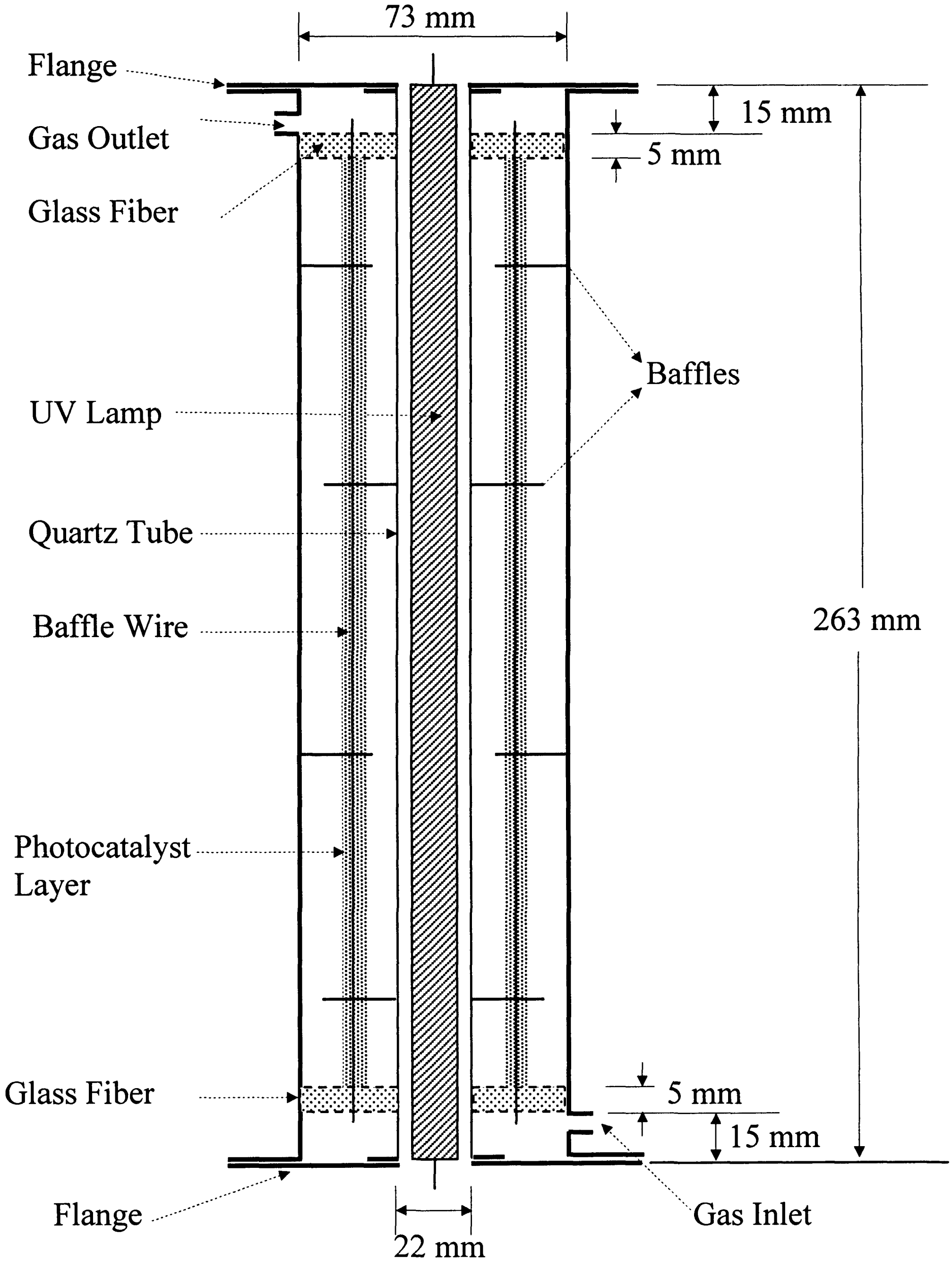


Figure 3.2 Parameters of the annular photocatalytic reactor with a baffle system inside

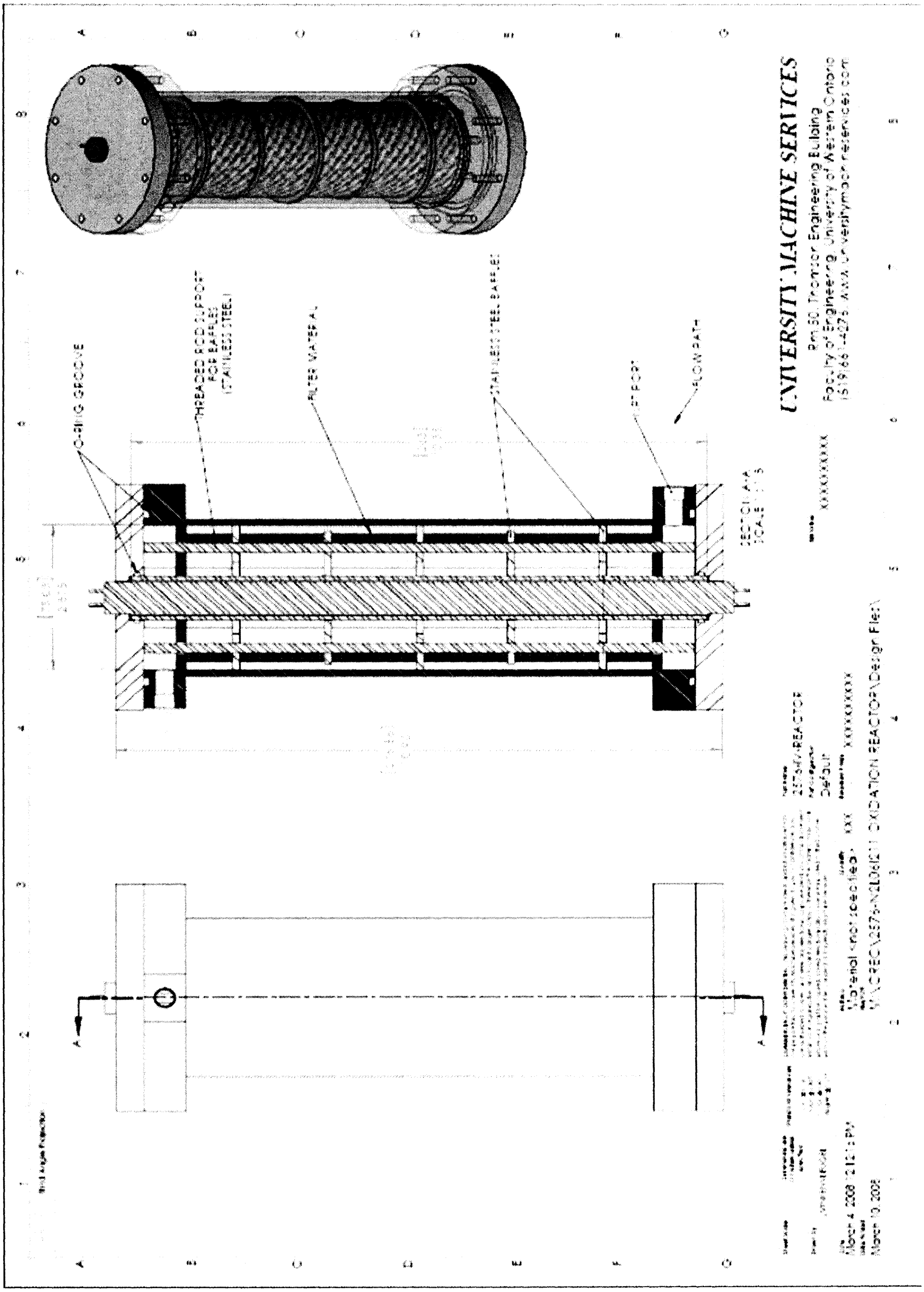


Figure 3.3 Design of the photocatalytic reactor-1

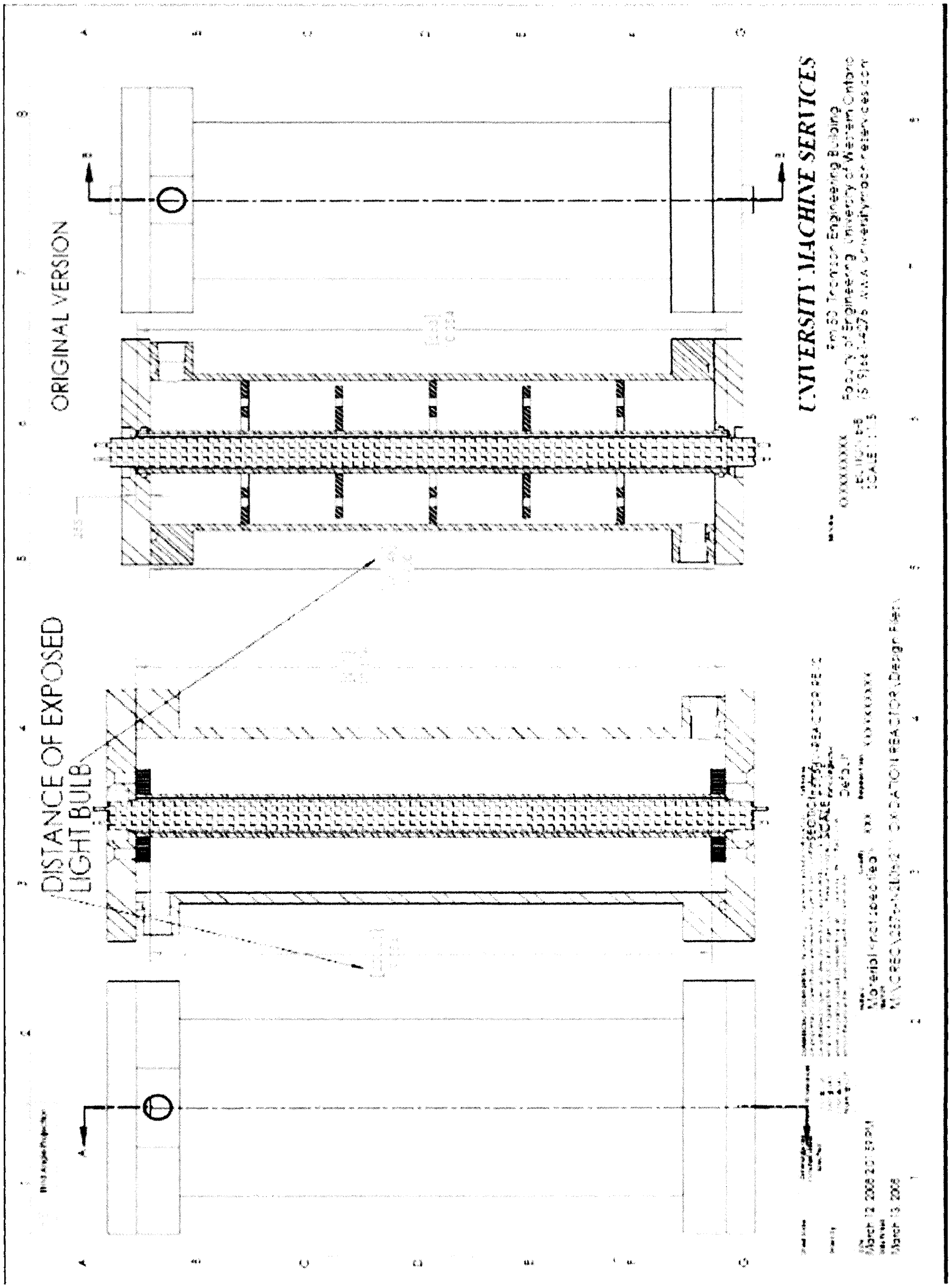


Figure 3.4 Design of the photocatalytic reactor-2

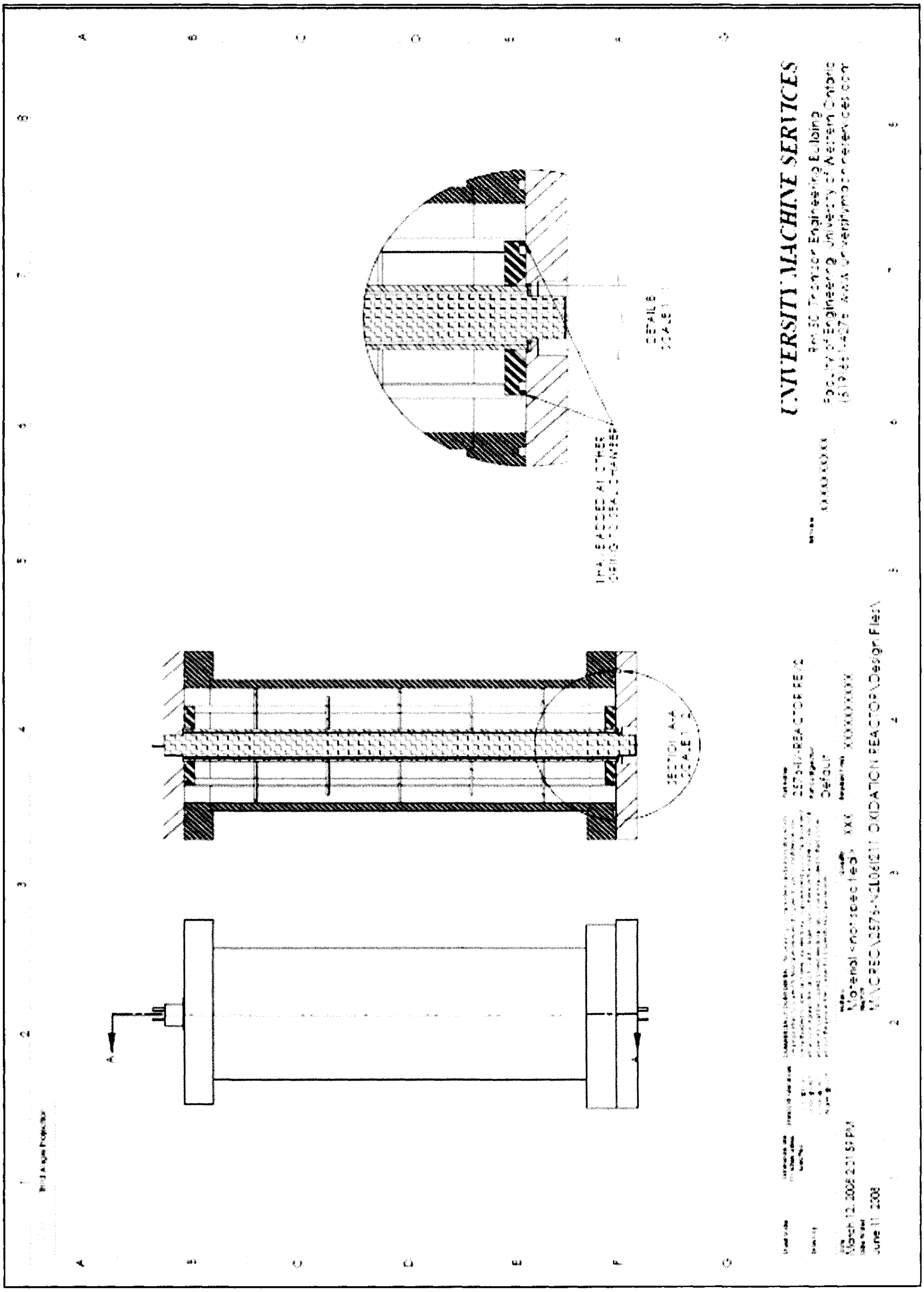


Figure 3.5 Design of the photocatalytic reactor-3

3.2.2 The Baffle System inside the Photocatalytic Reactor

A baffle system as shown in Figure 3.6 was used to improve the mass transfer efficiency of the reactants within the photocatalytic reactor. It is located at the centre of the annular photocatalytic reactor and can be easily put in or taken out of the inside of reactor. The effect of baffle system on the air flow in the photocatalytic reactor was shown in Figure 3.7.

The baffles were made of stainless steel. One group of baffles has the diameter of 73 mm, the same as the inside diameter of photocatalytic reactor. These baffles have a hole at the center with diameter of 30 mm. Another group of baffles has the diameter of 65 mm with a hole of 22 mm in diameter. There are six small holes in each baffle and six wires made of stainless steel are screwed in these holes. The position of each baffle can be adjusted by screwing along the metal wires. The baffles in these two groups were put together alternately by the metal wires to ensure a uniform flow in the reactor. The immobilized photocatalyst supported on activated carbon cloth can be conveniently located around the six metal wires.

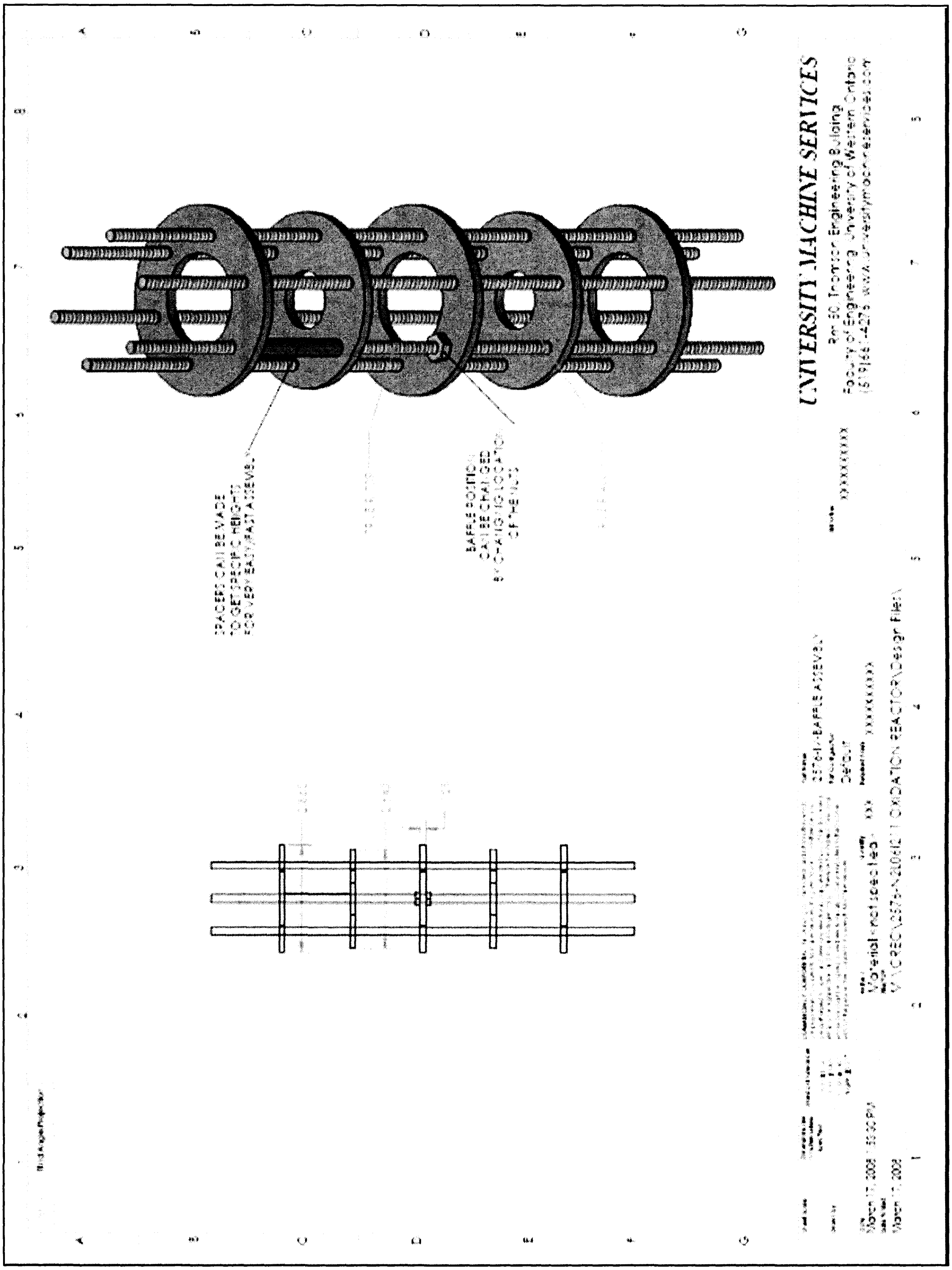


Figure 3.6 The baffle system located inside the photocatalytic reactor

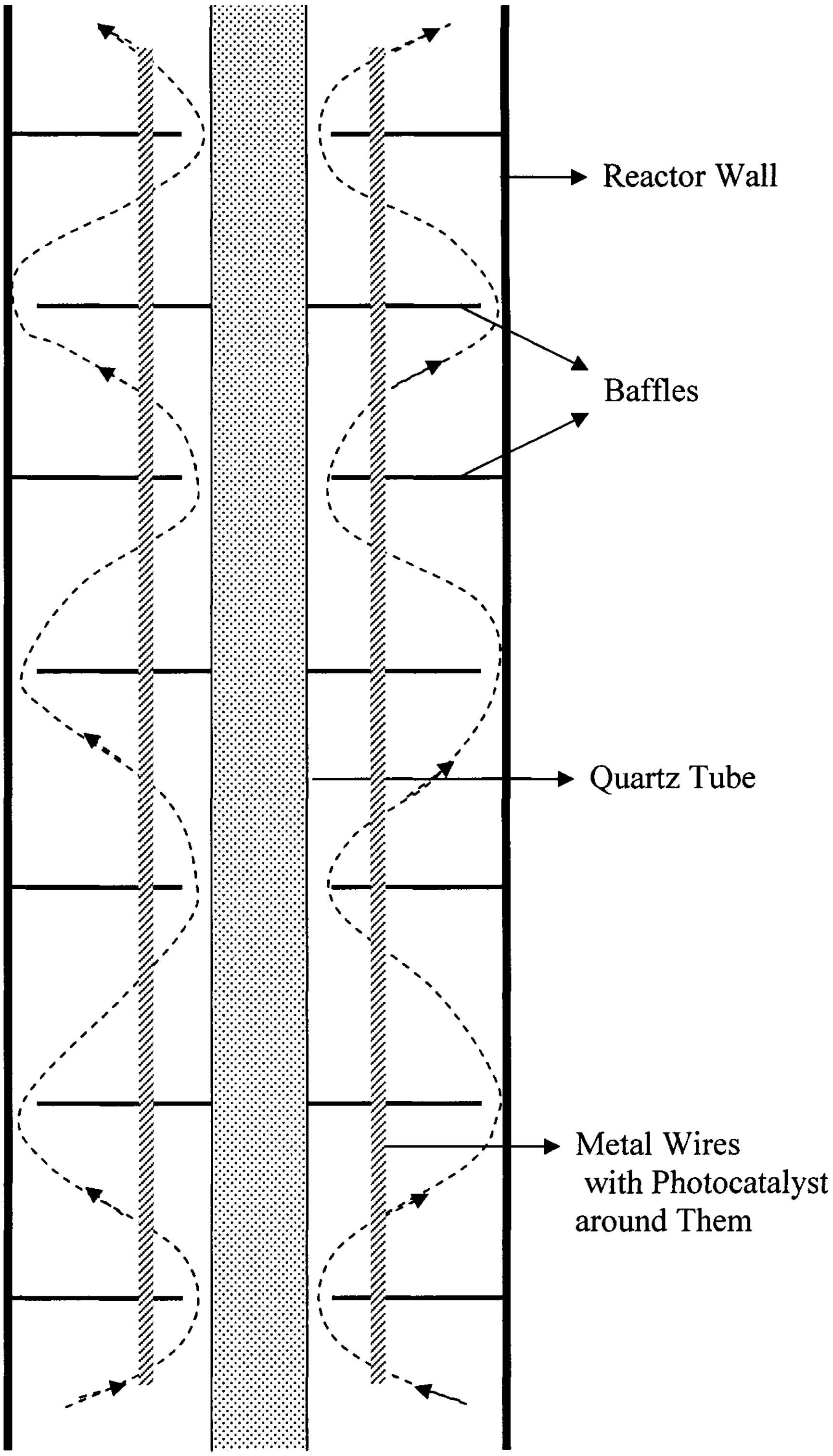
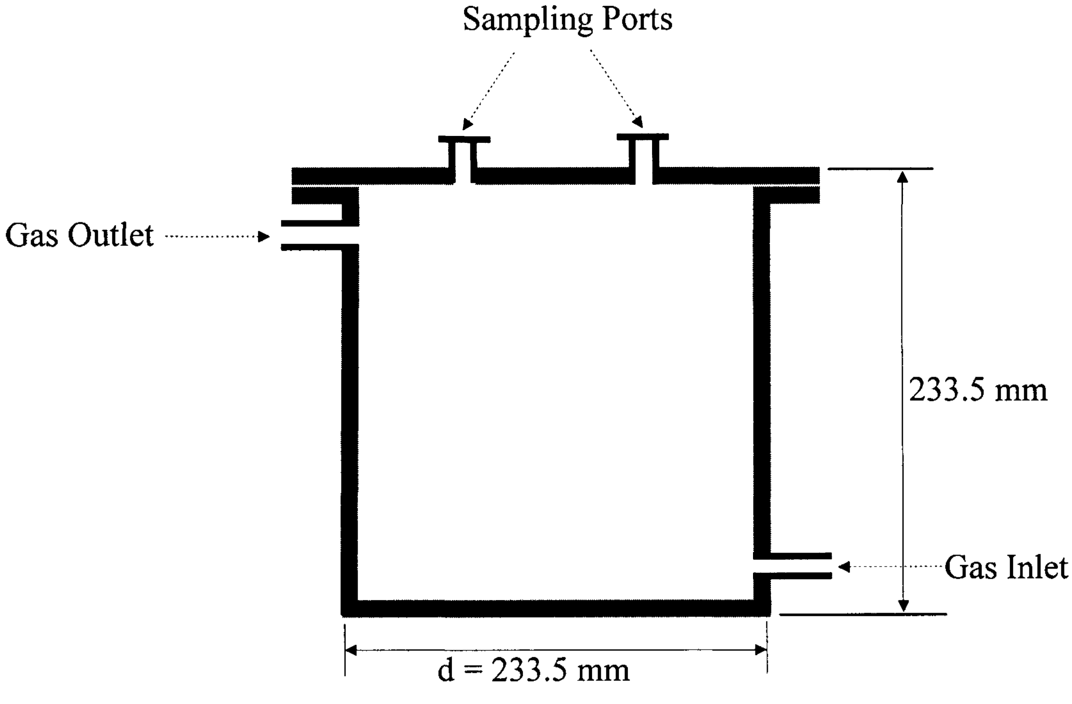


Figure 3.7 The effect of baffle system on the air flow in the annual photocatalytic reactor

3.2.3 The Gas Buffer Tank

A gas buffer tank made of stainless steel with a cylindrical structure was employed to generate an air flow with stable concentration of air pollutants by premixing the air flows. The design of the buffer tank was shown in Figure 3.8. There are gas inlet and outlet on the wall of the buffer tank which can be connected to a hose. The cover of the buffer tank is sealed by an O-ring to prevent the tank from gas leaking. Two sampling ports are located on the top of the buffer tank cover and sealed by silicone septa which are the same as those used for GC injectors.



Cylindrical Gas Buffer Tank

Figure 3.8 The design of the cylindrical gas buffer tank

Chapter 4

Photocatalyst Preparation and Evaluation

4.1 Photocatalyst Preparation

Titanium dioxide (TiO_2) powder used in this study for the photocatalyst preparation is Degussa P25 (Degussa, Germany). It is non-porous material with an approximate composition of 75% anatase and 25% rutile forms of TiO_2, a BET surface area of 50 ± 15 m^2/g and a primary particle size of 20 nm.

Two types of material were used as photocatalyst supports. One is borosilicate glass slides (microscope slides, 26 mm x 76 mm x 1 mm, Bio Nuclear Diagnostics Inc.); another is activated carbon cloth (Model 38002, Universal Replacement Carbon Pre-filter, Honeywell).

Photocatalysts were prepared using three methods: modified sol-gel method, dip coating method, and powder coating method. The photocatalyst identification and their corresponding preparation methods were listed in Table 4.1. Their detailed preparation methods were described as follows.

4.1.1 Modified Sol-Gel Method

The photocatalyst SGDS10 was prepared by the modified sol-gel method. First, 100 mL of silica colloid with 10 wt% SiO_2 was made by dilution of 30 wt% colloidal silica (Ludox AM-30 colloidal silica, 30wt% SiO_2 in water, Aldrich) by distilled water. Then 10g of TiO_2 P25 powder (Degussa, Germany) was added slowly into it, followed by stirring vigorously for 1 hour for better particle dispersion. Microscope slides (borosilicate glass, 26 mm x 76 mm x 1 mm, Bio Nuclear Diagnostics Inc.) as photocatalyst support were dipped into the above suspension for 2 minutes before they were pulled out manually at a constant speed of 0.5 cm/min. The glass slides with the first coating were dried at room temperature for 24 hours.

These coated glass slides were further coated with TiO_2 by a sol-gel process. They were soaked in TiO_2 sol for 2 minutes, then pulled out very slowly at a constant speed 0.5 cm/min. After drying at room temperature for 24 hours and 100 °C for 5 hours, they were calcinated in an oven at 600 °C for 1 hour with the ramp rate of 3 °C/min. The TiO_2 sol was prepared by titanium (IV) isopropoxide hydrolysis. The detailed process was described as follows (Chen and Dionysiou, 2006): (1) Prepare 100 mL of 0.5 M titanium (IV) isopropoxide (TTIP, 97 %, Aldrich) solution in 2-propanol ($\geq$99.8 %, Sigma-Aldrich). (2) Add 21.0 g of diethanolamine (DEA, 99%, Aldrich) into above 0.5 M TTIP solution with stirring at room temperature for 2 hours. The molar ratio of DEA/TTIP is 4. (3) Add 1.8 mL of distilled water dropwise into the above solution under vigorous stirring (H_2O/TTIP molar ratio = 2). The mixture was stirred for at least 5 hours and a clear and stable TiO_2 sol was obtained. This TiO_2 sol is stable for several months.

4.1.2 Powder Coating Method

The photocatalysts PCDS10, PCDS15 and PCDS20 were prepared by powder coating method. The preparation procedure is as follows: (1) TiO_2 P25 powder (Degussa, Gemany) was mixed well with acrylic resin powder (PPG Industries) and ground for 10 minutes to get the fine powder mixture. (2) The microscope slides (borosilicate glass, 26 mm x 76 mm x 1 mm, Bio Nuclear Diagnostics Inc.) were cleaned by acetone followed by distilled water. (3) The glass slides were heated in oven at 200 °C for 10 minutes. (4) The TiO_2-acrylic mixture was sprayed on the hot surface of glass slides by the spray gun of powder coating facility. (5) The glass slides with powder coating were heated in an oven at 200 °C for 15 minutes in order to form a fixed coating. The amounts of TiO_2 P25 powder in the mixtures were 10, 15, and 20 wt% for the photocatalysts PCDS10, PCDS15 and PCDS20, respectively. The powder mixture was coated on both sides of the glass slides.

The photocatalyst PC-30%SiO_2/AC, which used activated carbon cloth (Honeywell) as its support, was prepared by the powder coating method that has a little difference from the above method. First, the activated carbon cloth was sprayed by 30 wt% colloidal silica (Ludox AM-30 colloidal silica, 30 wt% SiO_2 in water, Aldrich) on its both sides. Then TiO_2 P25 powder (Degussa) was uniformly sprayed on the wet surface of activated carbon cloth by the spray gun of the powder coating facility. It was dried at room temperature for 24 hours, followed by drying at 105 °C for 6 hours. The wet colloidal silica sprayed on the activated carbon cloth surface acted as a binding material to hold the TiO_2 particles. This method avoided introducing polymer in the photocatalytically active coating of immobilized photocatalyst and the conditioning process by heating in oven was also not needed.

4.1.3 Dip Coating Method

The photocatalyst 10%TiO_2-30%SiO_2/AC was prepared by the dip coating method. The first step of dip coating is to make the dip coating suspension by adding 50 g of TiO_2 P25 powder (Degussa) into 500 mL of 30 wt% colloidal silica (Ludox AM-30 colloidal silica, 30 wt% SiO_2 in water, Aldrich), followed by stirring for 30 minutes. Then pieces of activated carbon (AC) cloth (Honeywell) were dipped into the above suspension for 2 minutes. After these soaked activated carbon pieces were drawn out from the above suspension gently, they were dried at room temperature for 24 hours then at 105 °C for 6 hours.

The photocatalysts 10%TiO_2-20%SiO_2/AC, 10%TiO_2-10%SiO_2/AC, and 10%TiO_2/AC were prepared using the same method except that the 20 wt% colloidal silica, 10 wt% colloidal silica, and distilled water were used respectively instead of 30 wt% colloidal silica. The 20 wt% and 10 wt% colloidal silica were made by diluting the commercial Ludox AM-30 colloidal silica with 30 wt% SiO_2 by distilled water.

Table 4.1 Photocatalyst prepared using different methods

Photocatalyst	**Preparation Method**
SGDS10*	Modified sol-gel
PCDS10**	Powder coating
PCDS15**	Powder coating
PCDS20**	Powder coating
10%TiO_2-10%SiO_2/AC***	Dip coating
10%TiO_2-20%SiO_2/AC***	Dip coating
10%TiO_2-30%SiO_2/AC***	Dip coating
10%TiO_2/AC***	Dip coating
PC- 30%SiO_2/AC***	Powder coating

* SGDS10 is the photocatalyst prepared by sol-gel method (SG) with double sides (DS) coated. TiO_2 content in the sol suspension is 10 (w/v)%.

** PCDC10 is the photocatalyst prepared by powder coating method (PC) with double sides (DS) coated. TiO_2 content in the powder mixture is 10 wt%. PCDS15 and PCDS20 were prepared by the same procedure except that TiO_2 content in the powder mixture is 15 and 20 wt%, respectively.

*** 10%TiO_2-10%SiO_2/AC is the photocatalyst prepared by dip coating method with activated carbon (AC) cloth as support. The dip coating suspension contains 10 (w/v)% TiO_2 and 10 (w/v)% SiO_2. 10%TiO_2-20%SiO_2/AC and 10%TiO_2-30%SiO_2/AC were prepared by the same procedure, but the dip coating suspension contains 20 and 30 (w/v)% SiO_2, respectively. The dip coating suspension of 10%TiO_2/AC consists of only 10 (w/v)% of TiO_2 and has no SiO_2 in it. PC-$SiO_2$30/AC is the photocatalyst with TiO_2 coated on activated carbon (AC) cloth prepared by powder coating (PC) method with the assistance of 30 wt% colloidal silica.

4.2 Photocatalyst Evaluation

4.2.1 Photocatalyst Evaluation Method

Experimental Setup for Photocatalyst Evaluation

The photocatalytic oxidation activity of prepared photocatalysts was evaluated by a batch reactor shown in Figure 4.1. The reactor was made of glass. An 8W UV-A lamp (Fluorescent Blacklight Blue Lamp F8T5/BLB, 8W, wavelength peak at 365 nm, VWR), located 2 cm above the photocatalyst, was mounted in a quartz tube. The photocatalyst was supported on three glass holders. The dimensions of the photocatalyst used in the batch reactor are 21.4 cm x 11.0 cm.

1000 mL of oxalic acid (OA) solution with initial concentration of either 0.005 M or 0.01 M was used as the evaluation solution. The extent of the oxalic acid degradation was an indication of the photocatalyst oxidation capability. The oxalic acid concentration was analyzed every one hour by taking 5.00 mL of oxalic acid solution from the batch reactor. The oxalic acid concentration versus reaction time was plotted for comparison of photocatalyst oxidation activity.

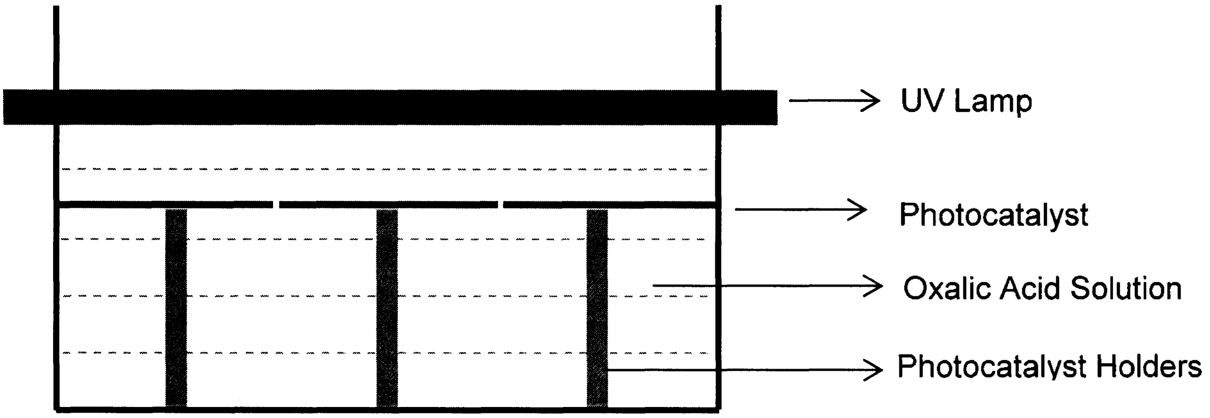


Figure 4.1 The batch reactor for photocatalyst activity evaluation

Evaluation Method for Photocatalyst Activity

The activity of prepared photocatalysts was evaluated by the method of oxalic acid (OA) degradation. Oxalic acid was used as model compound for the photocatalytic activity evaluation because it can be completely oxidized to carbon dioxide and water, and its concentration measurement by potassium permanganate titration is quick, accurate, and easy to operate.

The concentration of oxalic acid was measured by potassium permanganate ($KMnO_4$) titration. The reaction involved in the analysis process is a redox reaction which is expressed as

$$2\ MnO_4^- + 5\ C_2O_4^{2-} + 16\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$$

The following solutions need to be prepared for the photocatalyst evaluation:

(1) 0.01 M oxalic acid solution

0.9003 g of oxalic acid (anhydrous, ≥99 %, Aldrich) was dissolved in 20 mL of distilled water in a 100 mL beaker with stirring. Then this solution was totally transferred into a 1000 mL volumetric flask and diluted it to 1000.00 mL. The volumetric flask must be used in order to get the precise molar concentration of oxalic acid. This oxalic acid solution with the known molar concentration is used to standardize the $KMnO_4$ solution.

(2) 0.001 M potassium permanganate ($KMnO_4$) solution

0.1580 g of $KMnO_4$ (≥99.0 %, Fluka) was dissolved in 20 mL of distilled water in a 100 mL beaker with stirring, then it was diluted to 1000.00 mL using a 1000 mL volumetric flask. The accurate concentration of the prepared $KMnO_4$ solution was standardized by the above oxalic acid solution with known concentration. The concentration of $KMnO_4$ needs to be calibrated every one week.

(3) 3 M H_2SO_4

16 mL of concentrated H_2SO_4 (95.0-98.0 %, Aldrich) was dissolved in 84 mL water. Volumes were measured by graduated cylinders.

The procedure of oxalic acid (OA) concentration measurement by potassium permanganate titration is as follows:

(1) Transfer the oxalic acid sample for analysis

Measure 5.00 mL of oxalic acid solution accurately by a 5 mL transfer pipette and transfer it into a 125 mL Erlenmyer flask, followed by adding 2.5 mL of 3 M H_2SO_4 to the flask by a graduated cylinder.

(2) Titrate the oxalic acid sample using $KMnO_4$ solution

A 50 mL burette was used for the titration. A small amount of $KMnO_4$ solution was added into the oxalic acid sample solution in the 125 mL Erlenmyer flask by the burette till the pink color appeared and persisted. Then it was heated gently till the pink color disappeared. The solution was further heated to about 75 °C by a water bath. Titration of this warm solution was continued until a light pink color appeared and persisted again. Record the volume of $KMnO_4$ used.

The calibration curve for the oxalic acid concentration measurement by the potassium permanganate titration was shown in Figure 4.2.

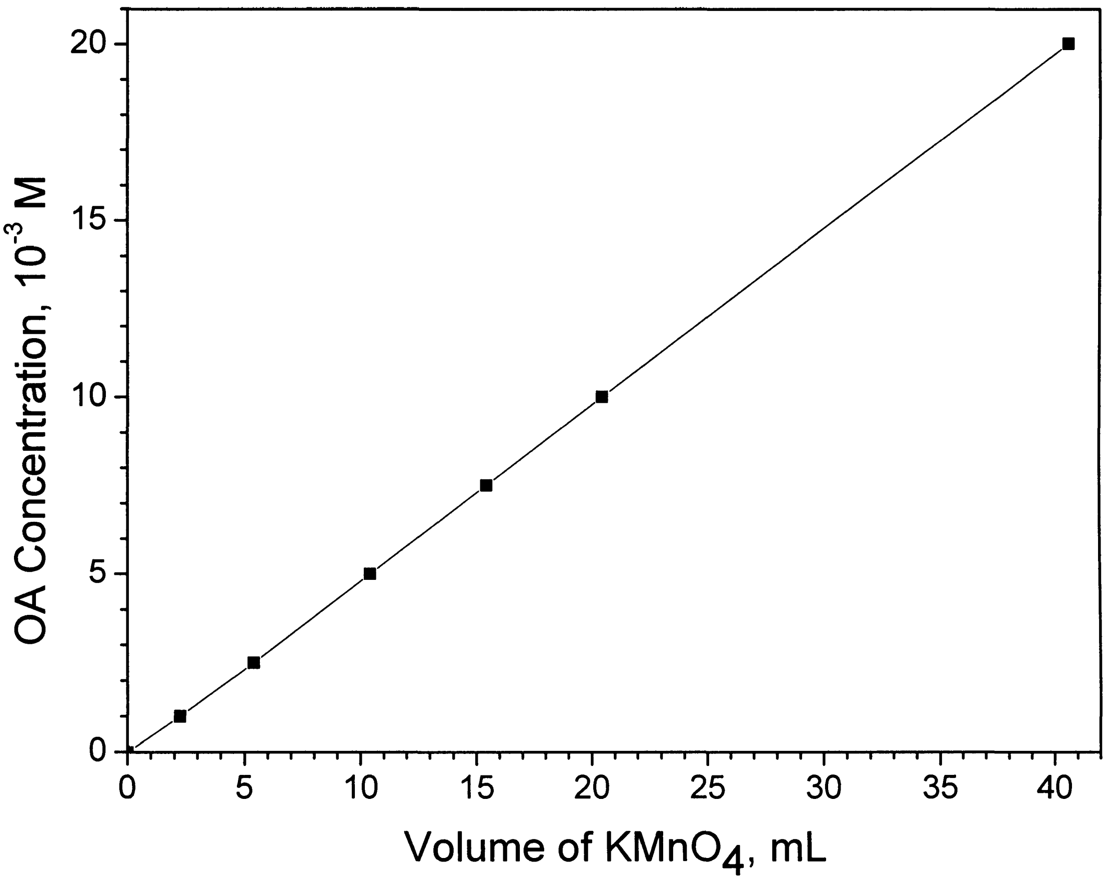


Figure 4.2 Calibration curve for oxalic acid (OA) concentration determination by the titration using 0.0009824 M of $KMnO_4$ solution

4.2.2 Photocatalyst Evaluation Results

Blank Tests for Photocatalytic Oxidation of Oxalic Acid

The batch reactor with an 8W UV-A lamp was used for the blank tests of photocatalytic oxidation of oxalic acid. The original concentration of oxalic acid was 0.005 M and 10%TiO_2-20%SiO_2/AC was used as the photocatalyst.

Two blank tests were carried out for the oxalic acid oxidation. One test used only UV irradiation and no photocatalyst was employed, while another test just had the photocatalyst but without UV light irradiation. For comparison, the oxalic acid degradation by photocatalytic oxidation using the UV light-activated photocatalyst 10%TiO_2-20%SiO_2/AC was also shown in Figure 4.3.

It was shown in Figure 4.3 that when either the UV light or the photocatalyst was used, only a very small amount of oxalic acid was eliminated This concluded that using only UV or photocatalyst, rather than their combination, has little effect on oxalic acid oxidation. Once both the photocatalyst and UV light were used simultaneously, the photocatalyst was activated by the UV irradiation and the photocatalytic reaction was initiated. It is obvious that the oxalic acid concentration was reduced greatly by the photocatalytic oxidation process.

Photocatalytic Oxidation Activity of Photocatalysts Supported on Glass Slide

Three photocatalysts with glass slide support, PCDS10, PCDS15 and PCDS20, were prepared by the powder coating method. Their preparation procedures are the same except that the amounts of TiO_2 P25 powder in the mixtures are different. The PCDS10 has 10 wt% of TiO_2 in the mixture, while the PCDS15 and PCDS20 has 15 wt% and 20 wt% of TiO_2, respectively. The glass slide support was coated on both sides for each photocatalyst.

The photocatalytic oxidation activity of the three photocatlysts are shown in Figure 4.4 by the degradation of oxalic acid with the initial concentration of 1×10^{-3} M. It was found from the results that the photocatalyst PCDS20 showed the highest activity for oxalic acid degradation. PCDS10 had the lowest oxidation activity, and PCDS15 presented the activity in the middle. For these three photocatalysts, the only difference is the TiO_2 content in the coating of each photocatalyst; thus their difference on photocatalytic oxidation activity can be related to their TiO_2 content in the coating. From the experimental results, it can be concluded that the activity on photocatalytic degradation of oxalic acid is increased with the increase of TiO_2 content in the photocatalyst coating for these three photocatalysts prepared by the powder coating method. PCDS20 has the highest TiO_2 content in the coating, thus the highest oxalic acid degradation activity was observed. Due to the lowest TiO_2 content, PCDS10 showed weakest photocatalytic oxidation performance.

The photocatalytic oxidation durability test was carried out for the photocatalyst PCDS20. A total of four runs were carried out. Each run used the same photocatalyst and was operated under exactly the same conditions as mentioned above. The test time for each run was 120 hours. The durability test results are shown in Figure 4.5. The results indicated that the photocatalytic oxidation activity of PCDS20 was decreased with the increase in the number of runs. After the first and second runs, the photocatalytic activity was obviously decreased. The decrease of photocatalytic activity can be attributed to the loss of TiO_2 particles in the coating of the photocatalyst. The photocatalyst PCDS20 was prepared by the powder coating method in which polymer was used as the binding material. During photocatalytic reaction under the UV irradiation, the polymer existing in the coating of photocatalyst can also be oxidized by the highly oxidative photo-generated hydroxyl radicals. As the result of this oxidation process, the decomposition of the binding polymer occurred, leading to the loss of the photocatalytically active component TiO_2 particles in the coating of the photocatalyst. The decrease of photocatalytic degradation activity was due to the loss of TiO_2 active component. After the third run, the activity did not show much change because there was no much TiO_2 lost in the photocatalyst coating.

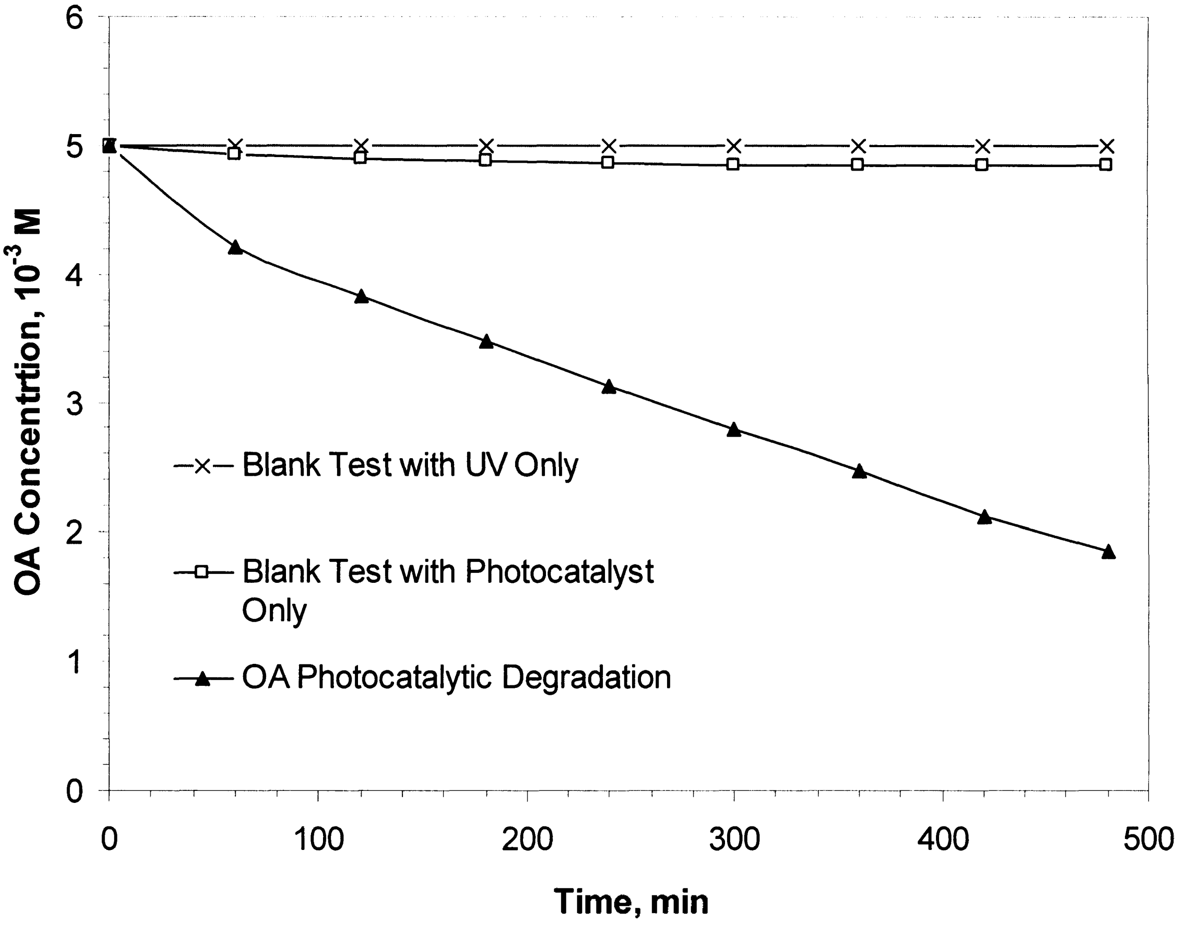


Figure 4.3 Blank tests for photocatalytic degradation of oxalic acid (OA)

Photocatalyst SGDS10 made by the modified sol-gel method was compared with PCDS20 prepared by the powder coating method for the photocatalytic degradation of oxalic acid. The most notable difference between these two photocatalysts is the coating composition on the glass support, which is determined by the preparation methods. Unlike PCDS20 with binding polymer mixed with TiO_2 particles in the coating (some of TiO_2 particles may be covered by the polymer after heat treatment), the SGDS10 made by modified sol-gel method has only TiO_2 particles existing in the coating and the TiO_2 particles were not covered. Due to the higher TiO_2 content in the photocatalyst coating, SGDS10 showed better performance for the oxalic acid oxidation. The results were shown in Figure 4.6.

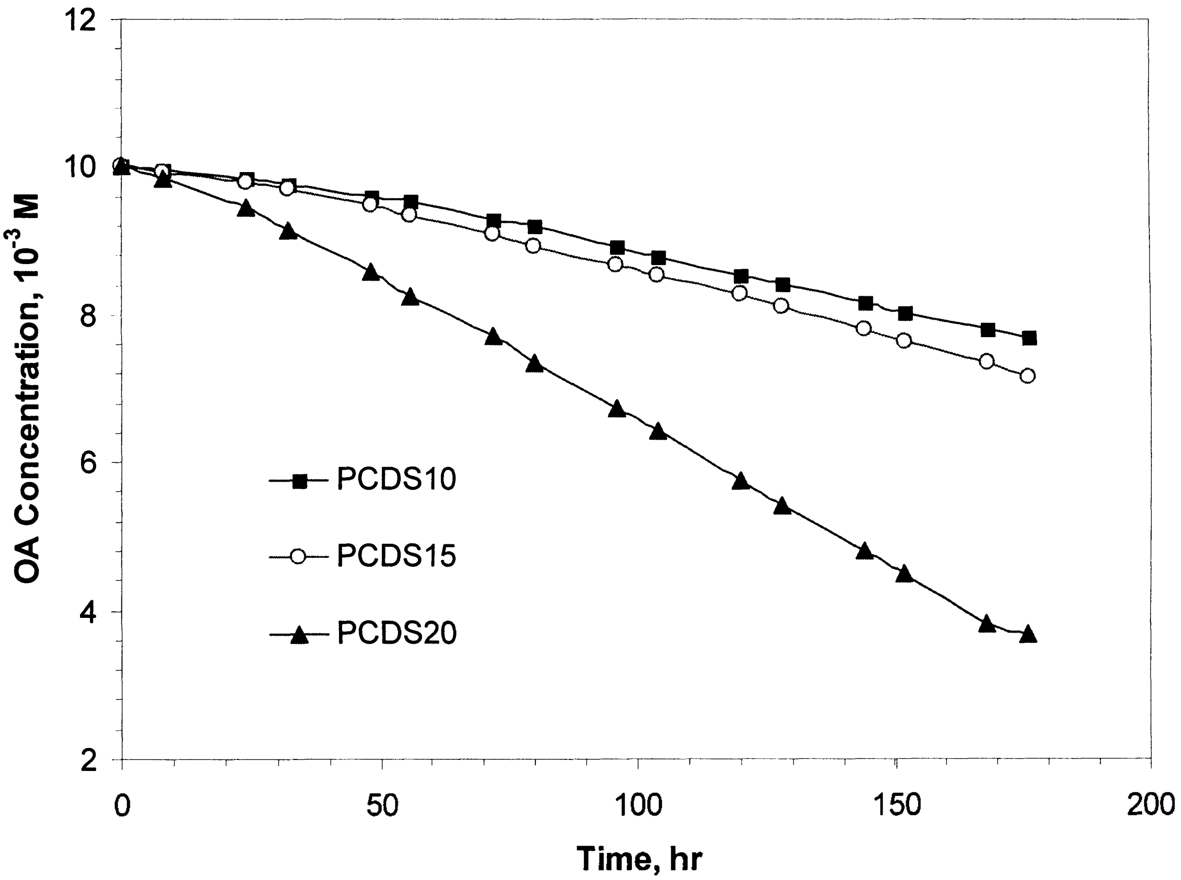


Figure 4.4 Photocatalytic degradation of oxalic acid using different photocatalysts supported on glass.

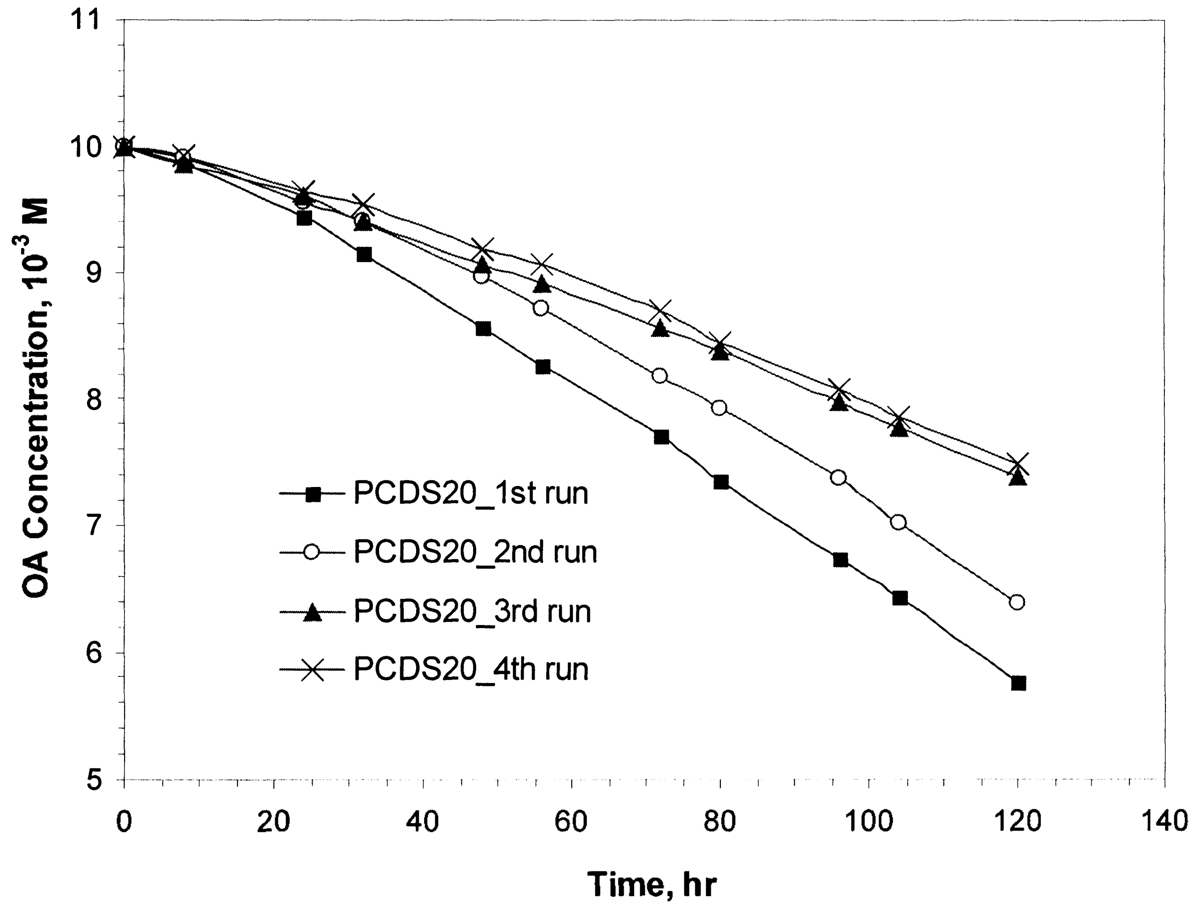


Figure 4.5 Photocatalytic durability test for the photocatalyst PCDS20

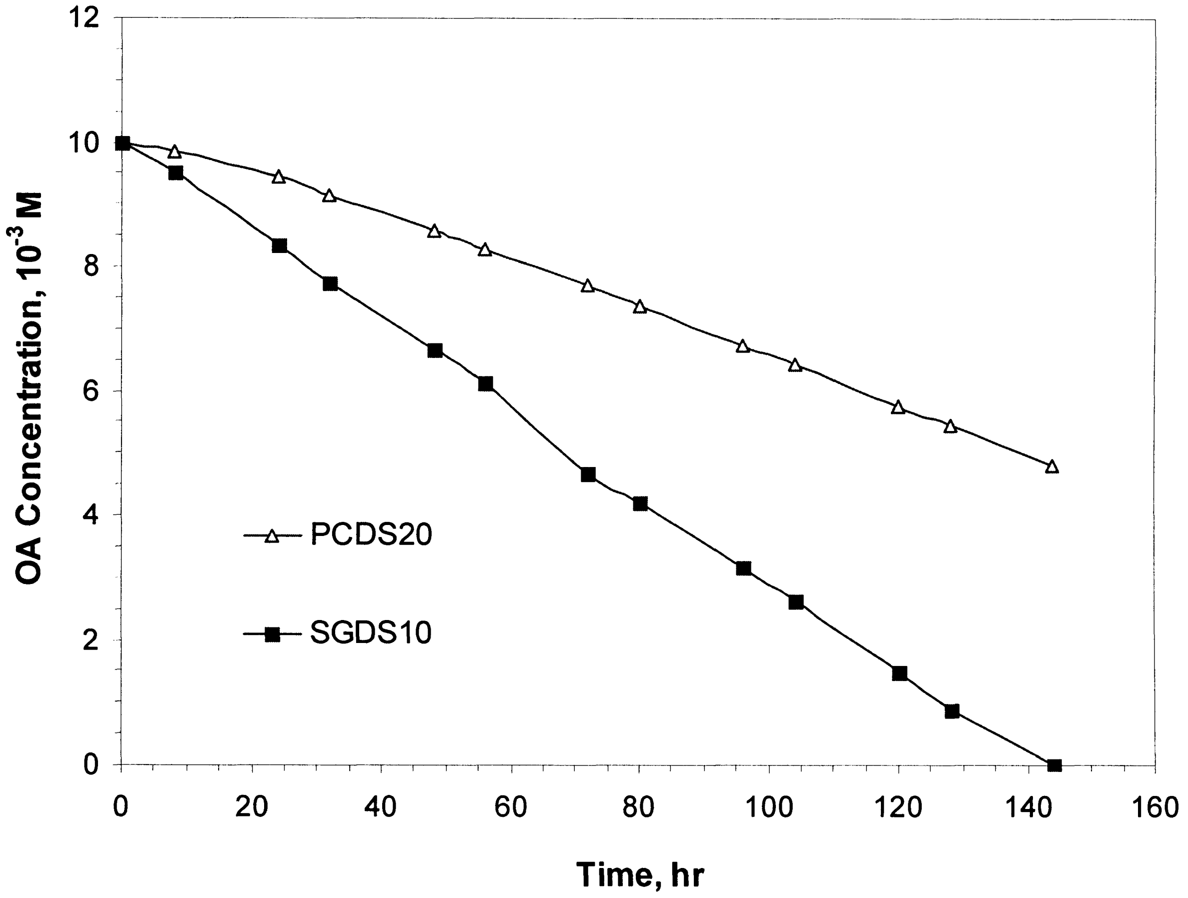


Figure 4.6 Comparison of oxalic acid (OA) degradation activity of photocatalysts prepared by different methods

* PCDS 20 was prepared by powder coating method while SGDS10 was prepared by modified sol-gel method.

Photocatalytic Oxidation Activity of Photocatalysts with Activated Carbon Cloth as Support

Four photocatalysts using activated carbon cloth as support were prepared by the dip coating method. All of the photocatalysts were made following the procedures in Chapter 4 (see pages 60 to 62). The dip coating suspensions were made by mixing TiO_2 P25 powder with colloidal silica with certain concentration of silica. The TiO_2 content in the mixed suspension is the same for all the photocatalysts, which is 10 %(w/v). The only difference for the photocatalysts 10%TiO_2-30%SiO_2/AC, 10%TiO_2-20%SiO_2/AC, 10%TiO_2-10%SiO_2/AC, and 10%TiO_2/AC is that 30 wt% colloidal silica, 20 wt% colloidal silica, 10 wt% colloidal silica, and distilled water were used respectively to make the dip coating suspensions for each photocatalyst.

The photocatalytic oxidation activities for the above four photocatalysts are shown in Figure 4.7. The results indicated that 10%TiO_2-10%SiO_2/AC and 10%TiO_2/AC have almost the same photocatalytic oxidation activities, but their activities are higher than that of 10%TiO_2-20%SiO_2/AC. Similarly the activity of 10%TiO_2-20%SiO_2/AC is higher than that of 10%TiO_2-30%SiO_2/AC. It was shown from the results that the greater the silica concentration in the dip coating suspension, the weaker the photocatalytic oxidation activity of the corresponding photocatalyst. The photocatalytic oxidation activity of 10%TiO_2-10%SiO_2/AC was also compared with that of PC-30%SiO_2/AC prepared by the powder coating method with activated carbon cloth as the support. The results in Figure 4.8 showed that the photocatalytic oxidation activity of PC-30%SiO_2/AC was only a little lower than that of 10%TiO_2-10%SiO_2/AC.

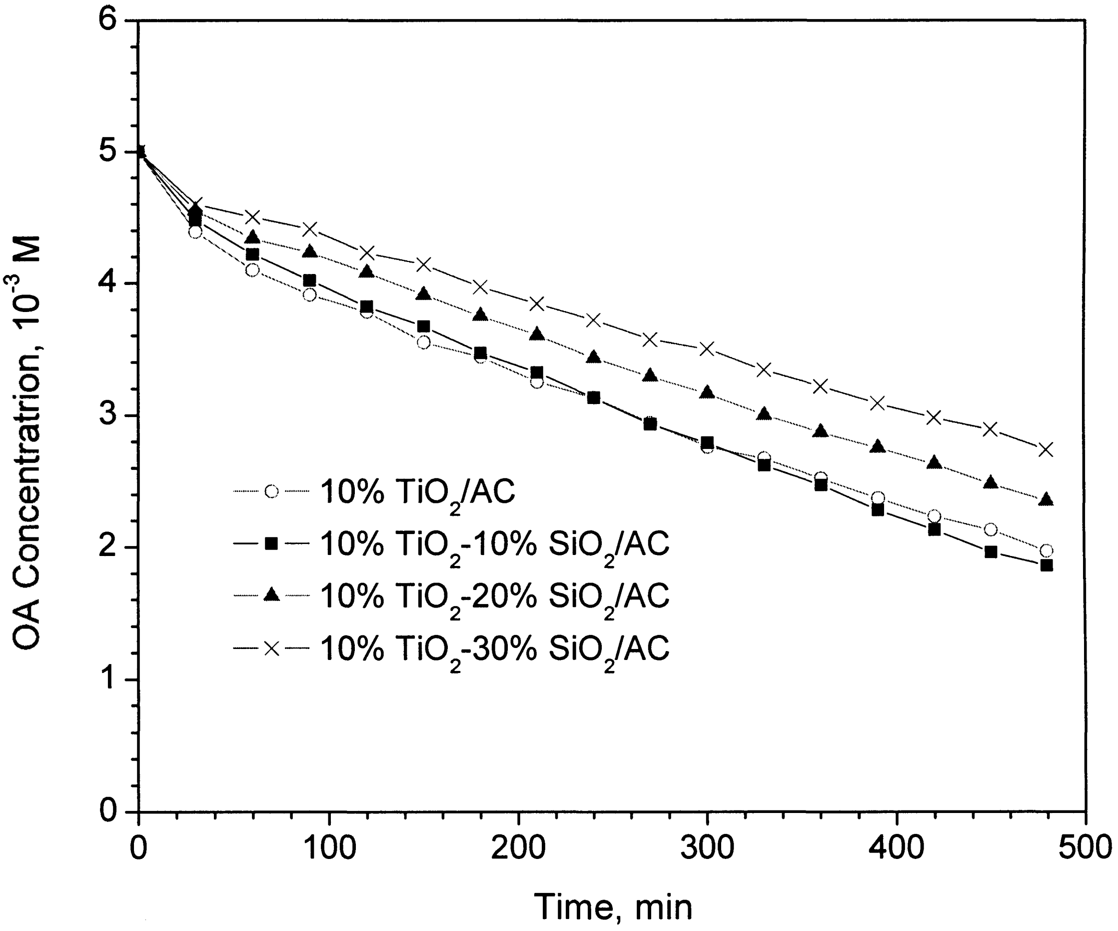


Figure 4.7 Photocatalytic degradation of oxalic acid using different activated carbon supported photocatalysts

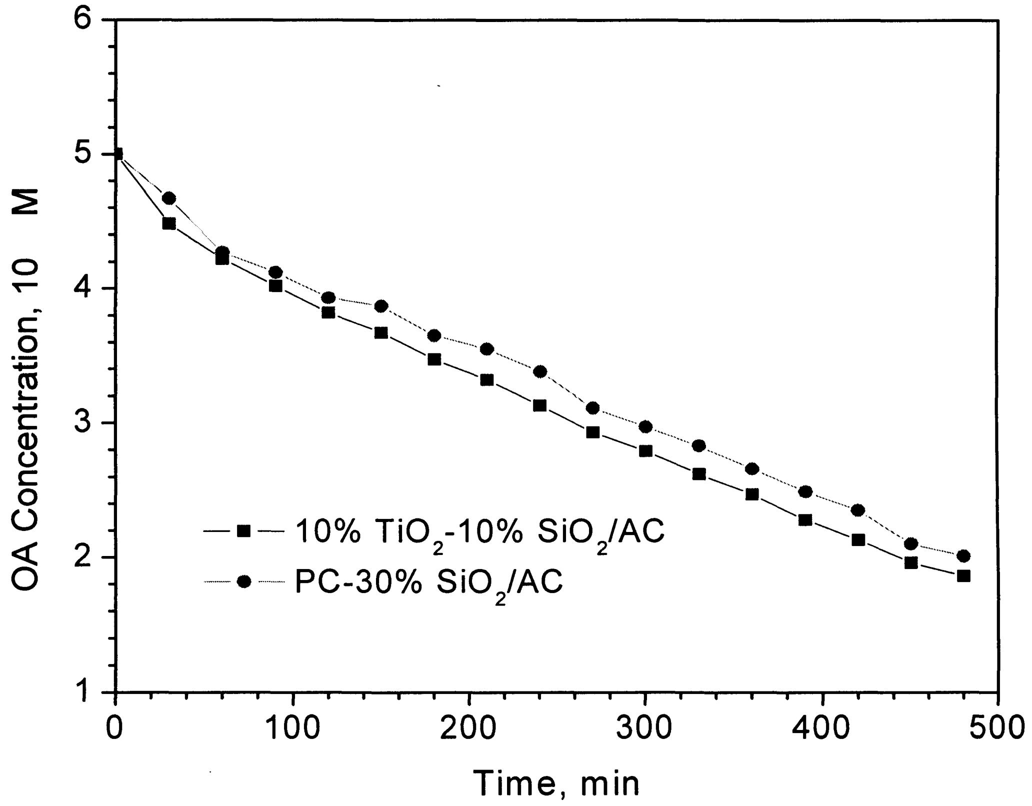
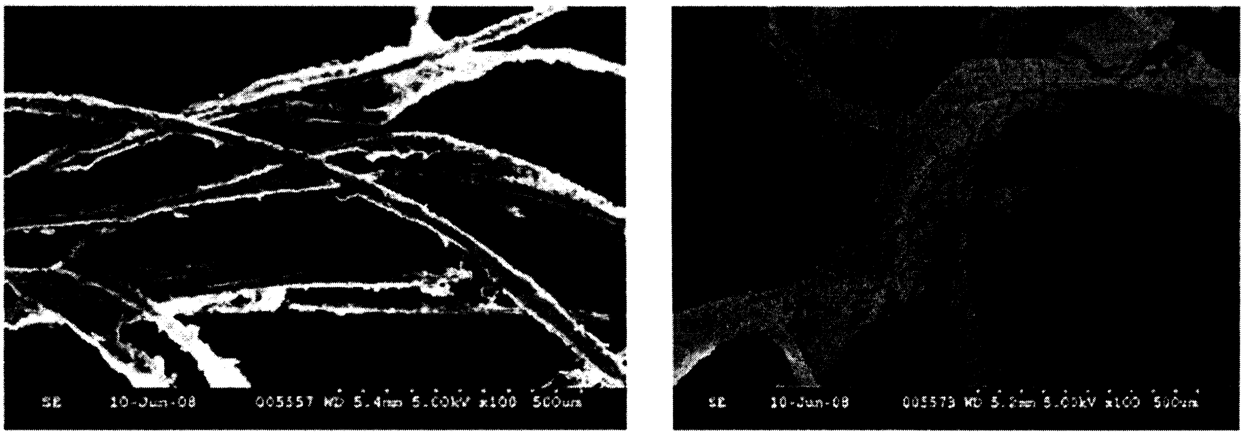


Figure 4.8 Comparison of oxalic acid (OA) photocatalytic degradation activity of activated carbon supported photocatalysts prepared by dip coating and powder coating methods

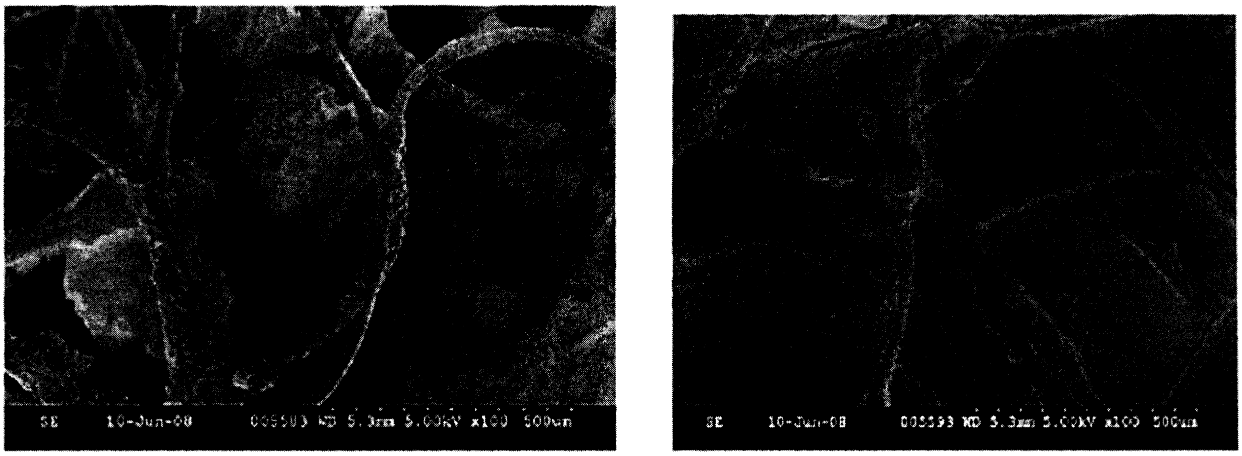
The main purpose of using colloidal silica in the dip coating suspension is to make it serve as a binding material to fix the TiO_2 particles firmly on the surface of activated carbon support because TiO_2 particles and activated carbon cloth have relatively weaker combination. But the negative effect of using silica is that it can cover a portion of TiO_2 particles in the coating of photocatalysts and thus lower the photocatalytic oxidation activity. The covering effect is more obvious for the photocatalyst prepared by the dip coating suspension with higher silica concentration, and this is why $10\%TiO_2$-$10\%SiO_2/AC$ and $10\%TiO_2/AC$ showed the higher photocatalytic oxidation activities.

Silica serving as the binding material was clearly shown by the SEM images in Figure 4.9. The images of scanning electron microscopy (SEM) of photocatalysts were taken by the Hitachi Variable-Pressure Scanning Electron Microscope (VP-SEM). The magnification of these images is 100 times. For the photocatalyst 10%TiO_2/AC, the TiO_2 particles were attached only on the surface of activated carbon fibers and there were few TiO_2 particles existing in the voids among fibers because no silica as binding material was used for the preparation of 10%TiO_2/AC. The photocatalysts 10%TiO_2-10%SiO_2/AC, 10%TiO_2-20%SiO_2/AC and 10%TiO_2-30%SiO_2/AC all used silica as the binding material in the preparation process; therefore, TiO_2 particles were filled among the activated carbon fibers. But TiO_2 was only loosely filled in the voids of activated carbon fibers for 10%TiO_2-10%SiO_2/AC due to the lower content of silica in the coating. For 10%TiO_2-20%SiO_2/AC and 10%TiO_2-30%SiO_2/AC, TiO_2 particles were full of voids among the fibers due to higher content of silica as the binding material.

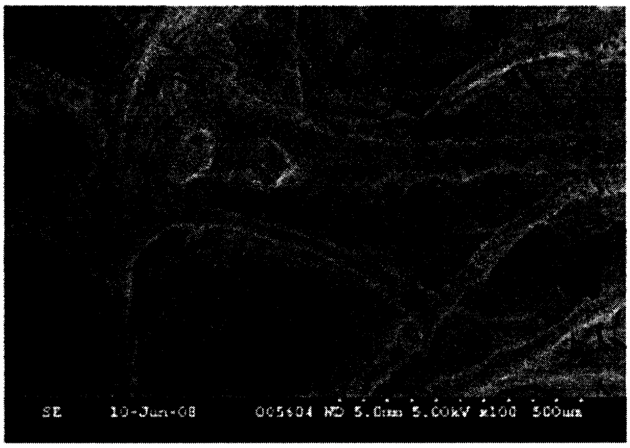
Figure 4.10 shows the SEM images of activated carbon-supported photocatalysts with the magnification of 5000 times. The images clearly illustrated that TiO_2 particles on the surface of photocatalysts 10%TiO_2/AC and 10%TiO_2-10%SiO_2/AC were in loose state, indicating that TiO_2 particles were not or seldom covered by silica. This explained why these two photocatalysts presented relatively higher photocatalytic oxidation activities. For photocatalysts 10%TiO_2-20%SiO_2/AC and 10%TiO_2-30%SiO_2/AC with increased silica contents, a large portion of TiO_2 particles was covered by silica molecules, which was shown by the smooth coating surfaces in Figure 4.10. The covering of TiO_2 particles by silica molecules accounts for the relatively lower photocatalytic oxidation activities of these two photocatalysts.



Activated Carbon Cloth (AC) **10%TiO_2/AC**

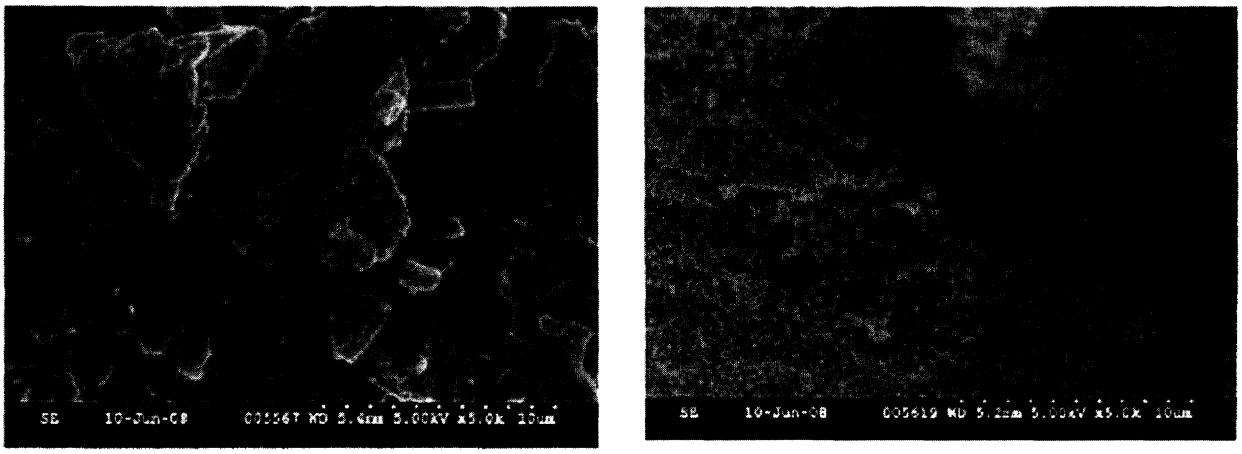


10%TiO_2-10%SiO_2/AC **10%TiO_2-20%SiO_2/AC**



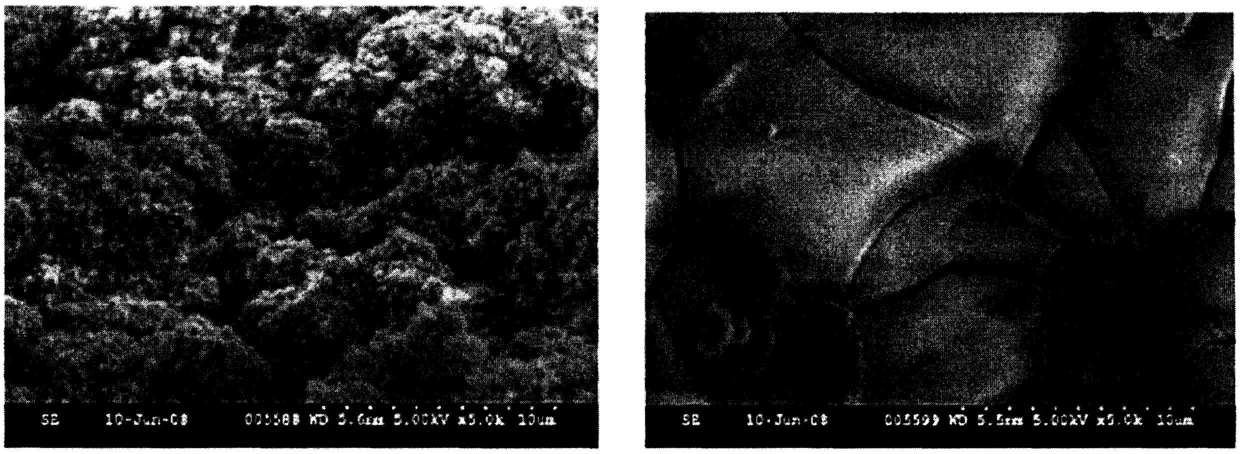
10%TiO_2- 30%SiO_2/AC

Figure 4.9 SEM images of photocatalysts with activated carbon cloth support prepared by dip coating method (Magnification × 100)



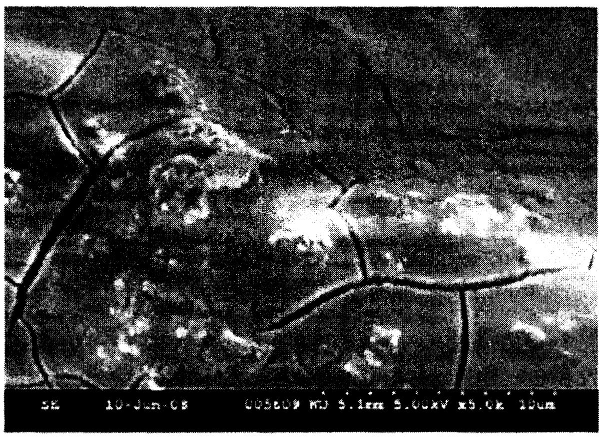
Activated Carbon Cloth (AC)

10%TiO$_2$/AC



10%TiO$_2$-10%SiO$_2$/AC

10%TiO$_2$-20%SiO$_2$/AC



10%TiO$_2$-30%SiO$_2$/AC

Figure 4.10 SEM images of photocatalysts with activated carbon cloth support prepared by dip coating method (Magnification × 5000)

Chapter 5

E. Coli K-12 Bioaerosol Disinfection in Indoor Air

5.1 E. Coli K-12Adsorption Equilibrium Test

In order to determine the Escherichia Coli (E. coli) K-12 inactivation effect of the indoor air purification device, adsorption equilibrium test was carried out with the photocatalyst 10%TiO_2-10%SiO_2/AC loaded inside the photocatalytic reactor. A blacklight blue lamp (F8T5/BLB, BULBTRONICS) with a peak emission at 365 nm (UV-A) and an energy output of 8 W was used as the light source for the photocatalytic reactor. The UV-A lamp was turned off during the adsorption test process. The air flow going through the bioaerosol nebulizing generator was 1.2 LPM, and an additional air flow with flow rate of 1.0 LPM was added to the air flow from the bioaerosol nebulizing generator, making the total flow passing the reactor being 2.2 LPM. The E. coli K-12 suspension in the bioaersol nebulizing generator was the 1/2000 dilution of the original suspension. The adsorption equilibrium tests were repeated under the same conditions for three times.

The results of the adsorption equilibrium tests are shown in Figures 5.1 and 5.2. Figure 5.1 shows the three parallel runs of the equilibrium tests, while Figure 5.2 is the average of these three runs. It was found that after 70 minutes the E. coli colony number (CFU) on the EMB agar plates becomes relatively stable. The average colony number on the surface of EMB agar plates from the samples collected after 70 min was denoted as N_a, and N is the colony number at a certain time. From the results of Figure 5.2 it is known that the adsorption equilibrium of the air contaminated by E. coli K-12 aerosol was reached after 70 minutes from the start of the run at the air flow rate of 2.2 LPM. So after 70 minutes the E. coli concentration in the outlet air flow of the photocatalytic reactor becomes stable. This adsorption equilibrium time was used for all the following E. coli K-12 inactivation tests. The UV-A lamp was switched on for the photocatalytic disinfection tests after the 70 minutes of equilibrium time.

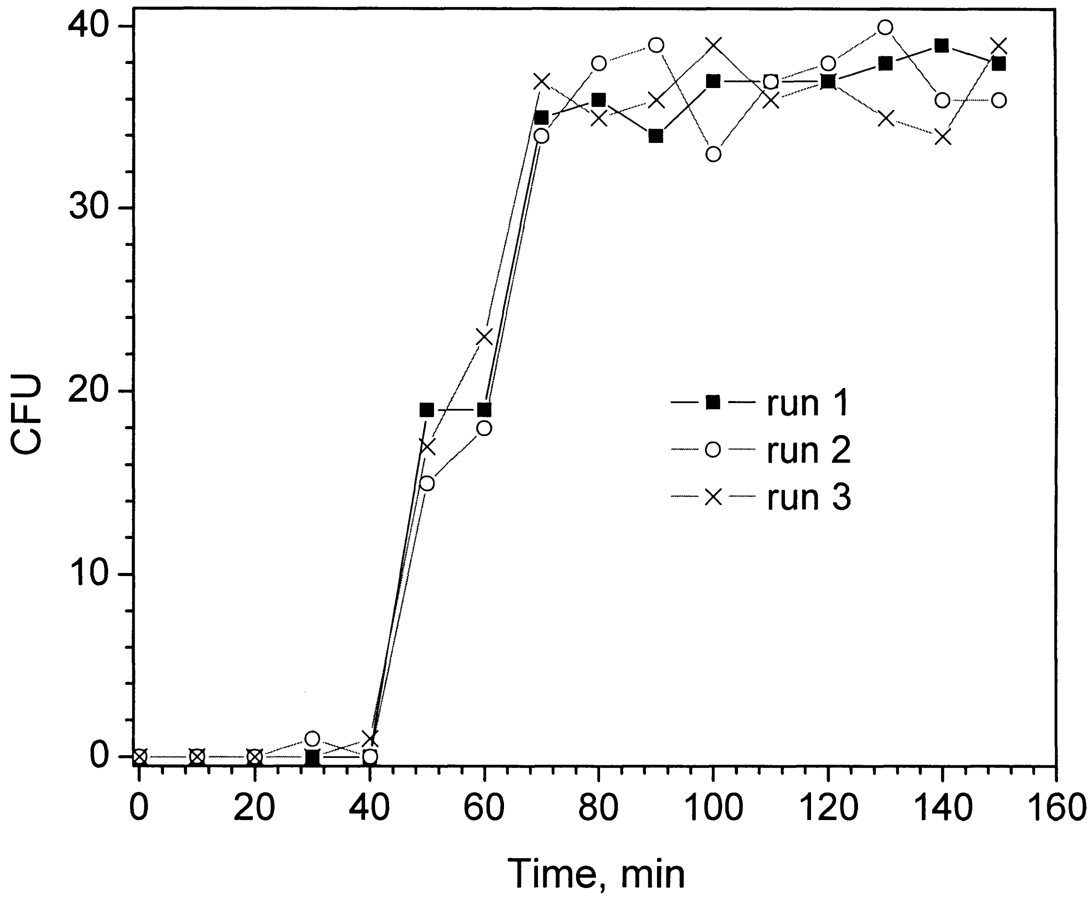


Figure 5.1 Three parallel runs of E. coli K-12 adsorption equilibrium test

*Test conditions: flow rate = 2.2 LPM; photocatalyst: 10%TiO_2-10%SiO_2/AC

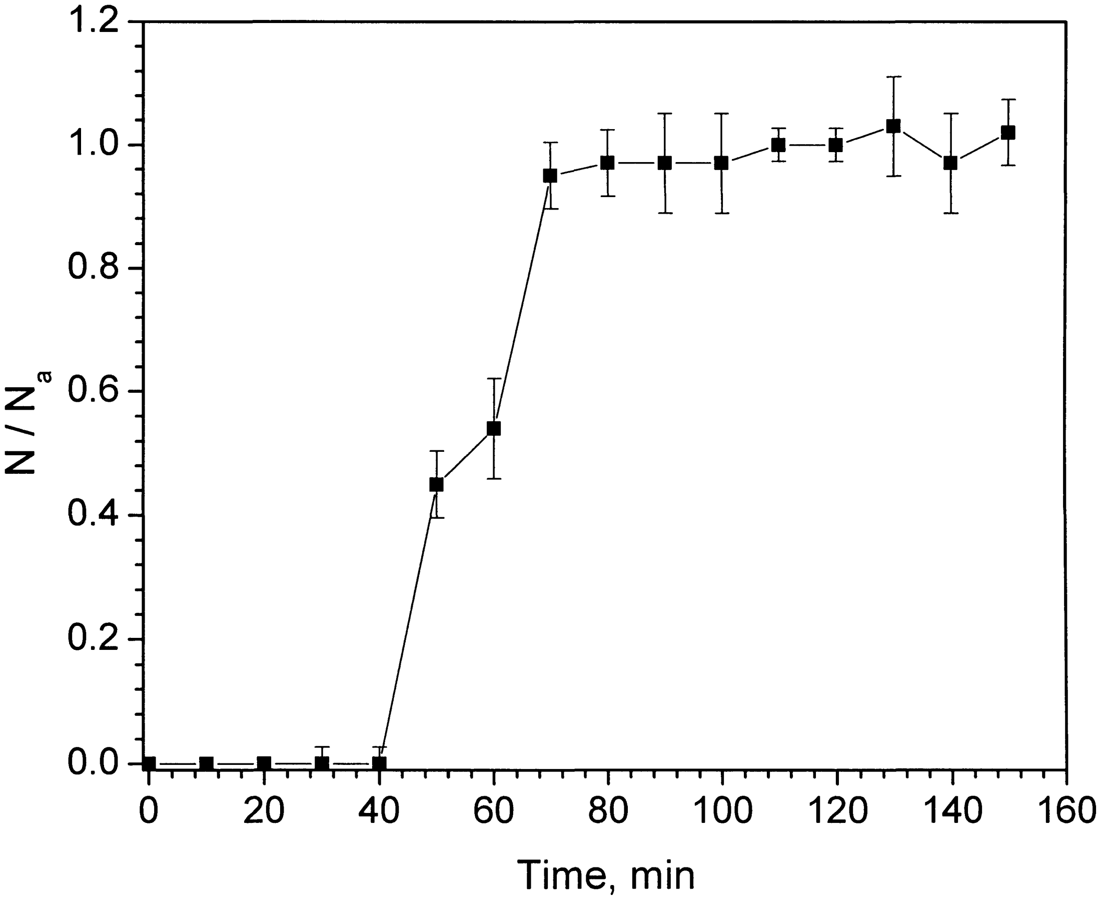


Figure 5.2 Average result of three parallel runs of E. coli K-12 adsorption equilibrium test *Test conditions: flow rate = 2.2 LPM; photocatalyst: 10%TiO_2-10%SiO_2/AC

5.2 E. Coli K-12 Photocatalytic Disinfection at Different Flow Rates

The effect of flow rate on E. coli K-12 disinfection was studied using 10%TiO_2-10%SiO_2/AC as photocatalyst irradiated by UV light with intensity of 7.09 mW/cm^2. Three flow rates of 1.2, 2.2 and 3.2 LPM were used for the tests. The air flow rate passing through the bioaerosol nebulizing generator is the same for all the three tests, which is 1.1 LPM. For the flow rate of 1.2 LPM, there is no additional air flow mixed with the air flow from the E. coli bioaerosol nebulizing generator, but for the flow rates of 2.2 and 3.3 LPM, additional air flows are needed with the flow rates of 1.0 and 2.0 LPM, respectively. The E. coli K-12 suspensions in the bioaerosol nebulizing generator were 1/2000, 1/1000, and 1/500 dilutions of the original suspension in LB broth respectively for the three air flows of 1.2, 2.2 and 3.2 LPM. When the adsorption equilibrium was reached after 70 minutes, the first sample was taken at $t = 0$ with the UV-A lamp off. The colony number (CFU) of the first sample was denoted as N_0. Immediately after the first sampling, the UV-A lamp was switched on and samples were taken every two minutes. The sampling time or the time for the air flow going through the single stage Anderson air sampler was 1 min. The E. coli colony number (CFU) is denoted N_t at the sampling time t after the UV-A lamp was turned on.

The effect of air flow rate on the E. coli K-12 disinfection was shown in Figure 5.3. The results suggested that E. coli K-12 can be completely disinfected for all the three flow rates of 1.2, 2.2 and 3.2 LPM. When the flow rate is 1.2 LPM, the E. coli K-12 was rapidly disinfected and after 6 minutes of UV-A irradiation there is no E. coli found in the outlet flow of the reactor. Once the air flow rate was increased to 2.2 LPM, the E. coli K-12 disinfection rate became slower than that with the flow rate of 1.2 LPM, but after 6 minutes of UV-A irradiation, the E. coli totally disappeared in the outlet flow. For the maximum air flow of 3.2 LPM, it took 14 minutes for the complete disinfection of E. coli through the photocatalytic process, indicating that the disinfection rate was the slowest in all of the three flows we used in the tests. The results for the effect of different flow rates on the disinfection of E. coli present in the air flow can be explained by the residence time. Smaller flow rate means longer residence time of E. coli K-12 bioaerosol in the photocatalytic reactor. The longer the E. coli K-12 stays in the reactor, the more possible it could be disinfected by the photocatalytic oxidation reaction.

Figure 5.4 shows the time for 80% and 50% E. coli disinfection at different flow rates. It was obvious that the time for the 80% and 50% E. coli disinfection was increased with the increase of air flow rates. The times for the E. coli disinfection were listed in Table 5.1.

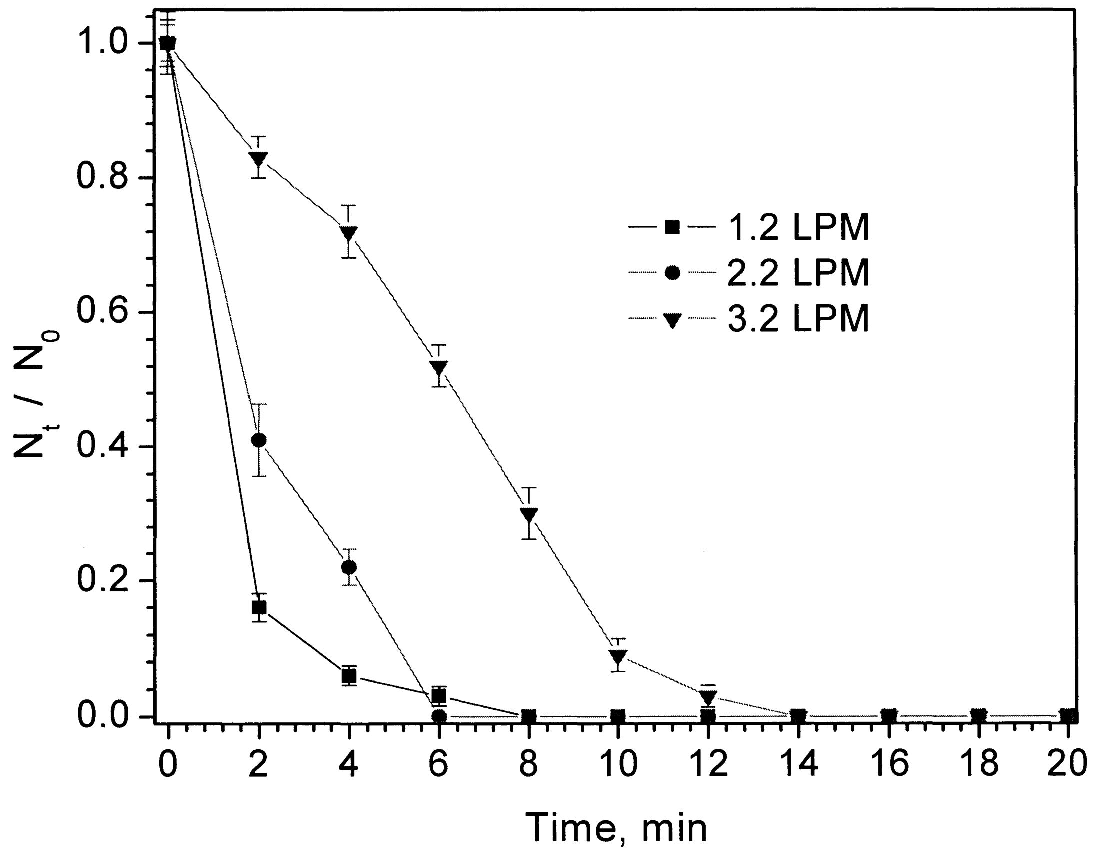


Figure 5.3 E. coli K-12 photocatatlytic disinfection at different flow rates

*N_0 is the E. coli K-12 colony number at t = 0, at which the UV light was turned on; N_t is the E. coli colony number at time t after the UV light was turned on.

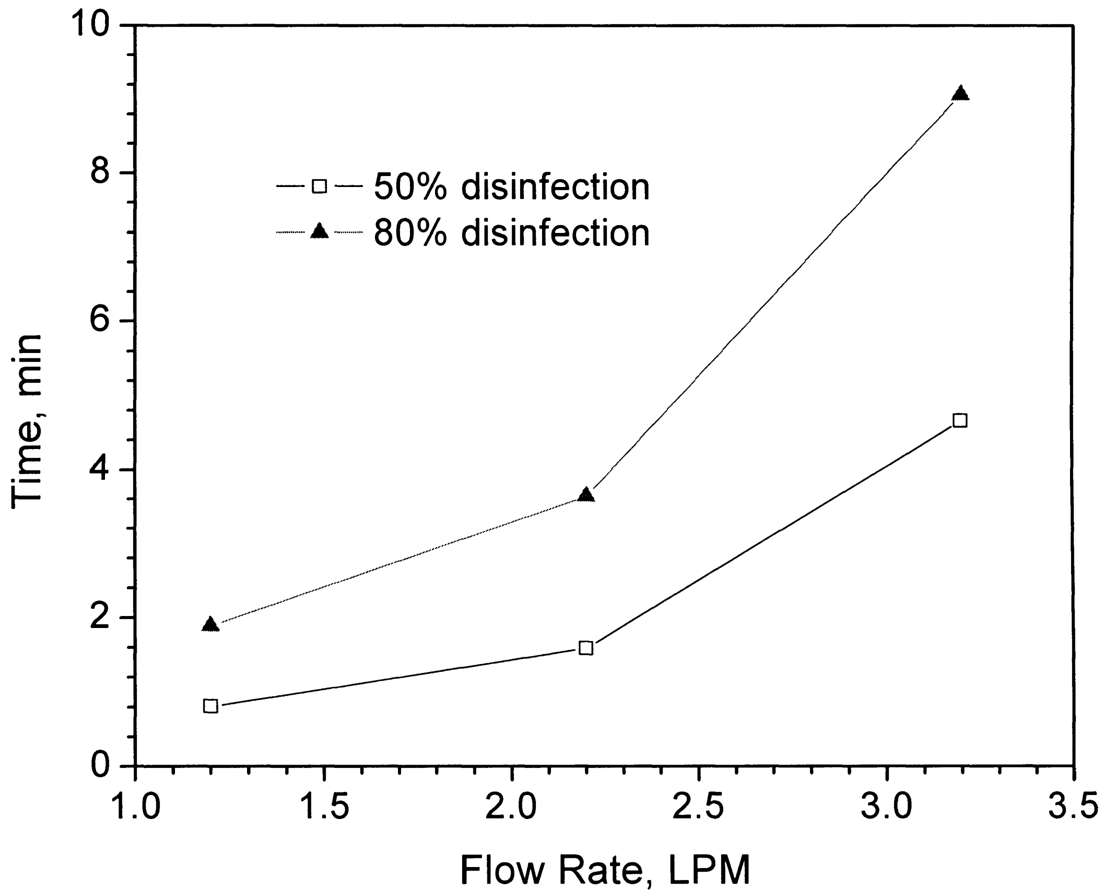


Figure 5.4 Time for 50% and 80% E. coli disinfection at different flow rates

5.3 E. Coli K-12 Disinfection under Different UV Intensities

Studies have shown that UV intensity can affect the bacteria disinfection significantly. Lin and Li studied the photocatalytic inactivation of Bacillus subtilis and Penicillium citrinum (Lin and Li, 2003). They found that the inactivation rate was higher under greater UV light intensity. The same conclusion was drawn in the study of Goswami et al. which stated that Gram-negative bacterium S. marcescens was more efficiently destroyed under stronger UV-A intensity (Goswami et al, 1997).

10%TiO_2-10%SiO_2/AC was used as the photoctalyst in the UV intensity effect study and the air flow rate used was 1.2 LPM. The E. coli suspension in the bioaersosol nebulizing generator was the 1/2000 dilution of the original E. coli suspension in LB broth. The UV-A intensities were measured at the outside surface of quartz tube surrounding the UV-A lamp.

Figure 5.5 shows the effect of UV intensity on the disinfection of E. coli K-12 present in air. With the UV intensity of 7.09 mW/cm^2, 83% of E. coli K-12 can be disinfected after 2 minutes of UV irradiation. But after 2 minutes of UV irradiation with the UV intensities of 5.78 or 5.05 mW/cm^2, only 2% or 4% of E. coli can be effectively inactivated respectively. It was found that the more intensive the UV light the more quickly the E. coli was disinfected. However, E. coli was completely inactivated after 8 minutes of UV illumination for all the three UV intensities. Figure 5.6 showed the time for 80% and 50% E. coli disinfection at different UV intensities. The times for the E. coli disinfection were listed in Table 5.1.

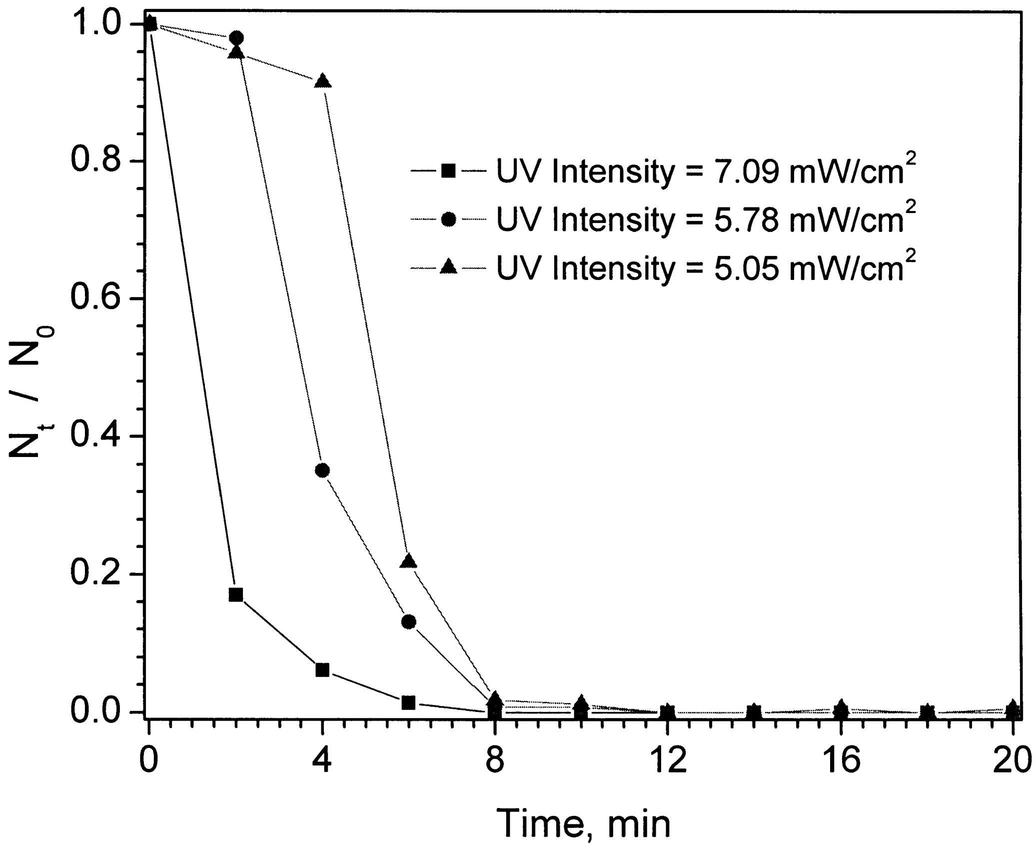


Figure 5.5 UV intensity effect on disinfection of E. coli K-12 in air

*N_0 is the E. coli K-12 colony number at $t = 0$, at which the UV light was turned on; N_t is the E. coli colony number at time t after the UV light was turned on.

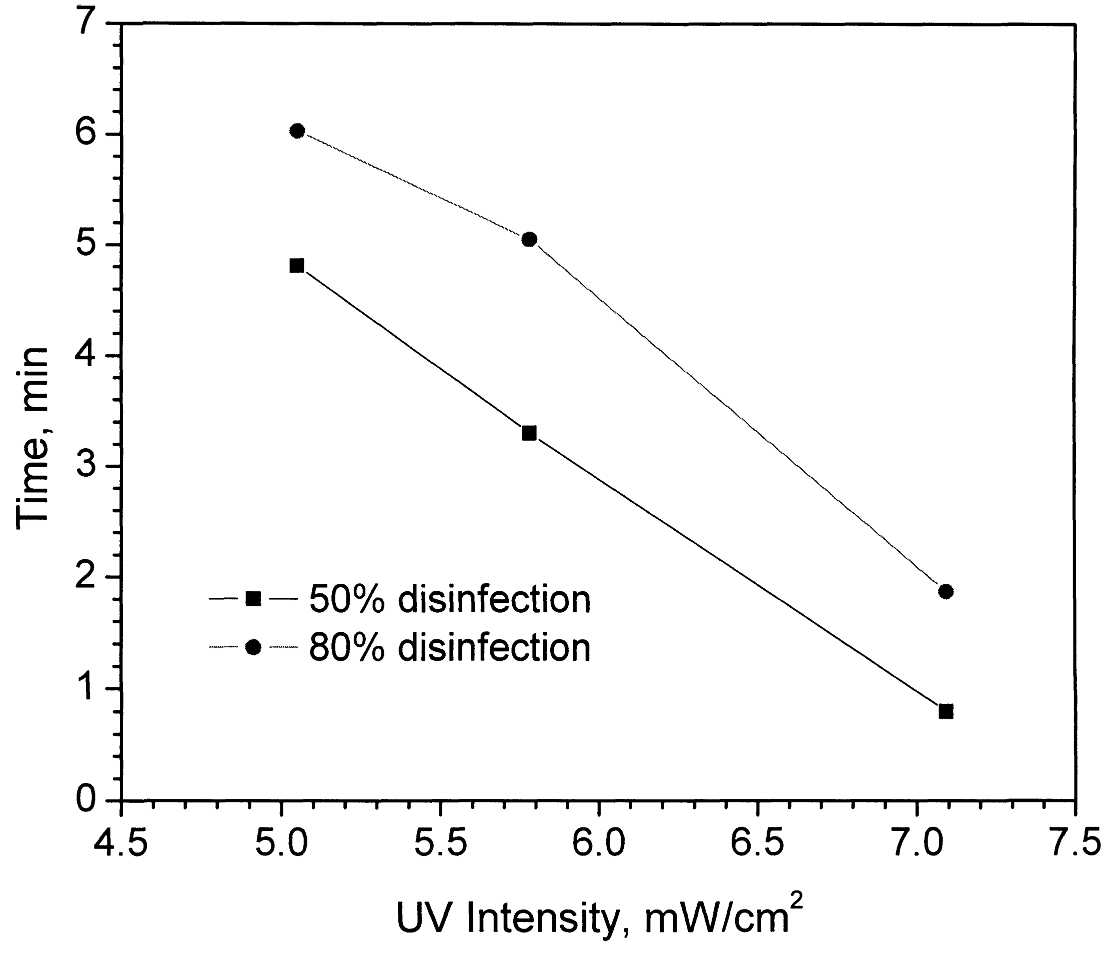


Figure 5.6 Time for 50% and 80% E. coli disinfection at different UV intensities

5.4 Effect of TiO_2 Loading on E. Coli K-12 Disinfection

The effect of TiO_2 loading on the E. coli K-12 disinfection was studied under the flow rate of 2.2 LPM and the UV intensity of 7.09 mW/cm^2. Photocatalysts prepared by the same procedure but with different amount of TiO_2 in the impregnation suspension were denoted as 1%TiO_2-10%SiO_2/AC, 4%TiO_2-10%SiO_2/AC, 7%TiO_2-10%SiO_2/AC, and 10%TiO_2-10%SiO_2/AC, which means 1, 4, 7 or 10 %(w/v) TiO_2 exists in the impregnation suspension when these photocatalysts were prepared. The detailed preparation methods for these photocatalysts were described in Chapter 4.

As shown in Figure 5.7, the E. coli K-12 disinfection rate increased when the TiO_2 loading increased from 1 to 10 %(w/v). This can be seen by the steeper lines of the photocatalysts with larger amount of loaded TiO_2. The higher E. coli disinfection rate is related to the generation of a larger amount of •OH radicals which has been proven to be a highly oxidative species for the elimination of the E. coli and other organic air contaminants. These photo-generated •OH radicals are potential biocide with strong oxidation potential and nonselective reactivity (Ireland et al., 1993). The higher TiO_2 loading leads to the generation of a larger number of •OH radicals, resulting in the faster E. coli K-12 inactivation rate. The results are consistent with the batch kinetic studies of Pal et al. who concluded that there is a linear relationship between inactivation rates of E. coli K-12 and TiO_2 loading (Pal et al., 2007).

Figure 5.8 showed the time for 80% and 50% E. coli disinfection with different TiO_2 loading. The times for the E. coli disinfection were listed in Table 5.1.

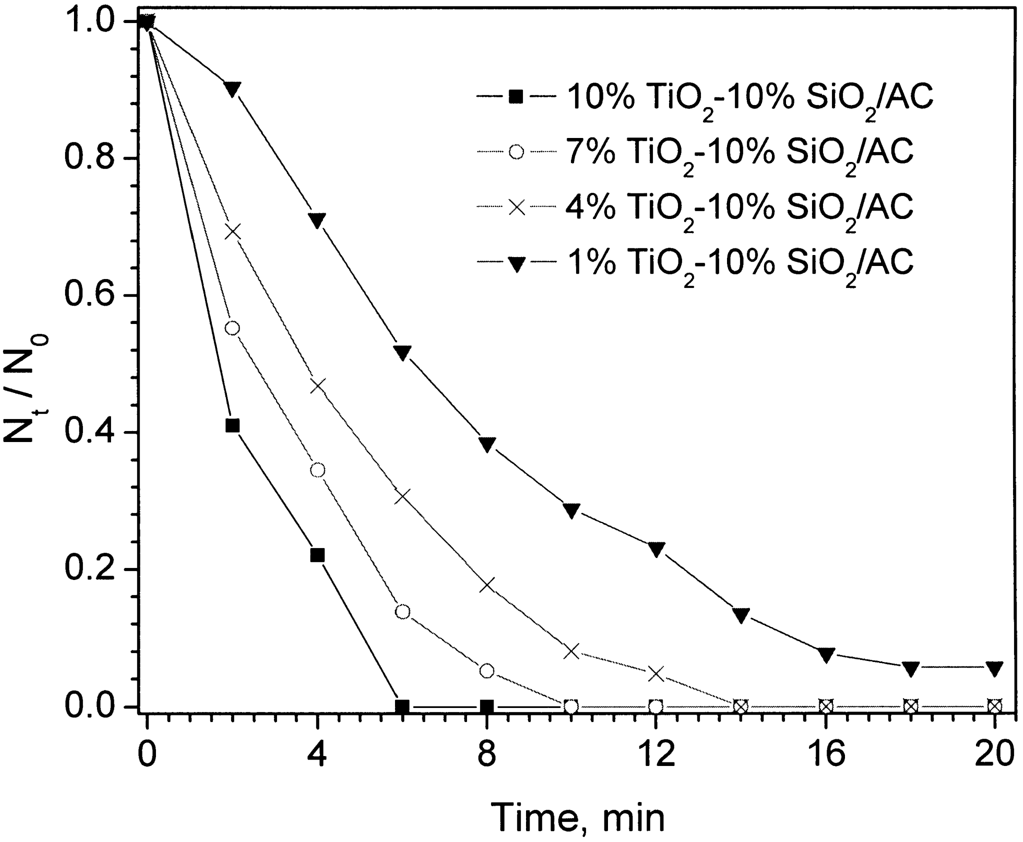


Figure 5.7 Effect of TiO_2 loadings on E. coli K-12 disinfection

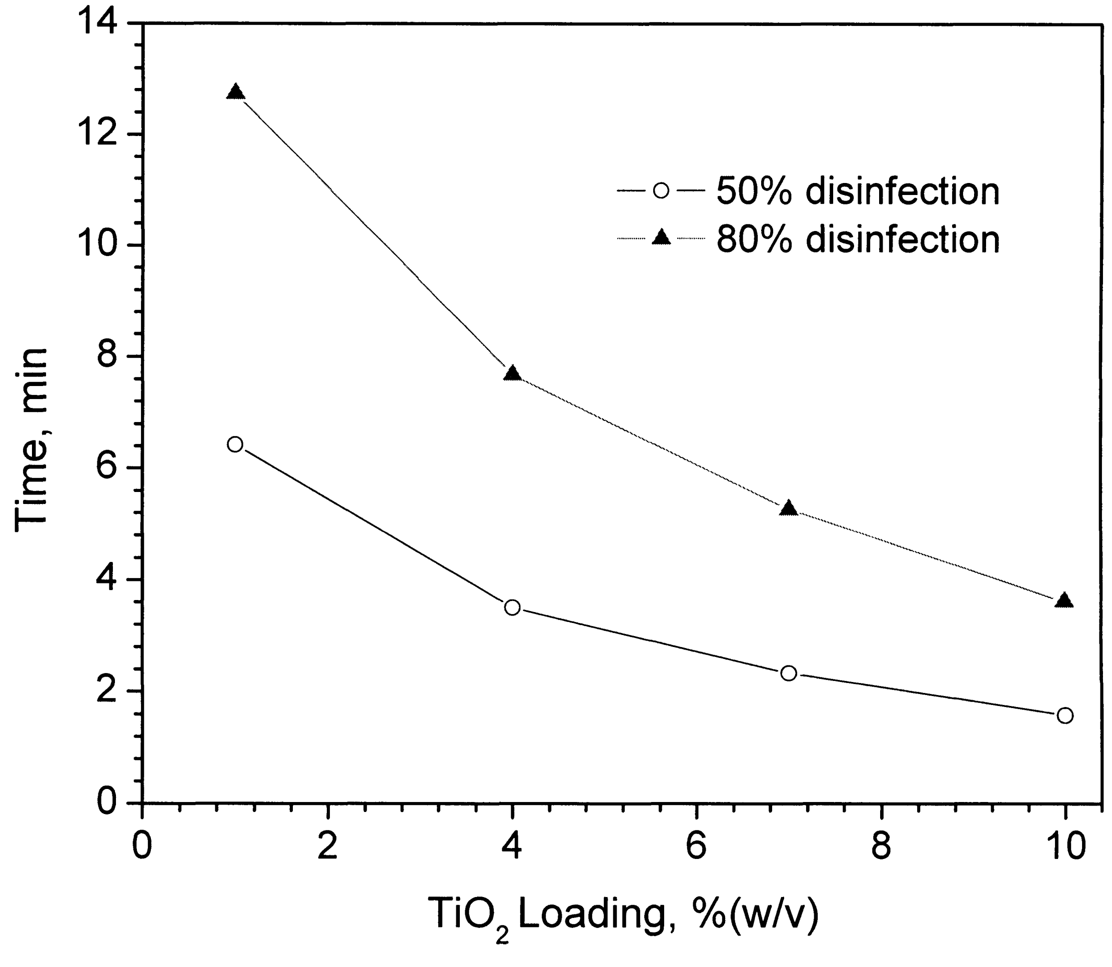


Figure 5.8 Time for 50% and 80% E. coli disinfection for photocatalysts with different TiO_2 loading

5.5 E. Coli K-12 Disinfection Using Photocatalysts Prepared by Different Methods

The result of E. coli K-12 disinfection using photocatalysts prepared by different methods is shown in Figure 5.9. The photocatalyst 10%TiO_2-10%SiO_2/AC was prepared by the dip coating method with the impregnation suspension of 10 %(w/v) TiO_2 in 10 wt% SiO_2 sol, while the photocatalyst 10%TiO_2/AC was prepared by the dip coating method as well but with the impregnation suspension of 10 %(w/v) TiO_2 in water. The photocatalyst PC-30%SiO_2/AC was prepared by the powder coating method. The tests were conducted under the flow rate of 2.2 LPM and the UV intensity of 7.09 mW/cm^2.

As indicated in Figure 5.9, the photocatalysts 10%TiO_2-10%SiO_2/AC and PC-30%SiO_2/AC have the relatively higher E. coli K-12 disinfection activity than 10%TiO_2/AC. The results showed that SiO_2 can promote the photocatalytic oxidation efficiency of the activated carbon supported photocatalysts. For the photocatalysts 10%TiO_2-10%SiO_2/AC and PC-30%SiO_2/AC, SiO_2 acted as the binding material that effectively held the active component TiO_2 powder on the surface of activated carbon support. But for the photocatalyst $TiO_2$10/AC, TiO_2 was loosely attached on the activated carbon surface and some TiO_2 particles were actually lost during the reaction process.

Figure 5.10 shows the times for 80% and 50% E. coli K-12 disinfection using photocatalysts prepared by different methods. The times for the E. coli disinfection were listed in Table 5.1.

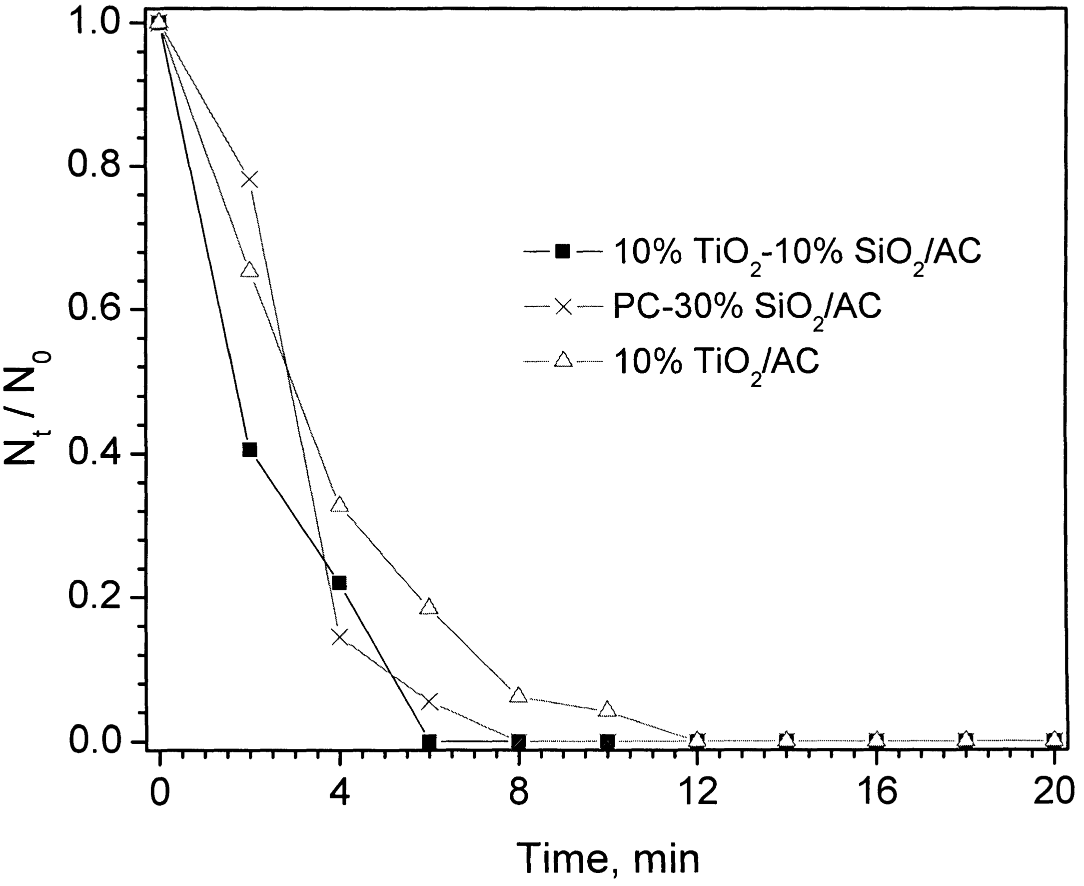


Figure 5.9 Effect of different photocatalyst preparation methods on E. coli K-12 inactivation

* 10%TiO_2-10%SiO_2/AC was prepared by the dip coating method with the silica sol.

10%TiO_2/AC was prepared by dip coating method without the silica sol.

PC-30%SiO_2/AC was prepared by the powder coating method.

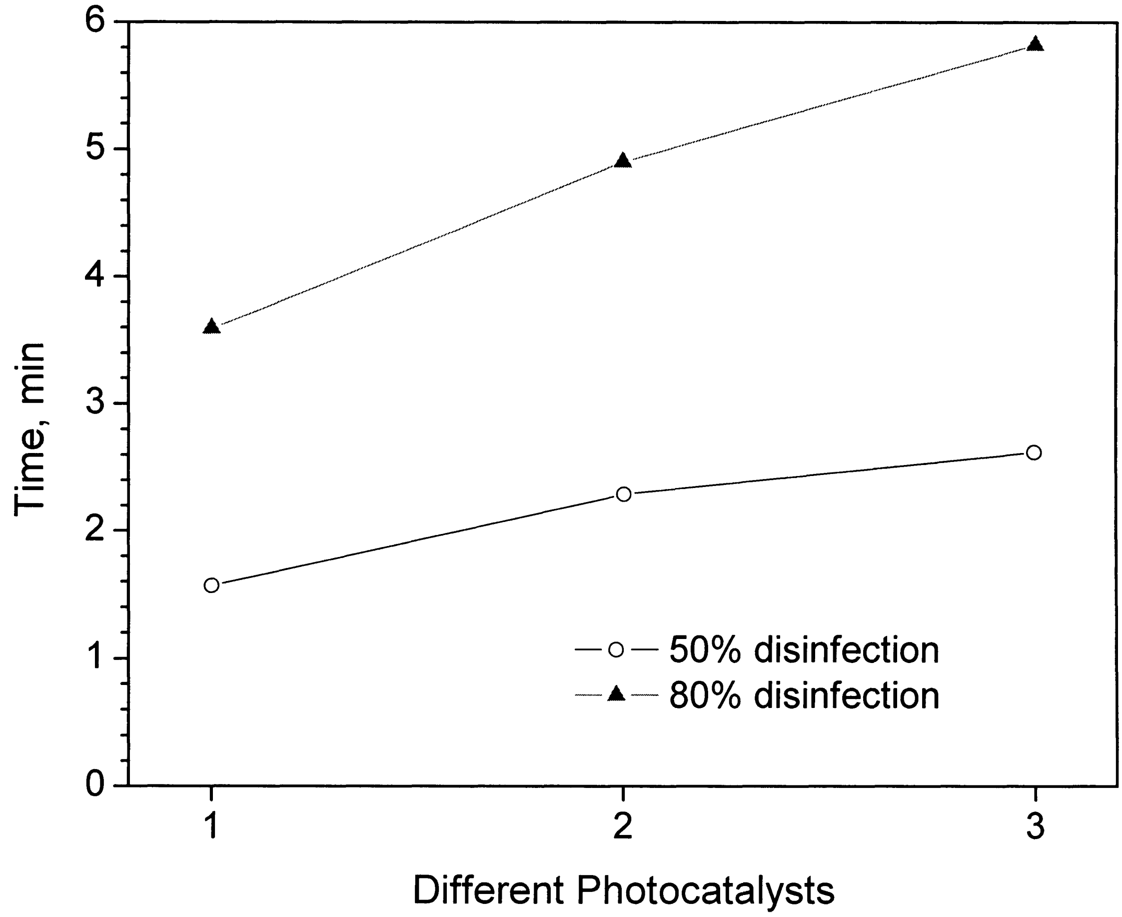


Figure 5.10 Time for 50% and 80% E. coli K-12 disinfection using photocatalysts prepared by different methods

* 1, 2, 3 denote 10%TiO_2-10%SiO_2/AC, PC-30%SiO_2/AC and 10%TiO_2/AC, respectively.

Table 5.1 Time for 50% and 80% E. coli disinfection under different parameters

Flow Rate	**UV Intensity**	**TiO_2 Loading***	**Photocatalyst**	**Disinfection Time , min**	
LPM	mW/cm^2	**%(w/v)**		**50%**	**80%**
*1.2***	7.09	10	10%TiO_2-10%SiO_2/AC	0.81	1.89
2.2	7.09	10	10%TiO_2-105SiO_2/AC	1.59	3.64
3.2	7.09	10	10%TiO_2-10%SiO_2/AC	4.66	9.06
1.2	*5.05*	10	10%TiO_2-10%SiO_2/AC	4.81	6.03
1.2	*5.78*	10	10%TiO_2-10%SiO_2/AC	3.30	5.05
1.2	*7.09*	10	10%TiO_2-10%SiO_2/AC	0.81	1.89
2.2	7.09	*1*	1%TiO_2-10%SiO_2/AC	6.42	12.73
2.2	7.09	*4*	4%TiO_2-10%SiO_2/AC	3.50	7.67
2.2	7.09	*7*	7%TiO_2-10%SiO_2/AC	2.33	5.26
2.2	7.09	*10*	10%TiO_2-10%SiO_2/AC	1.59	3.64
2.2	7.09	10	*10%TiO_2-10%SiO_2/AC*	1.59	3.64
2.2	7.09	—	*PC-30%SiO_2/AC*	2.29	4.90
2.2	7.09	10	*10%TiO_2/AC*	2.62	5.83

*TiO_2 loading %(w/v) denotes the TiO_2 content in the dip coating suspension.

** Changed parameters are indicated by italics.

Chapter 6

Conclusions

A highly effective photocatalyst is one of the main components of photocatalytic oxidation process for the indoor air purification. Photocatalysts were prepared by modified sol-gel, powder coating and dip coating methods. Borosilicate glass and activated carbon cloth were used as photocatalyst supports. Photocatalytic oxidation activities of the prepared photocatalysts were evaluated by the oxalic acid degradation in a batch reactor with an 8 W UV-A lamp as the irradiation source. Three photocatalysts, PCDS10, PCDS15 and PCDS20, were prepared by the powder coating methods on glass support. PCDS20 with higher TiO_2 content has the higher photocatalytical oxidation activity, but its activity decreased after use for longer time due to the coating decomposition caused by polymer oxidation. Photocatalyst SGDS10 prepared by the modified sol-gel method had higher oxidation activity than PCDS20 because the coating surface was totally composed of TiO_2 particles. Photocatalysts 10%TiO_2-10%SiO_2/AC, 10%TiO_2-20%SiO_2/AC, 10%TiO_2-30%SiO_2/AC, and 10%TiO_2/AC were prepared by the dip coating method using activated carbon cloth as the support. Each photocatalyst has 10 % (w/v) TiO_2 in the dip coating suspensions containing SiO_2 sol. The SiO_2 concentration in the suspensions is 10 wt%, 20 wt%, 30 wt%, and 0 wt% (distilled water only), respectively. It was found that 10%TiO_2-10%SiO_2/AC prepared using 10 wt% colloidal silica had the highest photocatalytic oxidation activity and relatively stronger coating. 10%TiO_2-20%SiO_2/AC and 10%TiO_2-30%SiO_2/AC showed lower photocatalytic oxidation activities because part of TiO_2 particles was covered by the silica molecules in the coating with higher silica contents. A photocatalyst PC-30%SiO_2/AC with activated carbon cloth as support was also prepared by the powder coating method. Its photocatalytic oxidation activity was found only a little weaker than that of 10%TiO_2-10%SiO_2/AC.

An indoor air purification device was developed at the laboratory scale. It is mainly composed of an annular continuous flow photocatalytic reactor, a baffle system inside the reactor, and a gas buffer tank. The photocatalytic reactor is the core of the whole device. A UV lamp is located in the centre of the reactor with photocatalyst around it. The gas buffer tank is used in order to obtain a stable flow of indoor air.

Disinfection of the E. coli K-12 as bioaerosol in indoor air was studied using the laboratory indoor air purification device. Photocatalysts with TiO_2 supported on activated carbon cloth were employed in the photocatalytic reactor. The adsorption equilibrium tests confirmed that the adsorption equilibrium of the air contaminated by E. coli K-12 aerosol in the reaction system was reached after 70 minutes. The effect of air flow rate on E. coli K-12 disinfection was studied under three flow rates of 1.2, 2.2 and 3.2 LPM. The results showed that although E. coli K-12 in air can be completely disinfected for all the three flow rates, it took longer time to totally inactivate them when the flow rate is relatively higher. UV intensity affects the disinfection of E. coli K-12 present in air. Three UV intensities were used in the tests which are 7.09, 5.78 and 5.05 mW/cm^2. With UV intensity of 7.09 mW/cm^2, 83% of E. coli K-12 can be disinfected after 2 minutes of UV irradiation, while after the same time of UV irradiation with intensities of 5.78 and 5.05 mW/cm^2, only 2% and 4 % of E. coli can be effectively disinfected respectively, indicating that higher UV intensity can significantly reduce the E. coli K-12 inactivation time. The effect of TiO_2 loading on E. coli K-12 disinfection was studied at the flow rate of 2.2 LPM. Photocatalysts prepared by the impregnation suspensions with 1, 4, 7 or 10 %(w/v) TiO_2 were used. The results showed that the E. coli K-12 disinfection rate increased when the TiO_2 loading going up from 1 to 10 %(w/v). E. coli K-12 disinfection in indoor air was also conducted using photocatalysts prepared by different methods. It was found that the E. coli K-12 disinfection efficiency can be improved by adding SiO_2 into the impregnation suspension when the activated carbon supported photocatalysts were prepared.

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