Photocatalysis in a novel semiconducting optical fiber monolithic reactor for wastewater treatment

Hongfei Lin
Louisiana State University and Agricultural and Mechanical College, hlin3@lsu.edu

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_dissertations
Part of the Chemical Engineering Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_dissertations/284
PHOTOCATALYSIS IN A NOVEL SEMICONDUCTING OPTICAL FIBER MONOLITHIC REACTOR FOR WASTEWATER TREATMENT

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by
Hongfei Lin

B.S. Tsinghua University, China, 1996
M.S. Tsinghua University, China, 2000
August, 2005.
ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude to my major advisor, Dr. Kalliat Valsaraj, for his insightful guidance, full support and continuous encouragement, which made this study possible.

I would also like to thank Dr. David Constant, Dr. Louis Thibodeaux, Dr. Benjamin McCoy, Dr. Karsten Thompson, and Dr. Jeffrey Hanor for serving on my committee.

I am grateful to Dr. Ravikrishna for sharing with me his vast experience and helping me design and fabricate the reactors. I also wish to thank all other colleagues in my group as they provided a very comfortable and friendly environment for my research. I also wish to express my thanks to Paul Rodriguez, Joe Bell and Frederick McKenzie, who helped me make the reactors.

My special thanks to my wife for her love, patience, encouragement and understanding. I also thank my parents, my brother and sisters for all their love and support.

This study was financially supported by a grant from the U.S. Environmental Protection Agency through the Gulf Coast Hazardous Substance Research center, Lamar University, TX.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................ ii

LIST OF TABLES .................................................................................................................. vi

LIST OF FIGURES ............................................................................................................... vii

ABSTRACT .......................................................................................................................... xi

CHAPTER I INTRODUCTION ............................................................................................... 1
1.1 PHOTOCATALYSIS IN WATER TREATMENT ............................................................ 1
1.2 OVERVIEW ................................................................................................................ 4
1.3 REFERENCES ............................................................................................................. 5

CHAPTER II BACKGROUND .............................................................................................. 6
2.1 INTRODUCTION ......................................................................................................... 6
2.2 PHOTOCATALYST ...................................................................................................... 7
  2.2.1 Titanium Dioxide ............................................................................................... 7
  2.2.2 Immobilization of TiO₂ Powder ....................................................................... 8
2.3 MECHANISM ............................................................................................................. 10
2.4 REACTION KINETICS ............................................................................................... 13
2.5 PHOTOCATALYTIC REACTOR DESIGN .................................................................... 16
2.6 EFFECTS OF OPERATING PARAMETERS .............................................................. 19
  2.6.1 Effect of Light Intensity .................................................................................. 20
  2.6.2 Effect of pH ................................................................................................... 20
  2.6.3 Effect of Initial Concentration ....................................................................... 21
  2.6.4 Effect of Temperature ................................................................................... 21
  2.6.5 Effect of Dissolved Oxygen ......................................................................... 21
2.7 REFERENCES ............................................................................................................. 21

CHAPTER III PHOTODEGRADATION IN A SLURRY BATCH REACTOR: REACTION MECHANISMS AND KINETICS .................................................................................................................. 29
3.1 INTRODUCTION ....................................................................................................... 29
3.2 EXPERIMENTAL ....................................................................................................... 31
  3.2.1 Materials .......................................................................................................... 31
  3.2.2 Photoreactor Assembly .................................................................................. 31
  3.2.3 Methodology and Analysis ............................................................................ 32
3.3 RESULTS AND DISCUSSION .................................................................................... 34
  3.3.1 Intermediates and Mechanism of DCB Degradation from Batch Experiments .......................................................................................................................... 34
  3.3.2 Intermediates and Mechanism of PAHs Degradation from Batch Experiments .................................................................................................................. 38
  3.3.3 Kinetics of Photodegradation of DCB and Intermediates ................................ 44
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Some examples of organic compounds that can be photomineralized on TiO₂</td>
</tr>
<tr>
<td>2.2</td>
<td>Methods of immobilization of TiO₂ and support substrates coated</td>
</tr>
<tr>
<td>2.3</td>
<td>Overview of photocatalytic reactor configurations</td>
</tr>
<tr>
<td>3.1</td>
<td>Mineralization of phenanthrene to carbon dioxide</td>
</tr>
<tr>
<td>3.2</td>
<td>Langmuir-Hinshelwood rate parameters and quantum efficiencies for DCB, DCP and CP degradation in the batch reactor</td>
</tr>
<tr>
<td>4.1</td>
<td>Physicochemical Properties of DCB and the PAHs</td>
</tr>
<tr>
<td>4.2</td>
<td>Steady State Fractional Removal of DCB and Apparent Rate Constants using Continuous flow, Immobilized Titania Reactors</td>
</tr>
<tr>
<td>4.3</td>
<td>Observed and expected chloride concentrations in selected continuous immobilized reactors using titania on quartz</td>
</tr>
<tr>
<td>4.4</td>
<td>Reaction rate constant and half life for two PAHs with and without titania catalyst</td>
</tr>
<tr>
<td>5.1</td>
<td>Comparison of photocatalytic reactors</td>
</tr>
<tr>
<td>7.1</td>
<td>Optical fiber monolith reactor model parameters</td>
</tr>
<tr>
<td>7.2</td>
<td>Estimation of model parameter, kₜ. Substrate: PHE.</td>
</tr>
<tr>
<td>7.3</td>
<td>Estimation of model parameter, kₜ. Substrate: DCB.</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic of various reactor configurations used in this work.......................... 4</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic representation of the processes occurring in and on semiconductor particles during the photocatalytic mineralization of organic molecules by oxygen................................................................. 10</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic of the batch slurry photocatalytic reactor set up. The reactor assembly is placed inside an aluminum box.......................................................... 32</td>
</tr>
<tr>
<td>3.2</td>
<td>The GC/MS trace of the solution from the batch reactor at various time intervals................................. 35</td>
</tr>
<tr>
<td>3.3</td>
<td>The changes in concentrations of DCB, DCP and CP in the batch reactor as a function of irradiation time.......................... 36</td>
</tr>
<tr>
<td>3.4</td>
<td>Proposed intermediates and reaction mechanism for the mineralization of DCB................................................................. 37</td>
</tr>
<tr>
<td>3.5</td>
<td>Proposed phenanthrene degradation mechanism (a) Scheme 1: the conversion of phenanthrene to 9,10-phenanthrenequinone. (b) Scheme 2: the various intermediates that result from 9,10-phenanthrenequinone identified by GC/MS. (c) Scheme 3: direct addition of hydroxyl and methyl radicals to phenanthrene................................................................. 39</td>
</tr>
<tr>
<td>3.6</td>
<td>GC/MS trace of the phenanthrene solution after 60 min of reaction in the batch mode................................................................. 41</td>
</tr>
<tr>
<td>3.7</td>
<td>The postulated mechanism of pyrene degradation mechanism and the intermediates identified by GC/MS................................................................. 42</td>
</tr>
<tr>
<td>3.8</td>
<td>Reciprocal initial rate versus reciprocal initial concentration for the parent compound (DCB) and the two intermediates (DCP and CP).......................... 45</td>
</tr>
<tr>
<td>3.9</td>
<td>The effects of (a) pH and (b) added hydrogen peroxide on the initial photodegradation of DCB in the batch reactor................................................................. 47</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic of the continuous annular photocatalytic reactor assembly and experimental set up................................................................. 53</td>
</tr>
<tr>
<td>4.2</td>
<td>Schematic of the reactor configuration: (a) multiple pass with feed recycle; and (b) single pass without feed recycle................................................................. 54</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>4.3</td>
<td>The influent and effluent concentrations of DCB and the overall removal efficiency in the reactor as a function of time</td>
</tr>
<tr>
<td>4.4</td>
<td>Feed and exit concentrations of phenanthrene and the conversion in the reactor as a function of time for: (a) multiple pass with feed recycle; and (b) single pass without feed recycle</td>
</tr>
<tr>
<td>4.5</td>
<td>Fractional conversion of phenanthrene in the continuous annular reactor using immobilized TiO$_2$ as a function of initial feed concentration</td>
</tr>
<tr>
<td>4.6</td>
<td>Effects of the flow velocity on (a) the overall rate of DCB degradation and (b) the mass transfer resistance in the continuous immobilized reactor using titania on quartz</td>
</tr>
<tr>
<td>4.7</td>
<td>Overall rate constants (a) and fractional conversions (b) for phenanthrene and pyrene in the continuous annular reactor as a function of feed velocity</td>
</tr>
<tr>
<td>4.8</td>
<td>Effects of the radiant flux on the overall rate constant of (a) 1,2-dichlorobenzene and (b) phenanthrene degradation in the continuous immobilized reactor using titania on quartz</td>
</tr>
<tr>
<td>5.1</td>
<td>A schematic of the optical fiber monolith reactor assembly and experimental setup</td>
</tr>
<tr>
<td>5.2</td>
<td>SEM images of TiO$_2$ layer on a quartz optical fiber that was coated with (a) 0.25 wt%; (b) 0.5 wt%; (c) 1.0 wt%; (d) 2.0 wt% TiO$_2$ slurry solutions</td>
</tr>
<tr>
<td>5.3</td>
<td>Thickness of TiO$_2$ coating on optical fibers with O.D. 400 µm versus concentration of TiO$_2$ slurry solution from which optical fibers were dip-coated</td>
</tr>
<tr>
<td>5.4</td>
<td>DCB and PHE concentration in the outlet and inlet streams as well as the overall removal efficiency as a function of time. (a) DCB; (b) PHE</td>
</tr>
<tr>
<td>5.5</td>
<td>The effect of initial feed PHE concentration on the removal efficiency</td>
</tr>
<tr>
<td>5.6</td>
<td>The effect of the liquid flow velocity on (a) the overall removal efficiency and (b) rate constant for DCB and PHE in the monolith reactor</td>
</tr>
<tr>
<td>5.7</td>
<td>The effect of thickness of the TiO$_2$ film coated on the optical fiber upon the overall rate</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>6.1</td>
<td>Schematic of experimental set up for measuring UV light intensity profile of a single optical fiber</td>
</tr>
<tr>
<td>6.2</td>
<td>Profile of UV intensity in a single cell of the monolith inserted with a coated optical fiber as the light conductor</td>
</tr>
<tr>
<td>6.3</td>
<td>Axial distribution of the cross-sectional light intensity along optical fiber with various TiO$_2$ film thickness and TiO$_2$-coated monolith channel</td>
</tr>
<tr>
<td>6.4</td>
<td>Absorbed, transmitted and unrefracted light distribution with a single TiO$_2$-coated optical fiber as a function of coating thickness</td>
</tr>
<tr>
<td>6.5</td>
<td>The effect of TiO$_2$ film thickness on the absorbed refracted light out of quartz fiber core</td>
</tr>
<tr>
<td>6.6</td>
<td>The effect of the tip light flux on the lateral light profile at the outer surface of a single optical fiber without TiO$_2$ coating</td>
</tr>
<tr>
<td>6.7</td>
<td>The profile of the penetrated refracted light with various thickness of the TiO$_2$ film on the optical fiber</td>
</tr>
<tr>
<td>6.8</td>
<td>Effect of fiber diameter on the penetrated refracted light. TiO$_2$ film thickness $\delta$ is 390 nm for both fibers</td>
</tr>
<tr>
<td>6.9</td>
<td>Profiles of the intensity of the light on the outer surface of the TiO$_2$ coating layer on the monolith channel wall and on the optical fiber</td>
</tr>
<tr>
<td>7.1</td>
<td>Schematic of a single monolith cell with a TiO$_2$-coated optical fiber inserted. The channel wall is also coated with TiO$_2$</td>
</tr>
<tr>
<td>7.2</td>
<td>Overall conversion for photocatalytic oxidation of (a) PHE and (b) DCB in continuous recycling multipass runs in an OFMR</td>
</tr>
<tr>
<td>7.3</td>
<td>Single-pass conversion for photocatalytic oxidation of (a) PHE and (b) DCB at different flow velocities in an OFMR</td>
</tr>
<tr>
<td>7.4</td>
<td>Single-pass conversion for photocatalytic oxidation of (a) PHE and (b) DCB at different input light intensities in an OFMR</td>
</tr>
<tr>
<td>7.5</td>
<td>Model simulation for photocatalytic oxidation of (a) PHE and (b) DCB in a single channel of OFMR. Radial profiles of the dimensionless concentration at different axial distances from the reactor inlet</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>7.6</td>
<td>Model simulation for photocatalytic oxidation of PHE in a single channel of OFMR. Radial profiles of the dimensionless concentration along the axial direction from the reactor inlet</td>
</tr>
<tr>
<td>7.7</td>
<td>Effect of fiber diameter on the overall conversion of PHE in recycling flow mode in multi-channel OFMR</td>
</tr>
<tr>
<td>7.8</td>
<td>Model simulation for photocatalytic oxidation of PHE in a single-pass run in the OFMR. Radial profiles of the dimensionless concentration along the axial direction from the reactor inlet</td>
</tr>
<tr>
<td>7.9</td>
<td>Model simulation for photocatalytic oxidation of PHE in a single-pass run in the OFMR. Effect of the reactor length on the single-pass conversion</td>
</tr>
</tbody>
</table>
ABSTRACT

The development of photocatalytic reactors is essential for the successful exploitation of heterogeneous photocatalysis on semiconductor particles, which has been shown to be an effective means of removing organic pollutants from wastewater streams. In this dissertation, a novel photocatalytic optical fiber monolith reactor (OFMR), which employed a ceramic multi-channel monolith as a support for TiO$_2$ and quartz fibers inserted inside the monolithic channels as both a light-transmitting conductor and a support for TiO$_2$, was developed for wastewater treatment by investigating the photocatalytic degradation of o-dichlorobenzene (DCB) and phenanthrene (PHE). This configuration provides a high surface area for catalyst coating per unit reactor volume, reduces the mass transport limitations, and allows for high throughput at low pressure drop. Using optical fiber to deliver UV light can remotely control the reactor.

The effects of water flow velocity, initial contaminant concentration, thickness of the TiO$_2$ film on the optical fiber and incident UV light intensity were investigated and optimized. The results showed mass transfer effects could not be ignored due to the relatively low flow Reynolds number. Optimum thickness of TiO$_2$ film on the optical fiber was found to be close to 0.4 µm in this study. The kinetics of DCB and PHE degradation were pseudo-first order. Greater apparent quantum efficiency was observed for the OFMR compared with that of the continuous annular reactor, which suggested that this novel reactor has the potential in photocatalytic applications.
The light distribution profile inside each cell of the monolith was quantitatively analyzed. The radiation field model with the fitting parameters was set up and validated. The two-dimensional heterogeneous convective-diffusion-reaction steady-state model of a multi-channel OFMR was developed by incorporating an empirical radiation field sub-model, an annular flow dynamics model and a Langmuir-Hinshelwood kinetics sub-model. Reasonable agreement was found between the model-predicted and experimentally observed photodegradation conversion data within the limits of experimental error, using the total rate constant as the only adjustable parameter. The model can be used to optimize the design parameters in an OFMR.
CHAPTER I
INTRODUCTION

1.1 PHOTOCATALYSIS IN WATER TREATMENT

The presence of harmful organic compounds in water supplies and in the discharge of wastewater from chemical industries, power plants, landfills, and agricultural sources is a topic of global concern. Traditional water treatment processes include filtration and flocculation, biological treatment, thermal and catalytic oxidation, and chemical treatment using chlorine, potassium permanganate, ozone, hydrogen peroxide and high-energy ultraviolet light [1-4]. All these water treatment processes, currently in use, have limitations of their own and none is cost-effective: (i) Phase transfer methods remove unwanted organic pollutants from wastewater, but they do not eliminate the pollutants entirely; (ii) Cost of biological treatment is low, however, some of the toxic compounds present are found to be lethal for microorganisms intended to degrade them, and there is a class of non-biodegradable organic products noted as biorecalcitrant organic compounds; (iii) While chemical treatments based on aqueous phase hydroxyl radical chemistry are powerful to oxidize toxic organic compounds present in water, these processes either use high-energy ultraviolet light or strong chemical oxidants of hazardous and therefore, undesirable nature [2,4]. Moreover, several intermediates, which are more hazardous, are formed in these processes, and because of very low efficiencies, overall treatment cost becomes high if destruction of intermediates and complete mineralization are to be achieved, especially for treating dilute wastewater streams [3].
Heterogeneous photocatalysis on metal oxide semiconductor particles is an advanced oxidation technology (AOT), which has been shown to be an effective means of removing organic pollutants from water streams [4]. Compared with traditional oxidation processes, heterogeneous photocatalysis has the following advantages [5-7]:

i. It utilizes low-energy ultraviolet light with semiconductors acting as photocatalysts and leads to complete mineralization of pollutants to environmentally harmless compounds.

ii. The photocatalytic reactions allow thermodynamically unfavorable reactions to occur and allow destruction of non-biodegradable refractory contaminants.

iii. While catalytic processes normally require high temperature or high pressure, photocatalytic oxidation is a promising technique for many purposes due to its ability to operate at or slightly above ambient conditions.

However, the rate of the photocatalytic reaction is determined by the illuminated surface area of photocatalysts, light irradiance, reactants adsorption rate, and the properties of photocatalysts. Generally, the rate is not significantly great due to the low photoefficiency. Thus commercialization of photocatalytic processes is still in its infancy.

Reactor design can alleviate some of the problems and increase the efficiency of the photocatalyzed process. However, there are four main barriers to scale-up of photocatalytic reactors. Firstly, the efficient exposure of the catalyst to light in a large scale reactor poses a challenge. Secondly, the illuminated catalyst area in contact with the water has to be maintained high. Thirdly, the mixing and mass transfer limitations in a large scale reactor have to be overcome. Finally, in any design for industrial application high wastewater throughput through the reactor should be attainable. Therefore, the
selection of an appropriate catalyst configuration is of utmost importance in a large scale reactor. There are mainly two types of configurations as far as the catalyst is concerned - either as a slurry of titania in suspension or immobilized on inert surfaces. Slurry reactors necessitate downstream separation and recycle of the catalyst and are inefficient and difficult to scale up. Therefore, immobilized reactors are preferred. Three types of immobilized photocatalyst reactors are known. The first category uses lamps external to the reactor with the catalyst coated on the reactor wall. The second category uses lamps placed within the reactor with the catalyst coated outside of the lamp housing or the reactor wall; these are termed immersion reactors. A third category comprises those in which light is distributed using fiber optic bundle or light tubes inside a monolithic structure that carries the catalyst on the inside reactor walls; these are termed distributive or monolithic reactors.

For this work we selected three different reactors for testing from among the three types described above. These are shown schematically in Figure 1.1. The differentiating features of the reactors are shown under the schematic. The first reactor is a batch one with lamps external to the reactor. The second one is a continuous reactor also with external lamps and titania immobilized on substrates (a quartz rod and a low density polyethylene tube). The third one is a monolithic reactor with titania coated on the inside surface of a ceramic monolithic and stripped fiber optic tube bundle is used to deliver light inside each of the cylindrical passageway. The last type of reactor has been suggested as a means to overcome the low photoefficiencies [8]. The objective of this research is to contribute to the body of knowledge on photocatalytic degradation of organic pollutants in dilute aqueous solutions, with a particular focus on aspects of the
design, modeling and experimentation of a novel photocatalytic optical fiber monolith reactor (OFMR) for wastewater treatment.

Fig. 1.1. Schematic of various reactor configurations used in this work.

1.2 OVERVIEW

The central theme in this work is the use of photocatalysis for decomposition of organic contaminants in wastewater streams in a novel photocatalytic optical fiber monolith reactor.

In Chapter 2, a brief background pertaining to the properties and utilization of photocatalysts, the mechanism of photocatalysis, the reaction kinetics analysis and the guidelines for photocatalytic reactor design are given.

The initial goal of this work is to investigate the reaction mechanism and kinetics of photocatalytic degradation of target organic compounds including dichlorobenzene
and phenanthrene. This aspect is analyzed in a slurry batch reactor and a continuous annular reactor with immobilized TiO$_2$ and is addressed in Chapters 3 and 4, respectively.

Chapters 5 to 7 describe experimental details and modeling of the optical fiber monolith reactor (OFMR). Experimental details and effects of operation variables are described in chapter 5. In chapter 6 we present the development of the light transmission and distribution model in a single cell of the OFMR. The model parameters are obtained by fitting the measured data with the model. The development of the reactor model and model validation are presented in chapter 7. Optimal design parameters are also given in this chapter.

The major conclusions from this work and directions for future work are presented in Chapter 8.

1.3 REFERENCES


CHAPTER II

BACKGROUND

2.1 INTRODUCTION

During the last decade, the number of references and related patents on heterogeneous photocatalytic removal of toxic and hazardous compounds from water and air are in the thousands. A variety of organic molecules can be photocatalytically oxidized and eventually mineralized according to the following general reaction [1-11]:

\[
\text{Organic Molecules} + O_2 \xrightleftharpoons[^{TiO_2, hv}]{\text{Mineral O H COOMoleculesOrganic}} \rightarrow CO_2 + H_2O + \text{Mineral Acids} \quad (2-1)
\]

An abbreviated list of compounds that have been demonstrated to be degradable via reaction (2-1) is given in Table 2.1. Often, local pollution problems impel researchers to investigate the degradability of a particular compound, and new compounds are continually being added to the list [6].

**Table 2.1.** Some examples of organic compounds that can be photomineralized on TiO\(_2\) (Revised based on Ref [6])

<table>
<thead>
<tr>
<th>Class</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>methane, isobutane, pentane, heptane, cyclohexane, paraffins</td>
</tr>
<tr>
<td>Haloalkane</td>
<td>mono-, di-, tri- and tetrachloromethane, tribromoethane, 1,1,1-trifluoro-2,2,2-trichloroethane</td>
</tr>
<tr>
<td>Aliphatic alcohols</td>
<td>methanol, ethanol, isopropyl alcohol, glucose, sucrose alkenes propene, cyclohexene</td>
</tr>
<tr>
<td>Aliphatic carboxylic acids</td>
<td>alcohols formic, ethanoic, dimethylethanoic, propanoic, oxalic acids</td>
</tr>
<tr>
<td>Alkenes</td>
<td>propene, cyclohexene</td>
</tr>
<tr>
<td>Haloalkenes</td>
<td>perchloroethene, 1,2-dichloroethene, 1,1,2-trichloroethene,</td>
</tr>
<tr>
<td>Aromatics</td>
<td>benzene, naphthalene, phenanthrene, pyrene</td>
</tr>
<tr>
<td>Haloaromatics</td>
<td>chlorobenzene, 1,2-dichlorobenzene, bromobenzene</td>
</tr>
<tr>
<td>Nitrohaloaromatics</td>
<td>3,4-dichloronitrobenzene, dichloronitrobenzene</td>
</tr>
</tbody>
</table>

(Table con’d.)
In this chapter, we will briefly review the photocatalyst, the mechanism of photocatalysis, the reaction kinetics and the reactor design.

2.2 PHOTOCATALYST

2.2.1 Titanium Dioxide

A semiconductor is a material whose valence band and conduction band are separated by an energy gap or bandgap. When a semiconductor molecule absorbs photons with energy equal to or greater than its bandgap, electrons in the valence band can be excited and jump up into the conduction band and thus charge carriers are generated [12]. This semiconducting character for various semiconductor particles, such as TiO$_2$, WO$_3$, ZnO, CdS and SnO$_2$, allows them to be used for photocatalytic studies. Among these semiconductors, TiO$_2$ or modified TiO$_2$ is the most commonly used catalyst for the photocatalytic oxidation of aqueous and gaseous pollutants, because it is highly photoactive, very photostable, biologically and chemically inert, nontoxic, the good adsorption/desorption rate of reactants (especially oxygen), and inexpensive as well [2,3,5-10,13-16]. The study of physicochemical principles of semiconductor-liquid
interface showed using TiO₂ for purifying waste water is especially suitable for small concentrations of the pollutant [17].

Titanium dioxide has three polymorphs: anatase (tetragonal), rutile (tetragonal) and brookite (orthogonal). There is growing evidence which suggests that anatase is more active than rutile for oxidative photocatalytic reaction [5,8-10,18]. Rutile is the thermodynamically stable form of TiO₂, into which anatase and brookite convert when heated above 500°C or 750°C, respectively [9,10].

There are many methods of producing TiO₂ nanopowders, such as chemical vapor deposition (CVD) [19], oxidation of titanium tetrachloride [20,21], sol–gel technique [22], thermal decomposition or hydrolysis of titanium alkoxides [23,24]. The most popular TiO₂ used in photocatalysis is commercial Degussa P25 produced by flame hydrolysis of TiCl₄ at temperatures greater than 1200 °C in the presence of hydrogen and oxygen. P25 is a mixture of anatase and rutile with the ratio about 70:30. The individual P25 particle is non-porous with rounded edges. While the size of particles is in the nano-scale, the average diameter of aggregates is approximately 1 micron [5,10]. In the experimental work described in the subsequent chapters of this work, we also utilized Degussa P25 TiO₂.

2.2.2 Immobilization of TiO₂ Powder

In numerous investigations, an aqueous suspension of the catalyst particles has been used. The use of TiO₂ in suspension is somewhat efficient due to the large surface area of catalyst available for reaction and is prevalent at the early stage of the photocatalytic research work. Some researchers have even developed pilot scale wastewater treatment systems using TiO₂ as an aqueous suspension [25,26]. However,
the use of suspensions requires the separation and recycling of the ultra fine catalyst from the treated solution. That is usually an inconvenient, time-consuming, expensive process, which adds to the overall capital and running costs of the plant. Moreover, the TiO$_2$ powder easily agglomerates in the aqueous solution thus losing its activity. Another problem is that the UV light penetration depth is very short in the non-transparent titania suspension because of strong absorption by catalyst and dissolved pollutants and thus the illumination area of the catalyst is still limited.

Table 2.2. Methods of immobilization of TiO$_2$ and support substrates coated [33]

<table>
<thead>
<tr>
<th>Method of immobilisation</th>
<th>Substrate coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dip coating from suspension</td>
<td>Glass beads; Glass tubing; Glass plate; Glass fibers; Tin oxide coated glass; Quartz; Silica gel; Sand; Poly-tetrafluoroethylene; Polyethylene</td>
</tr>
<tr>
<td>Sol gel method</td>
<td>Quartz; Optical fibers; Glass beads; Silica gel; Glass plate; Tin oxide coated glass</td>
</tr>
<tr>
<td>Electrochemical oxidation</td>
<td>Titanium</td>
</tr>
<tr>
<td>Thermal oxidation</td>
<td>Titanium; Titanium alloy</td>
</tr>
<tr>
<td>Anodisation of TiCl$_3$</td>
<td>Tin oxide coated glass, Ti, Pt, ad Au</td>
</tr>
<tr>
<td>Electrophoretic coating</td>
<td>Stainless Steel; Titanium; Titanium alloy; Tin oxide glass</td>
</tr>
</tbody>
</table>

In order to avoid the separation process, the catalyst can be immobilized onto a fixed solid support. When the catalyst is immobilized, there is inherently a decrease in the surface area available for reaction. In addition, the reaction occurs at the liquid-solid interface and the overall rate may be limited to mass transport of the pollutant to the catalyst surface and thus the overall removal efficiency also decreases [27,28]. The photocatalyst can be coated on various substrates such as the walls of the reactor, a support matrix, or a casing containing the light source [29-32]. Several different methods for the immobilization of TiO$_2$ on solid support substrates have been investigated and are listed in Table 2.2 [33]. The most common method of immobilization of TiO$_2$ is dip-
coating from TiO$_2$ suspension followed by drying and calcination since it is simple, low cost and effective. However, to get a uniform film, the coating procedure has to be repeated many times to build up any significant coating [34].

2.3 MECHANISM

![Schematic representation of the processes occurring in and on semiconductor particles during the photocatalytic mineralization of organic molecules by oxygen.](image)

Fig. 2.1. Schematic representation of the processes occurring in and on semiconductor particles during the photocatalytic mineralization of organic molecules by oxygen.

As we mentioned above, TiO$_2$ semiconductors consist of the valence band and the conduction band. Most electrons are located in the valence band at ambient temperatures. When TiO$_2$ is illuminated with photons with $\lambda < 380$ nm (the corresponding bandgap energy is greater than 3.2 eV), upon absorption of a photon by the TiO$_2$ particle, some electrons, e$^-$, are excited from the valence band to the conduction band, leaving holes, h$^+$, in the valence band, as illustrated in Figure 2.1. Before an excited electron recombines with the positive hole (moves down to the valence band) by releasing energy, if the excited electrons and holes are trapped at the TiO$_2$ surface and encounter electron acceptors and donors (i.e., oxidants and reductants), the electrons and holes can participate in redox half-reactions [1-11]. Since an n-type semiconductor has higher potential near the surface than in the bulk, the excited electrons move into the bulk and
the positive holes remain on the surface. This charge separation process causes the lifetime of the electron/hole pair to be longer and photocatalytic reaction to proceed more effectively.

The mechanism of photocatalytic oxidation using TiO$_2$ is complicated and still under discussion. The most widely accepted mechanism is as follows [5].

i. Charge carrier generation:

\[ TiO_2 + h\nu \rightarrow h_{vb}^+ + e_{cb}^- \]

ii. Charge carrier trapping:

\[ h_{vb}^+ + >\text{Ti}^{IV}OH \rightarrow \{ >\text{Ti}^{IV}OH^* \}^+ \]

\[ e_{cb}^- + >\text{Ti}^{IV}OH \leftrightarrow \{ >\text{Ti}^{III}OH \} \]

\[ e_{cb}^- + >\text{Ti}^{IV} \rightarrow >\text{Ti}^{III} \]

iii. Charge carrier recombination:

\[ e_{cb}^- + \{ >\text{Ti}^{IV}OH^* \}^+ \rightarrow >\text{Ti}^{IV}OH \]

\[ h_{vb}^+ + \{ >\text{Ti}^{III}OH \} \rightarrow >\text{Ti}^{IV}OH \]

iv. Interfacial charge transfer:

\[ \{ >\text{Ti}^{IV}OH^* \}^+ + \text{Reductant} \rightarrow >\text{Ti}^{IV}OH + \text{Reductant}^{*+} \]

\[ e_{tr}^- + \text{Oxidant} \rightarrow >\text{Ti}^{IV}OH + \text{Oxidant}^{*-} \]

Where \( >\text{TiOH} \) represents the primary hydrated surface functionality of TiO$_2$, \( h_{vb}^+ \) is a valence band hole, \( e_{cb}^- \) is a conduction band electron, \( e_{tr}^- \) is trapped electron, \( \{ >\text{Ti}^{IV}OH^* \}^+ \) is the surface-trapped valence band hole, and \( \{ >\text{Ti}^{III}OH \} \) is the surface-trapped conduction band electron. Characteristic times for the various steps range from 10 ps to 100 ns, except for electron scavenging by oxidant which is as slow as milliseconds.
Gerischer and Heller have suggested that reduction of oxygen is the rate-limiting step in most photocatalytic oxidations [35,36].

The redox potential for photogenerated holes is +2.53 V versus the standard hydrogen electrode (SHE). These holes can oxidize water or hydroxide ions to form hydroxyl radicals (OH$^\cdot$), whose redox potential is only slightly decreased. Both are more positive than that for ozone and are potent oxidants, which can directly oxidize organic molecules at the surface, eventually mineralizing them to CO$_2$, water and mineral acid [13]. In order for the oxidation process to proceed effectively, the photogenerated electrons must also be removed from the TiO$_2$ particle. Typically, oxygen is used as the electron acceptor. Oxygen can be reduced to the superoxide, O$_2$$^{-\cdot}$, which may also participate in the degradation reactions of the organic molecules, or be further reduced to hydrogen peroxide or water.

When the concentrations of e$^-$ and h$^+$ on the TiO$_2$ particle are high, they are likely to recombine to produce heat. The e$^-$ and h$^+$ can also become immobilized at surface defects, i.e., shallow traps [17,37]. While holes are usually powerful enough to initiate oxidation in either the free or trapped state, electrons can relax in traps below the reduction potential of O$_2$, called deep traps. The occupation of a deep electron trap inevitably leads to recombination with a hole, while the occupation of a shallow electron trap can also lead to transfer across the TiO$_2$/solution interface to O$_2$ [5,8,14,38].

Recombination and trapping of charge carriers accompanied by the competition with interfacial charge transfer determine the overall quantum efficiency, which is defined as the efficiency with which photons are utilized [39,40],

$$\phi = \frac{\text{moles of molecules transformed by photons}}{\text{moles of photons absorbed}}$$ \hspace{1cm} (2-2)
For heterogeneous photocatalysis, it is experimentally difficult to determine the intrinsic quantum yield because of light scattering off the semiconductor particles. Scattering losses can be significant, and have been determined to account in some cases for up to 70% of the incident photons [10,39,40]. To circumvent the problem of quantifying the number of photons absorbed, researchers often report photoefficiencies or apparent quantum efficiency [39,40],

\[
\phi_{\text{apparent}} = \frac{\text{moles of molecules transformed}}{\text{mols of incident photons}}
\]  

(2-3)

Quantum efficiency is usually low for aqueous phase photocatalysis of organic molecules, typically around a few percent. This is the main obstacle that has prevented this technology from being widely commercialized.

For photocatalytic systems in which the rate limiting step is interfacial charge transfer, improved charge separation and inhibition of charge carrier recombination is essential for enhancing the overall quantum efficiency of the photocatalytic process.

2.4 REACTION KINETICS

As mentioned above, the mechanism of photocatalytic oxidation is complicated and it is difficult to develop the reaction kinetics from elementary reaction steps. The rates of photocatalytic reactions depend largely on light irradiance and the characteristics of photocatalysts, which are much more complicated than that of thermal catalytic reactions. A variety of models have been derived to describe the kinetics of photocatalysis, but the most commonly used model is the Langmuir-Hinshelwood kinetic model [41-44]. The LH model relates the rate of surface-catalyzed reactions to the surface covered by the substrate, which assumes equilibrated adsorption of reactants and implies existence of a subsequent slow, rate-controlling surface step [45]. Due to the
complex reaction pathways, LH model is usually restricted to the analysis of the initial rate of degradation \( r_0 \) assuming no competition with reaction by-products. The simplest form of LH model is summarized as follows:

\[
-r_0 = k_{LH} \theta_0 = \frac{k_{LH} K C_0}{1 + K C_0}
\]  \hspace{1cm} (2-4)

The rate is the product of a specific rate constant \( k_{LH} \) for reaction of photogenerated surface species with the adsorbed substrate, the extent of adsorption being determined by \( K \). The role of other species such as intermediates and oxygen is interpreted as competing species [43]. However, many of the experimental results from photocatalytic studies fit the simple form of LH rate expression. This is probably due to the fact that reactor assemblies are simplified and that decompositions of trace contaminant in the water are tested in order to strictly reduce variables and to specify rate-determining steps.

While the Langmuir-Hinshelwood rate form is widely used in photocatalysis, recent research shows discord with this rate equation. Firstly, there is no correspondence between the value of \( K \) obtained from the fit of kinetic data and dark adsorption measurements [46]. Secondly, the LH parameters \( k \) and \( K \) have positive correlations [5]. Thirdly, the influence of both reactant concentration \( C \) and light intensity \( I \) exists in the same photocatalyzed reaction and both the rate constant \( k_{LH} \) and the apparent adsorption constant \( K \) depend on light intensity [47-49]. Alternatively, Ollis [50] presented a pseudo-steady state analysis based upon the stationary state hypothesis for reaction intermediates. In pseudo-steady state approach, reactant adsorption/desorption equilibria are assumed not to be established during reaction since the substantial reactivity of an active center (e.g. hole (\( h^+ \)), radical (OH\(^-\)) or electron (\( e^- \)), etc.) causes a continued displacement of the adsorbed reactant concentration from the coverage corresponding to
liquid-surface equilibrium. The pseudo steady state approach is given by the following equations:

$$-r_A = \frac{k_{cat}^{app} K_{diss}^{app}}{K_{diss}^{app} + C_A}$$  \hspace{1cm} (2-5)$$

where the apparent dissociation constant, the reciprocal of the apparent adsorption constant, exhibits an intensity dependence:

$$K_{diss}^{app} \equiv \frac{1}{K_{ads}^{app}} = \frac{k_{-1} + aI^n}{k_1}$$  \hspace{1cm} (2-6)$$

Both the apparent rate constant and dissociation constant depend on intensity raised to the same exponent. In contrast, the slow step approximation represented by LH rate equation depends on intensity only through the rate constant.

An empirical power rate law including the influence of light intensity was also proposed in the following form [51]:

$$r = kC_0^m I^n$$  \hspace{1cm} (2-7)$$

where I is the photon flux or light intensity. This approach fit each individual kinetic experiment but with different power-law exponents m and n, suggesting an intriguing dependence of all experimental variables without explicitly expressing their intimate relationships. The description indicates that m $\to$ 1 if n $\to$ 0, whereas n $\to$ 1 if m $\to$ 0. Therefore, the reaction orders m and n of photodegradation are interdependent.

Another well-known mechanistic/kinetic model, the Eley-Rideal (ER) model [47], assumes the organic reagent diffuses from the solution bulk onto the photocatalyst surface to interact with the activated state of the photocatalyst, which is different from Langmuir-Hinshelwood (LH) model whereby the organic reagent is pre-adsorbed on the photocatalyst surface prior to UV illumination.
2.5 PHOTOCATALYTIC REACTOR DESIGN

In spite of the potential of photocatalytic technology, development of a practical large-scale water treatment system has not yet been successfully achieved. Capital and operational costs of a photoreactor have to be lowered further to compete with the conventional processes. The design of a photocatalytic reactor is much more complicated than that of a conventional catalytic reactor since an additional engineering factor related to light illumination of catalyst becomes relevant, besides mixing, mass transfer, reaction kinetics, catalyst loading, etc. The high degree of interactions among the transport processes, reaction kinetics, and light absorption leads to a strong coupling of physico-chemical phenomena and a major obstacle in the development of photocatalytic reactors [52].

Several problems have to be solved for the effective design of photocatalytic reactor [53]: (i) the efficient exposure of the catalyst to light irradiation must be achieved since the catalyst shows no activity without photons of appropriate energy; (ii) the problem of poor photon energy absorption due to light scattering has to be considered regardless of reaction kinetics mechanisms; (iii) the reaction rate is usually slow compared to conventional chemical reaction rates, due to low concentration levels of the pollutants; (iv) large amounts of active and stable catalyst must be provided inside the reactor to provide large processing capacity. Among these restrictions, the illumination factor is of utmost importance since the amount of catalyst that can be activated determines the water treatment capacity of the reactor. Efficient reactor design must expose the highest amount of the activated stable catalyst to the illuminated surface and...
must have a high density of active catalyst in contact with the liquid to be treated inside the reactor.

In view of the above problems, new reactor configurations must address two important parameters: (i) light distribution inside the reactor through absorbing and scattering liquid to the catalyst, and (ii) providing high surface areas of catalyst coating per unit volume of reactor. The new reactor design concepts must provide a high ratio of activated immobilized catalyst to illuminated surface and also must have a high density of active catalyst in contact with liquid to be treated inside the reactor.

There are several categorizing methods for photoreactors in the existing literature. Based on the light type, reactors can be divided into two categories: reactors using solar light, and those using artificial light. Several comprehensive review articles have been published discussing the design of solar photocatalytic reactors [4,54,55]. Although our final goal is to utilize solar light, it will not be discussed in this dissertation since our project focuses on reactors using artificial light. Based on the deployed state of the catalyst, reactors can be categorized as slurry reactors and immobilized reactors. As mentioned in section 2.2.2, the reactors that use a suspended nano-sized catalyst have the inherent disadvantage that they require costly catalyst separation. Based on the arrangement of the light source and reactor vessel, all current photocatalytic reactor configurations fall under the categories of immersion type with lamp(s) immersed within the reactor, external type with lamps outside the reactor or distributive type with the light distributed from the source to the reactor by optical means such as reflectors or optical fibers. The distributive type has the inherent advantages of a fixed-bed design coupled with the reaction efficiencies of a slurry phase reactor. The distributive configuration
enhances the uniformity and distribution of activated photocatalyst within a given reaction volume relative to conventional fixed-bed reactor with the immersion type or external type light source. These characteristics reduce the mass transport limitations to photocatalytic reaction efficiency and allows for higher processing capacities. In addition, the possibility of light loss via absorption or scattering by the reaction medium is minimized since the light traveling distance is reduced. A summary of the most important reactor designs using artificial light is given in Table 2.3.

Table 2.3. Overview of photocatalytic reactor configurations

<table>
<thead>
<tr>
<th>Catalyst configuration</th>
<th>Arrangement of light source</th>
<th>Reactor configuration type</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry</td>
<td>Immersion</td>
<td>Annular reactor</td>
<td>Rideh et al. [56]; Pozzo et al. [57]; Romero et al. [58]; Salaices et al. [59]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thin falling film reactor</td>
<td>Yue [60]; Li Puma and Yue [61-65]; Almquist et al. [66];</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Taylor vortex reactor</td>
<td>Sczechowski et al. [67]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pulsed baffled tubular reactor</td>
<td>Gao et al. [68]; Fabiyi and Skelton [69]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Air-lift loop reactor</td>
<td>Sobczynski et al. [70]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fountain reactor</td>
<td>Li Puma and Yue [71-73];</td>
</tr>
<tr>
<td>Slurry</td>
<td>External</td>
<td>Swirl-flow reactor</td>
<td>Chen and Ray [74]; Mehrotra et al. [75]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bubble column reactor</td>
<td>Kamble et al. [76]; Yoshikawa et al. [77]; Lea and Adesina [78]</td>
</tr>
<tr>
<td>Immobilized</td>
<td>Immersion</td>
<td>Ultra-thin UV-tube lamps</td>
<td>Ray and Beenackers [79]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coated wall</td>
<td>Mazzarino and Piccini [80]; Mazzarino et al. [81]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Packed bed</td>
<td>Irazoqui et al. [82]; Dijkstra et al. [83]; Yamazaki et al. [84]; Raupp et al. [85];</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Taylor vortex reactor</td>
<td>Dutta and Ray [86]; Kabir and Ray [87]; Sengupta et al. [88]</td>
</tr>
</tbody>
</table>

(Table con’d.)
Immobilized Immersion Membrane Molinari et al. [89,90]; Bellobono et al. [91-93]; Gianturco and Vianelli [94]; Barni et al. [95];

Fluidized-bed Bhargava et al. [96]; Chiovetta et al. [97]; Pozzo et al. [57]; Haarstrick et al. [98]

Glass-mesh Serrano and de Lasa [99,100]; Topudurti et al. [101]

Immobilized External Fluidized-bed Dibble and Raupp [31]
Rotating disk Dionysiou et al. [102]
Thin film Balasubramanian et al. [103]; Lin and Valsaraj [104]; Arabatzis et al. [105]; Chang et al. [106]

Swirl-flow reactor Zhou and Ray [107]
Coated tube Dijkstra et al. [83]; Al-Ekabi and Serpone [108]

Immobilized Distributive Optical fiber reactor Hofstadler et al. [109]; Peill and Hoffmann [110-113,43]; Sun et al. [114]*; Choi et al. [115]*; Wang and Ku [116,117]*

Monolithic reactor* Sauer and Ollis [118]; Blano et al. [119]; Sanchez et al. [120]; Raupp et al. [121]; Son et al. [122]

Optical fiber monolith reactor Lin and Valsaraj [123]
Multiple tube reactor Ray [124]; Ray [52]

* For gas treatment.

2.6 EFFECTS OF OPERATING PARAMETERS

The rate of photomineralization of an organic compound by photocatalysis depends mainly on the nature and loading of the photocatalyst, reactor configuration, the nature and concentration of the compound, the temperature, wavelength, the radiant flux, the pH, the oxygen concentration, the presence of interfering adsorbing species and mass transfer (especially for immobilized TiO$_2$).
2.6.1 Effect of Light Intensity

At low light intensity and correspondingly low carrier concentrations, the rate of oxidation of a particular compound is proportional to light intensity, while at higher light intensity the rate is dominated by second-order charge carrier recombination and has a square-root dependence on light intensity [125-130]. The transition from one regime to the other depends on the photocatalyst material, but is typically above 1 sun equivalent (7x10^-5 Einsteins m^-2 s^-1) [126]. This transition depends on the (immobilized) catalyst configuration and on the flow regime in the photoreactor, and varies with each application [126]. The optimal light power utilization corresponds to the domain where the destruction rate is proportional to light intensity.

2.6.2 Effect of pH

The pH of an aqueous solution significantly affects all metal oxide semiconductors, including the surface charge on the semiconductor particles, the size of the aggregates formed and the energies of the conduction and valence bands. The adsorption of the contaminants and thus the rates of degradation will be maximum near the zero point charge of the catalyst [131]. The pH value of zero point charge for P25 has been measured as 6.25 [132]. At pH < 6 the TiO_2 surface accumulates a net positive charge, while at high pH the surface has a net negative charge. In accordance with Nernst’s law, varying the pH of the solution shifts the energies of the valence and conduction band edges, by 0.059 V per pH unit (at ambient temperature) [17,133]. This results in the valence band electrons becoming more potent and the conduction band holes less potent at higher pH.
2.6.3 Effect of Initial Concentration

Using low concentrations of pollutants is beneficial since the catalyst surface active sites may be saturated at high concentrations. According to the Langmuir-Hinshelwood reaction kinetics mechanism, for dilute solution \((C_0 < 10^{-3} \text{ M})\), the reaction is of the apparent first order, whereas the reaction is reduced to the zero order at high concentration \((C_0 > 5 \times 10^{-3} \text{ M})\) [6].

2.6.4 Effect of Temperature

Usually photocatalytic reactions do not require heating and are operated at room temperature due to photon activation. The temperature may increase with the release of energy because of the recombination of electron/hole pairs. When temperature increases above 80°C and tends to the boiling point of water, the exothermic adsorption of reactants becomes disfavored [6]. In the range of 20 - 80°C, the degradation rates usually weakly depend on the temperature [134].

2.6.5 Effect of Dissolved Oxygen

The primary role for oxygen in the photooxidation process is to act as an electron scavenger to prevent the recombination of charge carriers. No appreciable destruction was found in the absence of oxygen [83]. However, air can be safely used at commercial-scale operation instead of pure oxygen, which substantially decreases the operating costs [135].

2.7 REFERENCES


CHAPTER III

PHOTODEGRADATION IN A SLURRY BATCH REACTOR: REACTION MECHANISMS AND KINETICS

3.1 INTRODUCTION

Aqueous solutions that contain less than 3 mole percent of organic compounds are classified as “dilute” [1]. Large volumes of industrial wastewaters fall in this category. Organic contaminants are mainly chlorinated compounds and hydrocarbons. Dilute solutions treatment poses a challenge in separation science [2]. Most traditional operations such as distillation, solvent extraction, stripping, and absorption are either infeasible or uneconomical when applied to dilute solutions. Remediation technologies such as incineration, biodegradation, and steam stripping are also uneconomical because the compounds are toxic and/or require treatment of very large volumes of water. Adsorptive separations that involve concentrating organic compounds at a solid/water interface (e.g. alumina, titania, silica, and zeolite) appear to be promising since the adsorbent can be regenerated and reused [3]. Furthermore, surface catalytic oxidation technologies using chemical or photochemical agents are more appropriate for treatment and destruction of contaminants at dilute concentrations. Titania provides such a surface and has been used extensively for heterogeneous photocatalysis.

There are two classes of compounds that we were interested in our laboratory, viz., chlorinated benzenes and polycyclic aromatic hydrocarbons. Chlorinated aromatic compounds form an important class of organic pollutants in industrial wastewaters. They are typically present at sub-ppm concentrations, but are toxic. Most of them are highly hydrophobic and possess low vapor pressure and aqueous solubility. Aryl halide derivatives of benzene have many other uses in chemical synthesis, as pesticides and raw materials for pesticide manufacture and a diverse variety of other applications. 1,2-dichlorobenzene (DCB) is a manufactured organo-halogen compound and is used as a solvent for degreasing hides and wool. It also serves as a synthetic reagent for dye manufacture. Widespread uses over several decades have resulted in contamination of the environment and human exposure to DCB. It is used here as a candidate compound to represent the class of aryl halides. As another important class of organic pollutants in industrial wastewaters, polycyclic aromatic hydrocarbons (PAHs) form a class of refractory pollutants that are persistent in air, water and soil/sediment environments. They are produced as a result of fossil fuel energy usage, although some are of natural origin as well. Typically most PAHs such as phenanthrene (PHE) and pyrene (PYR) have small aqueous solubility and vapor pressure. As a result, they are hydrophobic and accumulate in organic rich environments such as soils, sediments and lipids in biota. Large molecular weight PAHs are toxic and difficult to treat in wastewaters.

In our preliminary batch slurry reactor study, we studied the mechanisms and intermediates for DCB and PAHs degradation on titania. It is important to assure that under the conditions we employed, degradation of DCB and PAHs does not lead to other harmful or toxic by-products. Accordingly, in this work we conducted a series of batch
tests with the primary purpose of identifying the intermediates in the aqueous phase using a gas chromatograph / mass spectrometer (GC/MS).

Using the batch reactor we also identified the kinetics of degradation of the parent compound and the dominant intermediates. The data obtained were also used to answer the question as to whether the process lends itself to complete mineralization of DCB and PAHs. We also evaluated the effects of pH, and the presence of other oxidants on the reaction of DCB.

3.2 EXPERIMENTAL

3.2.1 Materials

1,2-dichlorobenzene (DCB) of 98% purity was obtained from EM Sciences, Gibbstown, NJ. 2-chlorophenol (CP) and 2,3-dichlorophenol (DCP), both of 98% purity were obtained from Aldrich Chemicals, Milwaukee, WI. Phenanthrene (PHE, 98% pure) was also obtained from Aldrich Chemical Corporation. Powdered titania (P25) donated from Degussa Corporation, Akron, PA was used as the photocatalyst. The titania particle had a mean surface area of 60 to 70 m² g⁻¹, a mean particle diameter of 21 nm and the point of zero charge at a pH of 6.8.

3.2.2 Photoreactor Assembly

The reaction was conducted in the batch mode in cylindrical reactors made of quartz. The diameter of each reactor was 1.2 cm and the total height was 11 cm. The reactor had a tight screw cap at the top to prevent the escape of compounds from the head space. A magnetic stirrer at the bottom was used to keep the suspension stirred during the reaction. The reactions were conducted inside a constant temperature chamber (Figure 3.1). The temperature inside the chamber was kept constant at 40±2°C by means of a fan
and an automatic temperature controller (Omron ESC2-R40J, Omron Corp. Japan). Four UV lamps, each 15 W (λ > 302 nm) manufactured by UVP Inc., Upland, CA were used to provide UV light. The lamps were placed two on either side of the reactor assembly, facing each other, to provide uniform UV illumination of the reactor from both sides. The incident radiant flux at the reactor assembly from the lamps was 8.1 mW cm\(^{-2}\) as measured by a UVX radiometer obtained from UVP Inc, Upland, CA.

![Schematic of the batch slurry photocatalytic reactor set up](image)

**Fig 3.1.** Schematic of the batch slurry photocatalytic reactor set up. The reactor assembly is placed inside an aluminum box. 1a to d - UV lamps; 2 - holder for reactors; 3 - Fan; 4 - Temperature Control; 5 - Temperature sensor; 6 - Air inlet.

### 3.2.3 Methodology and Analysis

For DCB degradation, 10 mg TiO\(_2\) was added into 5 ml DCB aqueous solution of desired concentration in a quartz tube reactor and then magnetically stirred for 30 minutes in dark condition to reach the adsorption equilibrium. The pH was adjusted to the desired value by adding 1 M H\(_2\)SO\(_4\) or 1 M NaOH. The suspension was kept stirred and then irradiated using the UV lamp for different reaction times. The concentration at time zero was determined from an unexposed sample. Samples of known volume (5 mL) were taken out and filtered through a Millipore filter to remove TiO\(_2\) particles. The sample was then injected directly into the GC/MS.
For PHE degradation, since the aqueous solubility is too small, the PHE must be first adsorbed onto the TiO$_2$ particles from an ether solution since the solubility of PHE in ether was much higher than in water. Phenanthrene (0.0838 g) was first deposited onto 2.128 g of titania from an ether solution of phenanthrene. The solution was then magnetically stirred to disperse the TiO$_2$ particles and the ether was completely air-dried in the dark in a fume hood. A required amount (200 mg) of TiO$_2$ with adsorbed PHE was added to 100 ml of distilled water. The suspension was sonicated for 10 minutes in the dark and stirred for an additional 30 minutes in the dark to reach adsorption equilibrium. It was then transferred to the batch reactor and irradiated using the UV lamp for 1 to 3 hours duration. A blank experiment was also conducted without UV light irradiation to compensate for the experimental errors and determine the initial mass of phenanthrene adsorbed onto titania. The solution in the batch reactor was continuously purged with pure air at a constant flow rate and the carbon dioxide formed was collected by passing through two bottles of saturated barium hydroxide (200 ml each). Samples of known volume (5 mL) were taken out and filtered through a Millipore filter to remove TiO$_2$ particles. Both TiO$_2$ particles and aqueous solution were extracted using chloroform. The extracts were mixed together and concentrated to 2 ml using a gentle flow of nitrogen. The sample was then used for GC/MS analysis. The barium hydroxide from the bottles was filtered, baked in an oven and weighed to obtain the barium carbonate weight from which the amount of CO$_2$ collected was determined.

The DCB and the intermediates (DCP and CP) in the aqueous sample were analyzed using a Hewlett-Packard gas chromatograph/mass spectrometer (Model HP 5890 Series II) with a mass selective detector (HP 5971). A glass capillary column (60 m
long, 0.53 mm I.D) coated with SPB-20 was obtained from Supelco, Inc. The oven temperature was set at 70 °C initially, with a temperature ramp of 6 °C min\(^{-1}\) to a final temperature of 100 °C. The injector temperature was 180 °C and the detector temperature was also 180 °C. The carrier gas was helium at 0.565 ml min\(^{-1}\). Compound identification was done using the NBS mass spectral library. Chloride analysis was accomplished using a standard argentometric titration method [4].

The PAHs intermediates were analyzed using the same GC/MS system as above. A glass capillary column (30 m long, 0.25 mm i.d.) coated with DB-5 was obtained from Phenomenex. The oven temperature was held for 1 min at 45°C initially and temperature ramped at 30 °C min\(^{-1}\) to 130 °C which was held for 3 min and another temperature ramp of 12 °C min\(^{-1}\) to a final temperature of 325 °C. The injector temperature was 300 °C and the detector temperature was 325 °C. The carrier gas was helium at 0.571 ml min\(^{-1}\). Compound identification was done using the NBS mass spectral library.

3.3 RESULTS AND DISCUSSION

3.3.1 Intermediates and Mechanism of DCB Degradation from Batch Experiments

Although photooxidation is an efficient process for conversion of organics, it is important to make sure that the intermediates that were produced during the catalysis are not of higher toxicity than the parent compound. As a result, we conducted preliminary analysis of the reaction products and intermediates of DCB and PAH photodegradation.

Samples from the batch slurry reactor were taken at various times and analyzed on the GC/MS. Figure 3.2 shows the GC/MS traces obtained at 0, 20, 40, 60, 80 and 120 minutes after the photodegradation was started. Three compounds were identified, viz., the parent compound (1,2-dichlorobenzene), and two intermediates (2,3-dichlorophenol
and 3-chlorophenol). One other intermediate compound (catechol) was also detected, but at negligible concentrations only in a few experiments. The sample at 0 hours showed only the parent compound. However, the samples at 20 to 80 minutes showed both intermediates along with the parent compound. The samples at these intervals showed the two intermediates at declining concentrations along with an indication of the disappearance of the parent compound. The last sample showed no trace of the parent compound.

Fig. 3.2. The GC/MS trace of the solution from the batch reactor at various time intervals. The peak at 15.36 min represents the parent compound 1,2-DCB. The peak at 15.12 min represents 2-chlorophenol and that at 18.72 min represents 2,3-dichlorophenol.
compound indicating its complete disappearance and only tiny peaks for the two intermediate compounds. This shows that with time both the parent compound and the intermediates are being degraded. Figure 3.3 shows the concentration distributions of the parent compound (DCB) along with the intermediates, DCP and CP. Whereas DCB shows a first order decrease in concentration, DCP and CP shows an initial increase and subsequent disappearance. The relative concentrations of the intermediate compounds are much smaller than the parent compound. The important observation is that both intermediates show similar patterns indicating that both are being formed and degraded simultaneously.

Several investigators have shown that the main intermediates in the photodegradation of chlorinated aromatic compounds include chlorinated phenols, hydroquinones, catechol and pyrogallol [5-7]. It has also been shown that hydroquinones, catechol and pyrogallol convert to carbonyl compounds and acids as a result of ring

Fig. 3.3. The changes in concentrations of DCB, DCP and CP in the batch reactor as a function of irradiation time. Reactor liquid volume = 5 cm$^3$. 

![Graph showing concentration changes over time for DCB, DCP, and CP.](image)
opening before degradation to CO$_2$ [6,7]. However, others have contended that ring opening did not occur with chlorinated aromatic compounds [5].

Based on our observations of the GC/MS traces that we obtained, a mechanism for DCB degradation is proposed in Figure 3.4. In heterogeneous photocatalysis, the UV light excites TiO$_2$ to produce hydroxyl radicals (OH$^-$) as demonstrated by others [8]. The hydroxyl radical is the main reactant that attacks the meta position of DCB to generate 2,3-dichlorophenol (1). Chloro group is an ortho/para director for aromatic ring modification. Nucleophilic substitution by hydroxyl ion (OH$^-$) generates 2-chlorophenol (2), which subsequently may lead to the formation of hydroquinones (3b, 4b) or 1,2-dihydroxybenzene (catechol) (3a) and o-benzoquinone (4a). Similarly, successive nucleophilic substitution by OH$^-$ of 2,3-dichlorophenol (1) will lead to 1,2,3-trihydroxybenzene (pyrogallol) (6). Only the intermediates 1, 2 and 3a were observed in our GC/MS trace, while 4a was observed in a separate HPLC measurement. From

**Fig 3.4.** Proposed intermediates and reaction mechanism for the mineralization of DCB.
literature observations \[6,9,10\], we know that \(4a\) and \(6\) rapidly degrade to CO\(_2\). It has been reported that for monochlorobenzene degradation two other compounds, viz., chlorohydroquinone (\(3b\)) and hydroxyhydroquinone (\(4b\)) were also observed as intermediates \[10\]. In our work we did not observe either \(3b\) or \(4b\). It is known that these intermediates are rapidly degraded both by direct photolysis as well as photodecomposed on titania \[10\].

The ultimate products are, therefore, chloride ions in solution which were analyzed in a few experiments in the continuous immobilized reactor using titania supported on quartz as described later in this paper. We observed that the expected chloride concentration satisfactorily matched the experimentally observed chloride concentrations in the aqueous phase in the reservoir at the end of the experiment. Further, the solution changed acidic by 0.2 pH units. The pH variation, however, cannot be used to monitor the degradation, because it is affected by the dissociation of the intermediate compounds, the formation of organic acids during ring opening, and the adsorption of intermediates. The above observations lend support to the assertion that DCB is completely mineralized and do not produce other toxic products in our reactor.

3.3.2 Intermediates and Mechanism of PAHs Degradation from Batch Experiments

In contrast, intermediates analysis of two PAHs, phenanthrene and pyrene, photodegradation only shows partial mineralization which becomes a limitation of the heterogeneous photodegradation of PAHs. The plausible mechanism of phenanthrene degradation is shown in Figures 3.5 a to c.

HPLC and GC/MS analysis of the aqueous samples showed that 9,10-phenanthrenequinone was an intermediate in the degradation of phenanthrene. It is also a
known intermediate in the conventional direct UV photolysis of phenanthrene in natural water as described by various other investigators [11]. The e\textsuperscript{-}/h\textsuperscript{+} couple generated by UV (<380 nm) illumination of TiO\textsubscript{2} will generate highly oxidizing species as per the following sequence of reactions:

\[
\begin{align*}
TiO\textsubscript{2} + h\nu &\rightarrow e^- + h^+ \\
H_2O &\rightarrow H^+ + OH^- \\
OH^- + h^+ &\rightarrow OH \\
O_2 + e^- &\rightarrow O_2^-
\end{align*}
\]

(Figure con’d)

**Fig. 3.5.** Proposed phenanthrene degradation mechanism (a) Scheme 1: the conversion of phenanthrene to 9,10-phenanthrenequinone. (b) Scheme 2: the various intermediates that result from 9,10-phenanthrenequinone identified by GC/MS. (c) Scheme 3: direct addition of hydroxyl and methyl radicals to phenanthrene.

(Figure con’d)
The hydroxyl (OH$^-$) and superoxide (O$_2^-$) radicals are the primary oxidizing species in heterogeneous photocatalytic processes. The resulting hydroxyl radical attack on the 9-position of 1 (phenanthrene) and subsequent reaction with oxygen and superoxide radical will lead to the formation of 9,10-phenanthrenequinone (2). The plausible mechanism is shown in Scheme 1 in Figure 3.5. GC/MS peak area for this compound was very small in the early stages of the reaction and was non-existent in the later samples. This indicates
Fig. 3.6. GC/MS trace of the phenanthrene solution after 60 min of reaction in the batch mode.

- $t=21.53$ mins: 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester, (3)
- $t=21.74$ mins: 1,2-benzenedicarboxylic acid, diisooctyl ester, (4)
- $t=19.75$ mins: 9,10-Phenanthrene dione, (2)
- $t=19.30$ mins: 2-Phenanthrenol, (6)
- $t=18.93$ mins: 9,10-Dihydro-9,10-dihydroxyphenanthrene
- $t=17.64$ mins: Phenanthrene, 2-methyl-, (5)
- $t=16.59$ mins: [1,1'-Biphenyl]-2,2'-dicarboxaldehyde, (9)
- $t=16.43$ mins: Phenanthrene, (1)
- $t=15.53$ mins: 9H-Fluorene, 4-methyl-, (8)
- $t=14.24$ mins: Fluorene, (7)
that 9,10-phenanthrenquinone is a transient species and is probably easily oxidized to other species. Matsuzawa [12] has shown that 9,10-phenanthrenquinone undergoes photolysis by UV light to produce phthalic acid. Figure 3.6 shows the GC/MS trace of the aqueous solution containing phenanthrene and TiO$_2$ after 60 min of treatment in the batch reactor. Seven intermediates (3-9) were isolated and identified in the GC/MS trace for phenanthrene degradation. It is proposed that 9,10-phenanthrenquinone undergoes ring opening and subsequent reaction with the alkyl radicals generated by TiO$_2$ photooxidation to form the various aldehydes and esters (Scheme 2). The other intermediates 7 (fluorine) and 8 (9H-fluorene, 4-methyl) are believed to be formed by further hydroxyl radical attack on 9 ((1,1'-biphenyl)-2,2'-dicarboxaldehyde). Compounds 5 (phenanthrene, 2-methyl) and 6 (2-phenanthrenol) are formed by direct addition of •OH or •CH$_3$ radicals to the parent compound 1 (phenanthrene) and further elimination/rearrangement in some cases (Scheme 3). Aldehydes and esters have also been observed in the conventional photolytic oxidation (UV or ozone) of PAHs [11].

![Chemical structures](Fig. 3.7. The postulated mechanism of pyrene degradation mechanism and the intermediates identified by GC/MS.)

For pyrene, we observed two intermediates, viz., 11 (naphthalene, 1,2,3,4-tetrahydro-1-phenyl) and 12 (bis(2-ethylhexyl)phthalate) as shown in the Figure 3.7. The presence of 12 is once again indication of the formation of a quinone with a subsequent
ring opening reaction, which is similar to the reaction mechanism of phenanthrene photomineralization.

The CO₂ generated during the phenanthrene batch reaction was absorbed using saturated barium hydroxide solution. The amount of CO₂ is calculated from the weight of the barium carbonate. Table 3.1 displays the data from the mass balance in the batch reactor where the amounts of phenanthrene and CO₂ after 1 and 3 hours of reaction were determined. The mass of phenanthrene removed is 35% in 1 hour and 67% in 3 hours of reaction. However, only 28.6% of the reacted phenanthrene is converted to CO₂ in 1 hour and 40.1% in 3 hours of reaction. This indicates that although a substantial portion of phenanthrene on the titania surface has reacted photocatalytically, a fraction of the phenanthrene is converted to stable products via radical recombination mechanisms. This indicates that with large reaction times in a reactor there is the distinct possibility of formation of stable intermediates which can be more toxic than the parent compound. This fact was also noted for the photodegradation of naphthalene on titania [13]. This is a limitation of the heterogeneous photochemical degradation of polycyclic aromatic hydrocarbons.

**Table 3.1 Mineralization of phenanthrene to carbon dioxide**

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>Percent phenanthrene removed</th>
<th>Moles of phenanthrene removed</th>
<th>Moles of CO₂ for complete mineralization of phenanthrene</th>
<th>Actual moles of CO₂ observed</th>
<th>Percent conversion to CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.1</td>
<td>$9.108 \times 10^{-6}$</td>
<td>$1.275 \times 10^{-4}$</td>
<td>$3.469 \times 10^{-5}$</td>
<td>28.6</td>
</tr>
<tr>
<td>3</td>
<td>67.6</td>
<td>$9.653 \times 10^{-6}$</td>
<td>$1.352 \times 10^{-4}$</td>
<td>$5.422 \times 10^{-5}$</td>
<td>40.1</td>
</tr>
</tbody>
</table>
3.3.3 Kinetics of Photodegradation of DCB and Intermediates

The well known Langmuir-Hinshelwood mechanism for photodegradation on titania gives the following equation for the initial rate of the reaction in a batch reactor

\[-r_0 = \frac{kKC_0}{1 + KC_0}\]  \hspace{1cm} (3-1)

where \(-r_0\) is the initial rate in \(\text{mol l}^{-1} \text{min}^{-1}\), \(k\) is the reaction rate constant in \(\text{mol l}^{-1} \text{min}^{-1}\), \(K\) is the binding constant in \(\text{l mol}^{-1}\) and \(C_0\) is the initial solute concentration in \(\text{mol l}^{-1}\). The above equation can be linearized to obtain

\[-\frac{1}{r_0} = \frac{1}{kK} \frac{1}{C_0} + \frac{1}{k}\]  \hspace{1cm} (3-2)

The slope of equation (3-2) is \(1/kK\) and the intercept is \(1/k\), from which both \(k\) and \(K\) can be obtained. The data obtained for DCB was fitted to equation (3-2) as shown in Figure 3.8. DCP and CP were fed into the batch reactor individually and the disappearance rates were obtained separately. The degree of fit was satisfactory in each case. The rate constant \(k\) and the binding constant \(K\) for each reactant calculated from Figure 3.8 are given in Table 3.2. The quantum efficiency was obtained from the equation \(\varphi = (-\frac{dC}{dt})_0 / (\frac{d[hv]}{dt})_0\), where \((dC/dt)_0\) is the initial rate of degradation of DCB and \((d[hv]/dt)_0\) is the incident photon flux per unit volume. The initial rates were obtained from the initial slopes of the conversion versus time data in each case. The photon flux \((1.6 \times 10^{-6} \text{ mol s}^{-1})\) was obtained from the experimentally determined radiant flux of UV light falling at the reactor \((8.1 \text{ mW cm}^{-2})\). Note that \(k^* = kK\) represents the pseudo first-order rate constant at low concentrations of the contaminant. \(k\) is larger for DCP and CP compared to DCB indicating that the intermediates degrade much faster than DCB. The surface rate
constants, k’s for the three compounds are similar to those reported for other chlorinated compounds on titania [14].

![Fig. 3.8. Reciprocal initial rate versus reciprocal initial concentration for the parent compound (DCB) and the two intermediates (DCP and CP).](image)

**Table 3.2** Langmuir-Hinshelwood rate parameters and quantum efficiencies for DCB, DCP and CP degradation in the batch reactor

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k = kK/\text{min}^{-1}$</th>
<th>$k/\text{mol l}^{-1} \text{min}^{-1}$</th>
<th>$K/\text{l mol}^{-1}$</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>0.053 ± 0.012</td>
<td>$(9.2 \pm 0.9) \times 10^{-6}$</td>
<td>5656 ± 699</td>
<td>$7.2 \times 10^{-5}$ to $5.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>DCP</td>
<td>0.263 ± 0.111</td>
<td>$(9.6 \pm 8.7) \times 10^{-5}$</td>
<td>3664 ± 1538</td>
<td>$1.4 \times 10^{-3}$ to $1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>CP</td>
<td>0.044 ± 0.010</td>
<td>$(1.6 \pm 0.7) \times 10^{-5}$</td>
<td>2913 ± 648</td>
<td>$3.3 \times 10^{-4}$ to $1.5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The binding constants, K’s for the three compounds are large indicating high affinities for the titania surface. The binding constants increase in the order DCB > DCP > CP and are in accordance with their relative hydrophobicity as measured by their octanol-water partition constants. It is of interest to note that the K value determined here
for DCB (5656 l mol\(^{-1}\)) is larger than the value of 25 l mol\(^{-1}\) which was estimated from conventional equilibrium adsorption experiments conducted in the dark [15]. This was also demonstrated by others for a variety of other compounds [16]. A possible explanation is that the actual solute concentration accessible to the oxidizing species on the illuminated titania surface exceeds the equilibrium surface concentration of solute species in the dark experiments. This can be caused by induced photoadsorption or other primary reaction events at the surface that do not occur in the equilibrium adsorption experiments conducted in the absence of UV illumination [16].

Concentrations of DCB investigated in the batch experiments are in the range 0.1 to 0.5 mM. However, the concentrations encountered in most industrial wastewaters are much lower, a few \(\mu\)M or so. At these relatively low concentrations, the pseudo first order rate, \(-r = kKC\) would suffice to describe the oxidation rate of DCB in a batch reactor.

### 3.3.4 Effect of pH and Oxidants on the Degradation of DCB in the Batch Reactor

The effect of pH on the DCB degradation was ascertained in the batch reactor between pH values of 2 and 6.8. HNO\(_3\) was used for adjusting the pH to 2. The initial rates (-\(r_0\)) at different pH values are plotted in Figure 7a. Clearly the rate of degradation was larger at higher pH values. These points to the involvement of the hydroxyl ion in the photodecomposition of DCB as described by the proposed mechanism, since with increasing pH a larger concentration of OH\(^{-}\) is available for photodecolorination. This observation is supported by observations for other similar compounds [6].

The effect of an oxidant such as hydrogen peroxide on photochemical oxidation of organic compounds is somewhat less predictable since both positive and negative
influences are reported in the literature [17]. Hydrogen peroxide acts in two ways. In some cases it provides the necessary hydroxyl radicals by scavenging conduction band electrons. It also acts as a hydroxyl radical scavenger in some instances. In the present case, the effect of added hydrogen peroxide within a concentration range of 0 to 0.3 M is only marginal as shown in Figure 7b. Note that the stoichiometric ratio of oxidant to DCB is 1470 at the highest oxidant concentration. Not withstanding the marginal influence on the degradation of DCB, the cost of the oxidant and its residual concentration in treated water makes its use less attractive for industrial applications.

3.4 CONCLUSIONS

The slurry batch reactor investigated in this work is efficient in photodegradation, however, it is limited in the reactor throughput, i.e., only small volumes of water can be treated at any given time. This limitation can be alleviated using the monolithic reactor
design which is the next stage of our work. We identified the intermediates of DCB, PHE and PYR by GC/MS analysis and postulated the reaction mechanisms. DCB is completely mineralized and do not produce other toxic products in our reactor whereas PHE and PYE photodegradation only shows partial mineralization which becomes a limitation of the heterogeneous photodegradation of PAHs. Specifically, we have evaluated the effects of pH and additives (hydrogen peroxide and surfactant) on DCB degradation, and the kinetic rate constants for modeling the DCB degradation.

3.5 REFERENCES


CHAPTER IV

PHOTODEGRADATION IN A TITANIA THIN FILM REACTOR:
KINETICS AND MASS TRANSFER

4.1 INTRODUCTION

The selection of an appropriate catalyst configuration is of utmost importance in a large scale reactor. Our work in this field is directed primarily towards designing more efficient photochemical reactors [1,2]. Based on an exhaustive review of the literature and on model simulations we concluded that a monolithic reactor configuration would afford the optimum mass transfer rates and reactor throughput [2]. A ceramic monolithic reactor with titania coating that uses optical fibers for UV light delivery is the current focus of study in our laboratory. Optic fibers have quartz as the backbone material. In the monolithic reactor titania is immobilized on the fiber optic tubes and the ceramic monolith. Prior to detailed design, we need information on the mass transfer and photoreaction rate constants for compounds on titania film within the reactor. There are mainly two types of configurations as far as the catalyst is concerned - either as a slurry of titania in suspension or immobilized on inert surfaces. In the last chapter we only describe completely slurry batch reactor data that are not particularly useful for scale up of a continuous reactor. This chapter, therefore, explores laboratory data in a continuous
annular thin film reactor to elucidate kinetics, mass transfer, and radiant flux effects in the photodegradation process. The reaction kinetic parameters including the effect of radiance flux and the mass transfer characteristics are necessary for the design and evaluation of the optical fiber monolith reactor. We will discuss these in subsequent chapters.

4.2 EXPERIMENTAL

4.2.1 Materials

1,2-dichlorobenzene (DCB) of 98% purity was obtained from EM Sciences, Gibbstown, NJ. 2-chlorophenol (CP) and 2,3-dichlorophenol (DCP), both of 98% purity were obtained from Aldrich Chemicals, Milwaukee, WI. Two polycyclic aromatic hydrocarbons were considered, namely, phenanthrene (PHE, 98% pure) and pyrene (PYR, 98% pure), both obtained from Aldrich Chemical Corporation, Milwaukee, WI. PHE is a 3-ring compound, whereas PYR is a 4-ring compound. Both compounds have low aqueous solubility and vapor pressure, and are extremely hydrophobic as evidenced by their octanol-water partition coefficients. Table 4.1 lists the relevant properties of DCB, PHE and PYE. Feed solutions of contaminants were prepared by diluting a known amount of the saturated solution with distilled water.

Powdered titania (P25) donated from Degussa Corporation, Akron, PA was used as the photocatalyst. The titania particle had a mean surface area of 60 to 70 m$^2$ g$^{-1}$, a mean particle diameter of 21 nm and the point of zero charge at a pH of 6.8. In a few experiments, surface modification of titania was achieved using a fluorocarbon surfactant, potassium heptadecafluorooctane sulfonate (PFOS) of 98% purity purchased from Fluka Chemical Corporation, Milwaukee, WI.
Table 4.1. Physicochemical Properties of DCB and the PAHs

<table>
<thead>
<tr>
<th>Property</th>
<th>1,2-Dichlorobenzene</th>
<th>Phenanthrene</th>
<th>Pyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>147</td>
<td>178.24</td>
<td>202.26</td>
</tr>
<tr>
<td>Aqueous solubility / mg l(^{-1})</td>
<td>156</td>
<td>1</td>
<td>0.15</td>
</tr>
<tr>
<td>Vapor pressure / mm Hg</td>
<td>1.5</td>
<td>0.00025</td>
<td>4.5 \times 10^{-5}</td>
</tr>
<tr>
<td>log K(_{ow})</td>
<td>3.4</td>
<td>4.5</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Note: K\(_{ow}\) is the dimensionless octanol-water partition constant (molar concentration ratio). This parameter is a measure of the activity coefficient (hydrophobicity) of the compound in water. All values are at 25°C.

4.2.2 Continuous Photoreactor Assembly

Figure 4.1 is the schematic of the continuous annular photoreactor and ancillaries used in this work. A cylindrical quartz tube reactor (40 cm long and 6 mm I.D.) was fabricated and the catalyst immobilized on the appropriate substrate was then placed inside the quartz tube. Solution containing the contaminant was recirculated through the annular space within the reactor using an external pump at flow rates from 0.5 to 3.5 ml min\(^{-1}\). Four UV lamps (UVP Inc, Upland, CA) were placed around the reactor to give UV light intensity of 1 to 8 mW cm\(^{-2}\) at the reactor depending on the distance from the reactor. The incident light flux at the reactor was measured using a UVX radiometer obtained from UVP Inc., Upland, CA. The entire reactor was kept in a chamber where the temperature was controlled to 40 ± 2°C.

The reactor was configured for both single and multiple pass continuous modes of operation (Figure 4.2) for PAHs degradation. For the multiple pass experiments, the exit stream was mixed with the feed and continuously recycled. Both inlet and outlet concentrations decreased with time in this mode but provided constant steady state
For the single pass experiment, the exit stream was collected in a separate container. Periodic samples were obtained from the inlet and exit in both cases. Feed solutions containing PAHs at desired concentrations were fed to the reactor at the bottom using a pump at various flow rates up to 3.5 ml min\(^{-1}\). The feed solution was prepared by diluting a saturated solution of the target PAH in distilled water.

### 4.2.3 Catalyst Configuration

Powdered titania was immobilized by depositing it on the outside surface of two different materials. Low density polyethylene (LDPE) tube of 37.6 cm length and 3.2 mm O.D. was used as the first substrate for DCB degradation. The second substrate was a quartz rod that had a length of 38 cm and 3 mm O.D. Of the various technologies
available for immobilization of titania on quartz, silica, glass and polymers, we used the dip-coating technique [3]. After roughening the outer surface of the LDPE tube using sand paper, and blocking the open ends, it was dipped into a 12.3 wt% titania dispersed in aqueous solution for 30 minutes. The wet-coated LDPE tube was heated in a furnace (30°C to 75°C temperature ramp) for 2 hours. The heating and coating were repeated two times. The final coated LDPE tube was washed with a large amount of distilled water and then dried at ambient temperature. For the quartz rod, a slightly different method of coating was used. The 20 wt% titania solution was stirred with a magnetic bar for 1 hour and then the rod was dipped into the suspension for 15 min. It was then slowly taken out and dried in a furnace for a few hours at 150°C. The rod was again placed in the slurry solution and returned to the furnace. This process was repeated 6 times. The rod was finally rinsed with water, redried in the furnace at 150°C, and cooled to room temperature before use.

Fig. 4.2. Schematic of the reactor configuration: (a) multiple pass with feed recycle; and (b) single pass without feed recycle.
4.2.4 Methodology and Analysis

To start the experiment, an aqueous solution of known pH was first recirculated through the reactor to obtain a constant surface charge on the titania. Subsequently, the feed solution was circulated through the reactor without UV light for approximately 30 min so that the inlet and outlet concentrations remained same indicating that steady state adsorption on titania was achieved. The UV light was then switched on and the feed and exit concentrations were monitored to obtain the conversion in the reactor. This step was continued until steady state conversion was achieved under the given flow conditions. For the experiment involving surface modification of titania, the surfactant (PFOS) solution was recirculated through the reactor immediately following the pH adjustment step. Subsequently DCB was spiked into the recirculating solution in the reservoir along with the PFOS.

The DCB in the aqueous sample was analyzed using a Hewlett-Packard gas chromatograph/mass spectrometer (Model HP 5890 Series II) with a FID detector. A glass capillary column (60 m long, 0.53 mm I.D) coated with SPB-20 was obtained from Supelco, Inc. The oven temperature was set at 150 ºC.

PHE and PYR in the exit and feed streams were determined by direct injection into a Hewlett Packard liquid chromatograph (HP 1100) equipped with a UV/Visible diode array detector. The aqueous solution was directly injected into the HPLC. The column used was Phenomenex Envirossep-PP (125 x 3.2 mm). The parameters and HPLC conditions used for the analysis were that for the US EPA Standard Method No. 8270 [4].
4.3 RESULTS AND DISCUSSION

4.3.1 Analysis of the Continuous Reactor Data

As indicated earlier (see also Figure 4.2), the continuous flow reactor was operated in either single or multiple pass mode. In the single pass mode, the feed concentration was maintained constant and the exit stream was not recirculated. In the multiple pass mode, the exit stream was recirculated through the reactor after mixing with the feed in the reservoir. In the multiple pass mode, both the feed and exit streams declined in concentrations with time. The steady state fractional removal per pass is defined as $x = 1 - \frac{C}{C_F}$, where $C$ is the effluent concentration and $C_F$ is the feed concentration of the reactor. Note that $x$ is independent of the initial concentration in the reservoir.

There is one essential difference between a continuous flow and a batch reactor, namely, the extent of mixing and therefore the rates of mass transfer from the liquid to the titania surface. Whereas the mass transfer rate could be very large and not limiting for a batch reactor with titania in suspension, the rate would be finite and limiting for the case of titania immobilized on an inert support. Overall mass balances on the solute in the liquid and solid phase in a continuous reactor at steady state give the following equations:

**Liquid Phase:**

$$u \frac{\partial C}{\partial z} + k_m a_v (C - C_s) = 0$$  \hspace{2cm} (4-1)

**Solid Phase:**

$$k_m a_v (C - C_s) = k \frac{K C_s}{1 + K C_s}$$  \hspace{2cm} (4-2)

In the above equations, $C$ is the bulk aqueous concentration (mol cm$^{-3}$), $C_s$ represents the aqueous concentration near the surface of titania film (g cm$^{-3}$). Note that in equation (4-2) a Langmuir-Hinshelwood mechanism was assumed for the degradation of target.
pollutants on titania. From the isotherm data for DCB (Table 3.2 and inset of Figure 3.8) we see that at concentrations < 0.2 mM used in the continuous experiments the isotherm is linear. Moreover, the aqueous solubility of PHE and PYE is even much less than that of DCB (Table 4.1). Therefore we can assume that $K_C \ll 1$. Under these conditions the solid phase mass balance can be approximated to

$$\text{Solid Phase: } k_m a_v (C - C_s) = kK C_s$$  \hspace{1cm} (4-3)

Using equation (4-3) to obtain $C_s$ and substituting in equation (4-1) and solving the resulting differential equation we obtain the following solution for the fraction removal per pass, $x$, at steady state [5]

$$x = 1 - \frac{C}{C_F} = 1 - \exp \left[ -k^* \frac{L}{u} \right]$$  \hspace{1cm} (4-4)

where $k^*$ represents the apparent rate constant (min$^{-1}$), $L$ is the length of the reactor (cm) and $u$ represents the velocity of the fluid through the reactor (cm min$^{-1}$). The product $k^* \frac{L}{u}$ is the reaction Damkohler number, Da. $k^*$ takes into account both the rate of the reaction at the surface of the immobilized catalyst and the mass transfer of the reactant to the surface [5,6]. This is given by the following equation

$$\frac{1}{k^*} = \frac{1}{kK} + \frac{1}{k_m a_v}$$  \hspace{1cm} (4-5)

where $k$ is the rate constant (mol l$^{-1}$ min$^{-1}$), $K$ is the Langmuir-Hinshelwood parameter (l mol$^{-1}$), $k_m$ is the mass transfer coefficient from liquid-to-catalyst surface (cm min$^{-1}$) and $a_v$ is the total effective catalyst area per unit volume of the reactor (cm$^2$ cm$^{-3}$). In equation (4-5) the two terms on the right-hand side represent respectively the reaction rate and mass transfer resistances.
Equation (4-4) can be used to obtain the apparent rate constant $k^*$ from known experimental values of $x$.

$$k^* = -\frac{u}{L} \ln(1 - x)$$  \hspace{1cm} (4-6)

This is useful in understanding the influence of different parameters on the response of a reactor and comparing the different immobilized systems.

**Fig 4.3.** The influent and effluent concentrations of DCB and the overall removal efficiency in the reactor as a function of time. Flow velocity is 2.8 cm min$^{-1}$.

Figure 4.3 shows an example where the overall DCB removal efficiency as well as the inlet and outlet concentrations are plotted as a function of time operated in the multiple-pass mode. The concentration at both the inlet and outlet of the reactor decreased with time. Tracer experiments with chloride showed that the reactor was in plug flow with a residence time of 17.7 min at a flow rate of 0.60 ml min$^{-1}$. The time shown on the x-axis reflects the number of passes in the plug-flow tubular reactor. Using
an average residence time of 15.8 min, one can estimate that at 500 minutes the number of passes is approximately 31. The overall removal of DCB per pass from water remained constant and the process is therefore at quasi steady state. Table 4.2 summarizes the steady state fractional removals (x), the apparent rate constants, and other parameters for the continuous experiments described in this paper. The chloride ion concentrations determined in selected experiments are shown in Table 4.3.

**Table 4.2.** Steady state fractional removal of DCB and apparent rate constants using continuous flow, immobilized titania reactors.

<table>
<thead>
<tr>
<th>Reactor type and Conditions</th>
<th>Number of trials</th>
<th>Steady State Fractional Removal, x</th>
<th>Apparent Rate Constant, k’ / min⁻¹</th>
<th>Loading of titania, mg cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz without surface modifier</td>
<td>20</td>
<td>0.253 ± 0.040</td>
<td>0.022 ± 0.005</td>
<td>7.03</td>
</tr>
<tr>
<td>Quartz without surface modifier</td>
<td>3</td>
<td>0.292 ± 0.080</td>
<td>0.029 ± 0.009</td>
<td>0.19</td>
</tr>
<tr>
<td>Quartz with PFOS as surface modifier</td>
<td>16</td>
<td>0.364 ± 0.080</td>
<td>0.034 ± 0.009</td>
<td>7.03</td>
</tr>
<tr>
<td>LDPE without surface modifier</td>
<td>13</td>
<td>0.436 ± 0.084</td>
<td>0.042 ± 0.011</td>
<td>1.6</td>
</tr>
<tr>
<td>LDPE with PFOS as surface modifier</td>
<td>10</td>
<td>0.508 ± 0.088</td>
<td>0.053 ± 0.013</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Note: Flow velocity through the reactor was 2.8 cm.min⁻¹ in all cases. The illumination intensity was 8.1 mW cm⁻². Initial concentration of DCB in the reservoir was <0.2 mM in all experiments.

**Table 4.3.** Observed and expected chloride concentrations in selected continuous immobilized reactors using titania on quartz.

<table>
<thead>
<tr>
<th>Initial DCB concentration, mM</th>
<th>DCB conversion efficiency</th>
<th>Expected chloride concentration in the feed reservoir, mM</th>
<th>Observed chloride concentration in the feed reservoir, mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.48</td>
<td>0.25</td>
<td>0.24</td>
<td>0.17</td>
</tr>
<tr>
<td>0.46</td>
<td>0.25</td>
<td>0.23</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Figure 4.4a and b show the PHE concentration in the exit and inlet streams for the two cases for a given feed velocity of 7.26 cm min⁻¹. The steady state removals are also shown in the Figures. The time shown on the x-axis for the multiple pass experiment reflects the number of passes in the plug-flow reactor. Using an average residence time of
5.2 minutes, one can estimate that at 400 minutes, the number of passes is 77. The overall removal per pass remained steady and the process is therefore at quasi steady-state. Note
that the steady state removals remained a constant in both cases. As a result, the observed rate constant $k^*$ was also similar in both cases. Therefore, we conclude that both modes of operation are equivalent in extracting reaction rate parameters for PAHs.

4.3.2 Comparison of Immobilized Titania on Different Substrates on the DCB Degradation

As shown in Table 4.2, the fractional removal of DCB using titania on LDPE was $(43.6 \pm 8.4)$ %. The efficiency under the same conditions for titania on quartz was $(25.3 \pm 4.0)$ %. The respective rate constants were $0.042$ and $0.022 \text{ min}^{-1}$. These differences are probably due to differences in the binding characteristics between titania on LDPE and quartz, better surface coverage of titania due to surface conditioning of LDPE as opposed to the quartz surface used without pretreatment, and possibly even different electron-hole interactions on the two substrates. Scanning electron micrographs of titania on LDPE indicated that the surface was highly porous and fractured and presented a large surface area. The fracturing of the film is due to contraction and stress on drying. The quartz coated with titania displayed a smooth surface. The rate constants obtained can be used to determine the reactor length required to achieve a desired separation using equation (4-6).

If a 90% removal of DCB is desired in a single pass under the same conditions of flow velocity $(2.8 \text{ cm min}^{-1})$ and UV intensity $(8 \text{ mW cm}^{-2})$, the length of the reactor required will be 1.6 m for titania on LDPE and 3.0 m for titania on quartz.

The thickness of the surface film estimated from the titania loading on the two substrates and the mean density of titania $(3.7 \text{ g cm}^{-3})$ was $19 \mu$m $(7.03 \text{ mg cm}^{-2})$ on quartz and $4 \mu$m $(1.6 \text{ mg cm}^{-2})$ on LDPE. It is known that the coating thickness does play a role in the degree of photocatalytic activity of supported titania, and that an optimum coating thickness is about $1 \mu$m [7]. For example, in our work when the titania loading on
quartz was reduced to 0.19 mg cm\(^{-2}\), which is equivalent to approximately 0.5 \(\mu\)m surface thickness, the rate constant was 0.029 \(\pm\) 0.009 min\(^{-1}\) as compared to 0.022 \(\pm\) 0.005 min\(^{-1}\) with 19 \(\mu\)m thickness. Previous work indicated that the photocatalytic degradation rate increased with increased catalyst loading up to a maximum and increasing the load beyond had no significant effect [8]. The rates can be interpreted on the basis of per gram of the catalyst or per cm\(^2\) of the underlying substrate [9]. For the present case, the rates on either basis are larger for titania coated on LDPE than quartz. It was also observed that in both cases, the reuse of the coated titania tended to reduce the overall efficiency slightly, though not appreciably.

One experiment was conducted with titania as a slurry in the continuous reactor. The rate constant obtained in the case was only 0.011 min\(^{-1}\). The mass of TiO\(_2\) used in the suspension reactor was similar to that used for titania immobilized on quartz, and five times larger than that used for titania immobilized on LDPE. Thus, we concluded that the activity of titania immobilized on either LDPE or quartz is superior to that used as a slurry suspension. When particles are suspended in water, besides casting shadows, particle aggregation occurs and, inefficient use of light by titania surface results. Moreover, particles of titania immobilized on LDPE or quartz are more effectively dispersed than powdered titania in suspension. The important disadvantage in using powdered titania as a suspension is the difficulty in maintaining a homogeneous dispersion in a tubular reactor.

4.3.3 Effects of Surface Modification of Titania on the DCB Degradation

The pH of the solution affects the reaction rate on titania by changing the surface charge of a mineral oxide such as titania. In the present case all experiments were
performed at an initial pH of 4.0. At pH values less than the point of zero charge (6.8 for titania), the surface is positively charged and hydrophilic and, therefore not favorable for adsorption of hydrophobic compounds such as DCB. Since adsorption of DCB is necessary to affect the photocatalysis, modifying the surface characteristics to increase the affinity of organic compounds will improve the reaction efficiency. We have shown in batch slurry reactor studies that a UV resistant, non-degraded anionic fluorinated surfactant (PFOS) can make the surface of titania more hydrophobic at pH values less than 6.8 [10]. This occurs via the formation of hemi-micelles on the titania surface wherein the long chain fluorocarbon surfactant tails are presented to the water. It was shown that the DCB adsorption increased linearly with the PFOS adsorption, and therefore the reaction rate also increased proportional to the PFOS adsorbed on the surface. Table 4.2 shows this effect in the continuous immobilized reactor that uses a surface-modified titania on both LDPE and quartz. The conversion using the modified titania surface increased over the unmodified titania surface. The added aqueous concentration of PFOS in the feed reservoir was 0.93 mM and the pH was 4.0 in both cases. This type of in-situ surface modification using reusable surfactants may prove beneficial only in those cases where the presence of residual surfactants in treated wastewater can be tolerated, such as in some industrial wastewater treatment operations where the process water is recirculated, and where the surfactants do not interfere with other downstream processes. If the wastewater downstream cannot tolerate any surfactant, then a second stage recovery process will have to be maintained to remove and reuse the surfactant in the upstream photocatalysis unit. It should, however, be
recognized that the use of a fluorinated surfactant is nowadays discouraged due to the environmental persistence of PFOS [11].

Surface modification can also be achieved by permanently changing the surface characteristics of titania. Several such methods are currently reported in the literature. For example, Rajh et al [12] reported that chelating agents such as arginine and salicylic acid improved the electron transfer characteristics from the titania conduction band to the adsorbed molecule. Chandrasekharan and Kamath [13] reported that adsorption of gold nanoparticles on titania films improved the interfacial charge-transfer kinetics of the titania/gold composite surface. Similar observations were also reported by Li and Li [14]. Capping colloidal titania particles using long-chain alkyl xanthates are also known to improve the electron transfer characteristics [15]. In some cases, however, surface modification affects the photocatalytic activity of titania adversely, such as the coating of iron oxides [16].

4.3.4 Effects of Feed Concentration on the PAHs Degradation

The effect of PHE concentration upon fractional conversion was studied for the range between 100 µg l\(^{-1}\) to 1,200 µg l\(^{-1}\). This is shown in Figure 4.5 for a feed velocity of 7.26 cm min\(^{-1}\). It was observed that the fractional conversion did not show any discernible difference or trend in the range of concentrations investigated. Noting that the maximum concentration used was the aqueous solubility of PHE, and that the photodegradation of PHE is not a function of the concentration, it is clear that the adsorption on titania is in the linear region of the Langmuir adsorption isotherm. Only
under these circumstances will equations (4-5) and (4-6) be valid. This also underscores the fact that the linear isotherm assumption for PHE on titania is valid at concentrations as large as the saturation solubility of PAHs. In other words, the saturation adsorption capacity for PAHs on titania is never reached. Recent adsorption studies of PHE on titania and alumina also corroborate this conclusion [17,18].

The quantum yield for the photooxidation was obtained from \( \phi = \frac{k^*C}{d[h v]/dt} \),

where \( d[h v]/dt \) is the incident photon flux per unit volume. The incident photon flux was 1.6 x 10^{-6} mole s^{-1} at the reactor obtained from the measured UV intensity of 8 mW cm^{-2}. The quantum yield obtained varied from 3.7 x 10^{-5} to 2.7 x 10^{-4} for PHE at aqueous concentrations varying from 0.77 to 6.7 μM. The low values are attributable to the low PHE concentrations in water. Since oxidation processes involve secondary reactions...
between primary radicals (hydroxyl and superoxide) and substrates, the quantum yield will depend on substrate concentration.

4.3.5 Effects of Flow Velocity and Mass Transfer on the DCB and PAHs Degradation

**Fig. 4.6.** Effects of the flow velocity on (a) the overall rate of DCB degradation and (b) the mass transfer resistance in the continuous immobilized reactor using titania on quartz.

The fractional removal at steady state for the degradation of DCB using titania immobilized on quartz decreased with liquid flow velocity increasing from 0 and 10 cm min\(^{-1}\). Using equation (4-6) the apparent rate constants (\(k^*\)) were obtained. Now from equation (4-5), since the value of \(kK\) is known (Table 3.1), we can obtain the mass transfer coefficient, \(k_m a_v\). Further the percent of the total resistance (1/\(k^*\)) that is the mass transfer resistance represented by the term 1/\(k_m a_v\) can also be obtained. The value of the overall rate constant is plotted in Figure 4.6a. The mass transfer rate coefficient and the mass transfer resistance are plotted in Figure 4.6b. Primarily the small value of \(k_m a_v\) at low flow velocities is due to small activated surface area to volume ratio, \(a_v\). This is an inherent drawback of an immobilized reactor. We see that as flow velocity increases, the
mass transfer resistance term becomes less and less important. At the largest flow velocity of 8.8 cm min\(^{-1}\), which corresponds to a Reynolds number of 10.4, the percent mass transfer resistance is 33%. In general, if the rate is influenced by the mass transfer term, then the apparent rate constant should increase with flow velocity, \(u\). Beyond a certain value, \(k^*\) is solely reaction-rate controlled and mass transfer resistance becomes unimportant. Equation (4-5) bears this out, since it states that the maximum value of \(k^*\) is \(kK\) which is obtained from the batch reactor which was operated under completely mixed conditions where mass transfer is not limiting.

Fig. 4.7. Overall rate constants (a) and fractional conversions (b) for phenanthrene and pyrene in the continuous annular reactor as a function of feed velocity.

For the photodegradation of PAHs in the same continuous annular reactor, the effect of the liquid feed velocity on the rate constant is shown in Figure 4.7. Figure 4.7a shows the variation in \(k^*\) at flow velocities ranging from 0.5 to 15 cm/min. Both PHE and PYR showed similar trends. The value of the overall rate constant appears to be independent of \(u\) at values greater than 7 cm min\(^{-1}\), while it shows a linear dependence at
smaller flow velocities. Notice, however, that the conversion, x decreased as u increased (Figure 4.7b). For a given reactor length, increasing u decreases the residence time, \( \tau \) and hence the overall conversion of PHE and PYR decrease. However, since \( k^* \) is logarithmically related to the fractional conversion, x (Equation 4-6), increased velocity increased \( k^* \) as shown in Figure 4.7a. There is a specific reason for the dependence of rate constant on u. For this we turn to Equation (4-5) which represents the magnitude of mass transfer and intrinsic reaction terms on the overall rate constant. Equation (4-5) shows that the overall resistance to conversion (\( 1/k^* \)) is the sum of the mass transfer resistance (\( 1/k_{ma_v} \)) and that due to intrinsic reaction (\( 1/kK \)). The intrinsic reaction term is independent of u while the mass transfer resistance decreases as u increases [2,5,19]. \( k_m \) represents the mass transfer of the compound from the aqueous phase to the catalyst surface through the aqueous boundary layer; this is called the diffusion limited or mass transfer controlled regime. Increasing u decreases the boundary layer resistance in the liquid phase, and consequently decreases the term \( 1/k_{ma_v} \) and increases the overall rate constant, \( k^* \). Once the mass transfer limitation is overcome at high u, the conversion is limited only by the intrinsic reaction rate which is independent of u. Thus at high flow rates (> 7 cm min\(^{-1}\)) we reach the reaction limited region. The delineation of this region is of importance in designing our photocatalytic monolithic reactor using immobilized catalysts.

An important observation from Figure 4.7a is that the intrinsic reaction rate constant (\( k^* = kK \) at u > 10 cm min\(^{-1}\)) for PYR is 1.6 times larger than that for PHE under similar conditions of flow and UV illumination intensity (Table 4.4). This difference is primarily a result of the higher adsorption constant K for PYR than for PHE due to the
much larger hydrophobic nature of PYR. This is evident from the fact that logarithm of the octanol-water partition constant is 4.57 for PHE as opposed to 5.13 for PYR (Table 4.1). In Table 4.4, we also list the photolysis rate constants for the two PAHs in pure water as it occurs under UV illumination. As noted, these rate constants are much lower than the titania-catalyzed process.

**Table 4.4. Reaction rate constant and half life for two PAHs with and without titania catalyst**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Phenanthrene</th>
<th>Pyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film titania catalyzed&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intrinsic reaction rate constant (min&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.166 ± 0.006</td>
<td>0.270 ± 0.021</td>
</tr>
<tr>
<td>Half life (min)</td>
<td>4.2 ± 0.2</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>Aqueous photolysis (without titania catalyst)&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction rate constant (min&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>5.4 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.0234</td>
</tr>
<tr>
<td>Half life (min)</td>
<td>1283</td>
<td>29</td>
</tr>
</tbody>
</table>

<sup>a</sup> These values are applicable for the reactor geometry that we have used and valid for the reaction rate controlled regime, where u > 7 cm min<sup>-1</sup>.

<sup>b</sup> The photolysis of PAHs were conducted in pure water in the presence of oxygen at wavelengths > 290 nm [20].

4.3.6 Effects of Radiant Flux on the DCB and PAHs Degradation

The UV light intensity at the reactor was varied by changing the distance of the UV lamps from the reactor. The radiant flux corresponds to approximately 20% of the total electrical power consumed in the reaction. Figure 4.8a shows the influence of the radiant flux on the overall rate constant of the degradation of DCB using titania immobilized on quartz. The radiant flux at the reactor was varied by changing the distance of the lamps within the reactor. It has been confirmed that for all photochemical reactions the rate is proportional to the radiant flux up to a certain value. It is generally
known that above a certain UV photon flux, the reaction rate dependency goes from first order in the reactant concentration to a one-half order; the transition occurring at different intensities for different compounds and reactor configurations [21]. As shown in Figure 4.8a, the direct proportionality of the steady state removal shown in Figure 4.6 confirms the photo-induced nature of the activation of the degradation of DCB. Figure 4.8b shows

Fig. 4.8. Effects of the radiant flux on the overall rate constant of (a) 1,2-dichlorobenzene and (b) phenanthrene degradation in the continuous immobilized reactor using titania on quartz.
the influence of the radiant flux on the overall steady state degradation of PHE using titania immobilized on quartz. That the reaction rate constant increased linearly with the UV illumination intensity up to 2 mW cm$^{-2}$ and thereafter showed smaller changes up to 8 mW cm$^{-2}$. From our results we conclude that an optimum UV intensity of 2 mW cm$^{-2}$ is required for our reactor configuration for the photocatalytic decomposition of PHE.

4.4 CONCLUSIONS

The continuous annular reactor using immobilized titania suffers from limitations of low mass transfer, low exposure of surface area of titania to light and difficulty to scale-up. These limitations can be alleviated using the monolithic reactor design in the following chapters. The work described here has given us essential information needed towards the construction and operation of a monolithic reactor. Specifically, we have evaluated (a) the effects of substrates for immobilization of titania, (b) the flow rate and mass transfer characteristics in a annular reactor configuration such as that to be used in a distributive monolithic reactor, (c) the effects of radiant flux density and surface modification of titania, and (d) the kinetic rate constants for modeling the degradation of DCB and PHE in the monolithic reactor.

4.5 REFERENCES


CHAPTER V

DEVELOPMENT OF AN OPTICAL FIBER MONOLITH REACTOR FOR PHOTOCATALYTIC WASTEWATER TREATMENT*

5.1 INTRODUCTION

The selection of an appropriate catalyst configuration is of utmost importance in a large-scale reactor to provide a large amount of activated photocatalyst per unit volume of liquid treated without loss of the processing capability for the reactor. The majority of photocatalytic reactors, which is a variation of the annular or tubular reactors, suffers from low light utilization efficiencies and mass transport limitations and is limited to laboratory-scale.

In order to meet this reactor design challenge, a novel reactor named optical fiber reactor (OFR) was developed. Marinangeli and Ollis [1-3] first proposed that optical fibers could be used for both remote light transmission and as a solid support for photocatalysts. Experimental application of the idea was demonstrated by Hofstadler et al. [4] who designed a TiO$_2$-coated quartz fiber reactor and used it in the photodegradation of 4-chlorophenol in water. Peill and Hoffmann [5-7] developed, characterized, and modeled an optical fiber reactor (OFR) system for photomineralization of pentachlorophenol, 4-chlorophenol, dichloroacetate, and oxalate in water. Similar batch-type OFR systems were easily devised to use for the photocatalytic degradation of gaseous organic pollutants such as benzene or acetone in air streams [8,9]. The OFR system enhances the uniformity and distribution of the UV light within a given reaction.

volume and allows for the remote delivery of and thus can be used for the in situ treatment of contaminated sites in the environment. However, immobilization of TiO$_2$ on an optical fiber also creates its own problems. In an OFR system, since the contaminants diffusion direction is opposite to the light transmission direction, the charge carriers can be generated relatively far from the liquid-catalyst interface and, consequently, are more susceptible to recombination loss [8]. Also the internal mass transfer resistance within the TiO$_2$ film further lows overall reaction rate. Another drawback of an OFR reactor is that the configuration does not effectively utilize the entire reactor volume. The optical fibers usually take up 20-30% of the reactor volume but provide relatively low surface area of the coating support since the optical fiber is usually thin.

On the other hand, as a unique catalyst support, a honeycomb monolith, which contains a large number of small channels in parallel through which the reacting fluid flows and the catalyst is deposited on the walls of the monolithic channels, can provide a high surface-to-volume ratio and allow high flow rates with low pressure drop. Moore et al. [10] found that a honeycomb monolith substrate has 10~100 times higher specific surface area than that of plates and beads type substrates with the same outer dimensions. Moreover, the monolithic reactor is easy to scale-up by increasing the number of the channels. Several monolithic reactors were used in the treatment of air streams by photocatalysis [11-14]. However, the efficiency of these reactors was hindered since limited UV light could penetrate through the cells of the honeycomb substrate.

In our study, a multi-channel optical fiber monolith reactor (OFMR) with distributed optic fibers inside a ceramic monolithic structure, which combined the advantages of the optical fiber reactor (OFR) and the monolith reactor, was constructed
and tested to provide high photon utilization within a physically compact reactor system. In this configuration, stripped optical fibers coated with thin TiO$_2$ film, which allows the UV light to radially refract out of the fibers, were used as both light distributors and support for photocatalysts. Moreover, thick TiO$_2$ films formed on the inner wall of the monolith channels, which can be illuminated by the refracted UV light out of the optical fibers, provides extra photoreaction sites. Since the surface area of the TiO$_2$ coating layer on the channel wall is larger than that of the TiO$_2$ thin film on the optical fiber, the higher surface area of the illuminated catalyst in the given reactor volume is obtained in an OFMR, compared to an optical fiber reactor. Thus, a higher overall reaction efficiency can be reached.

1,2-dichlorobenzene (DCB) and phenanthrene (PHE) are selected as the model contaminants in water as we did in our preliminary works using conventional reactors [15,16]. Experiments were performed under conditions that were relevant to the evaluation of the design of the optical fiber monolith reactor. A comparison of the overall degradation efficiencies of the present reactor with those of a batch slurry reactor and a continuous annular reactor was made to test the feasibility of the reactor.

5.2 EXPERIMENTAL

5.2.1 Materials

1,2-dichlorobenzene (DCB) of 98% purity was obtained from EM Sciences, Gibbstown, NJ. Phenanthrene of 98% purity was obtained from Aldrich Chemicals, Milwaukee, WI. Powered titania (P25) donated from Degussa Corporation, Akron, PA was used as the photocatalyst. The TiO$_2$ crystallites had a mean surface area of 60-70 m$^2$ g$^{-1}$, a mean particle diameter of 20 nm and the point of zero charge at a pH of 6.8.
5.2.2 Characterization of TiO$_2$ Coating

Two kinds of Multimode quartz optic fibers (3M Power-Core FT-1.0-UMT and FT-400-UMT) with a diameter of 1 mm and 400 $\mu$m respectively were purchased from Thorlab, Newton, NJ and used as the light conductor. The optic fiber wire was cut to multiple pieces with equal-length of 90 cm. A section of the single fiber was then stripped for a desired length. Firstly, the fiber was completely stripped of its protective buffer using a wire stripper and the inner polymer cladding was then removed mechanically with a sharp razor (for large fibers) or a fine sand paper (for small fibers). The stripped fibers were then wiped with a soft tissue soaked in acetone to remove polymer residues on the fiber. After these procedures, the quartz core was completely exposed. Inspection through a microscope found no polymer cladding remaining on the surface of stripped fiber core. A dip-coating method was used to immobilize TiO$_2$ particles on the outer wall of the quartz optic fiber and the inner walls of the monolith substrate. TiO$_2$ suspensions in deionized water were prepared and dispersed by sonication and magnetic stirring. The adhesion of TiO$_2$ particles to quartz is primarily through electrostatic interactions. TiO$_2$ suspensions of 0.125, 0.25, 0.5, 1, 2, and 5 wt % were used to coat the optical fibers, while a 20 wt % suspension was used to coat the monolith channels. The exposed quartz core was dipped into a well-stirred TiO$_2$ slurry solution for 10 minutes, and then air-dried at 260°C for 30 minutes using a heat gun. The dip-drying procedure was repeated twice and then rinse with plenty of deionized water in order to wash out the loosely bound TiO$_2$ particles. The coated fiber was then air-dried at room temperature for 24 hours. Selected coated optic fibers were cut into several 1-cm pieces and gold-coated by using a sputter coater for determination of thickness and surface
roughness of the TiO$_2$ film by a scanning electron microscope (SEM) (Cambridge Model S-360). Dip-coating the monolith channels was similar to that on the optic fibers except that the TiO$_2$-coated monolith block was fired in a furnace at 300°C for 1 hour.

5.2.3 Multi-channel Optical Fiber Monolith Reactor

![Diagram of the optical fiber monolith reactor assembly and experimental setup](image)

**Fig. 5.1.** A schematic of the optical fiber monolith reactor assembly and experimental setup. Note that the reactor was operated in the continuous recycle mode. Samples were taken at S1 and S2 to determine the overall removal efficiency.

The experimental assembly for the multi-channel photocatalytic monolith reactor is shown in Figure 5.1. The reactor consists of a light source, a coated optical fiber bundle, a coated multi-channel monolith block, a reaction vessel and a reservoir. The main body is a ceramic honeycomb monolith with 61 cylindrical channels obtained from
Applied Ceramics, Atlanta, GA. All 61 channels are utilized for the optical fiber with a diameter of 0.4 mm, but only 19 channels are utilized for the fiber with a diameter of 1 mm. The rest of channels were blocked permanently by using high temperature resisted epoxy if large fibers were used. The cross-sectional area of fiber bundles of both types of fibers is same, 0.785 cm$^2$. The length of the monolith block is 30 cm with a channel diameter of 3 mm. The multiple cylindrical channels was coated on the inside wall with TiO$_2$ using the dip-coat method. Then the coated monolith block was placed inside a cylindrical stainless steel container fabricated with flanges at either end. One TiO$_2$-coated fiber was inserted through each channel in the monolith. Every channel was thus an independent reaction unit. Each fiber passed through perforated plates at the top and bottom of the cylindrical monolith, thus maintaining their center position in each flow channel. The head cover on the top end was attached with provisions for fluid inlet and fiber optic passage. The length of upper parts of optical fibers outside the monolithic reactor is 60 cm. These unstripped parts of optical fibers were then bundled and polished.

Two types of 500 W Xe short arc lamp, Osram XBO 500W/R and Osram XBO 500W/H, which were obtained from Spectral Energy Corporation, NY, were used as the UV radiation source. The former type of lamp can provide higher light intensity and is used for the OFMR with small fibers to ensure that both TiO$_2$-coatings are well illuminated. Light was delivered to the fiber optic bundle from the UV light source, through a collimator, a reflecting mirror, a UV band pass filter (310-380 nm), a condenser lens and finally focused on the polished end of the fiber optic bundle. The incident angle is adjusted at 85°. The influent feed stream was pumped into the reactor in an upflow mode and then recycled through the reactor after mixing in the reservoir. The
solution in the reservoir was well mixed by magnetic stirring. Thus the overall operation was in the continuous recycle mode with multiple passes through the reactor. The volume of the reservoir was 900 mL. The inlet and outlet samples were collected at valve ports S1 and S2 respectively. The bypass line from the outlet of the pump to the reservoir was used to adjust the flow rate of the water stream passing the reactor. Samples were collected in 2 ml vials with a cap and septum.

5.2.4 Methodology and Analysis

The DCB or PHE solution was recirculated through the reactor in the dark (i.e., without UV light) for 2 hours to ensure that adsorption equilibrium was reached. At 2 hours the UV lamp was turned on. The decline in the concentration of DCB or PHE in the reservoir was obtained by periodic analysis of the aqueous phase and the overall reaction loss of DCB or PHE was obtained by sampling the influent and effluent every 10-20 min interval. The DCB in the aqueous sample was analyzed using a Hewlett-Packard gas chromatograph (Model HP 5890 Series I) coupled with a mass spectrometer (HP 5971). The PHE in the aqueous sample was analyzed using a Hewlett-Packard High Performance Liquid Chromatograph (HP 1100). The detailed description can be found in chapter 3 and 4. The incident UV light intensity was measured by a UV radiometer (UVP UVX radiometer) coupled with a 365 nm sensor (UVX-36 long wave sensor).

5.3 RESULTS AND DISCUSSION

5.3.1 Thickness of the Coated Optical Fiber

SEM images of TiO$_2$ layer on a quartz optical fiber with a diameter of 0.4 mm that was coated with 0.25, 0.5, 1.0, 2.0 wt% TiO$_2$ slurry solutions are compared in Figure 5.2 (cross-sectional view), which indicates that the thickness of TiO$_2$ layer was uniform
around the surface of the fiber. TiO2 coating on a larger fiber with a diameter of 1 mm was found to have a similar thickness for a given concentration of TiO2 slurry solution. As shown in Figure 5.3, the thickness was found to be 0.4-1.7 μm for TiO2 layers generated from slurry solutions containing 0.25 - 2 wt% of TiO2. The thickness of the TiO2 layer formed on the surface of the fiber increased almost linearly with increasing TiO2 content in aqueous solution from which the dipping was carried out. Wang and Ku [9] also observed the linear increase of TiO2 coating thickness with increasing the content of TiO2 slurry solution.

**Fig. 5.2.** SEM images of TiO2 layer on a quartz optical fiber that was coated with (a) 0.25 wt%; (b) 0.5 wt%; (c) 1.0 wt%; (d) 2.0 wt% TiO2 slurry solutions.
5.3.2 Kinetics of Photodegradation of DCB and PHE OFMR

The photocatalytic degradation rate of DCB or PHE depends on the concentration of adsorbed reactant and could be explained using the Langmuir-Hinshelwood kinetics [15, 16]. The monolith photocatalytic reactor was operated in a semi-batch mode with continuous recycle of the feed solution. A known volume of the feed solution was stored in the reservoir. The effluent from the reactor was mixed with the feed solution in the reservoir and recirculated through the reactor.

Figure 5.4a and 5.4b show the PHE and DCB concentration in the exit and inlet streams as well as the overall removal efficiency as a function of reaction time. The optical fiber was coated with 0.25 wt% TiO$_2$ sol and the thickness of the TiO$_2$ film was approximately 0.4 μm, which is comparable with the wavelength of UV-A light. The monolith channel was coated with 20 wt% TiO$_2$ sol and the thickness of the TiO$_2$ film is

![Fig. 5.3. Thickness of TiO$_2$ coating on optical fibers with O.D. 400 μm versus concentration of TiO$_2$ slurry solution from which optical fibers were dip-coated.](image-url)
approximately larger than 10 μm which can fully absorb the incident light. Based on our

Fig. 5.4. DCB and PHE concentration in the outlet and inlet streams as well as the overall removal efficiency as a function of time. (a) DCB; (b) PHE. The flow velocity was 2.31 cm min⁻¹; the optic fibers were coated with 0.25 wt% TiO₂ slurry solution; dₐ = 0.4 mm.
observation, although the total length of the coated small fiber is 30 cm, the light is almost extinct after 5 cm from the top. Therefore, the effective reactor length is only 5 cm and the residence time is about 2.16 min at the given flow velocity \( v = 2.314 \text{ cm min}^{-1} \). At 120 min the number of the passes through the reactor is approximately 55. The overall removal of DCB per pass from water remained constant and the process is therefore at quasi-steady state. For DCB, a steady-state conversion of about 17.8\% was obtained under the same condition of flow velocity, \( v = 2.314 \text{ cm min}^{-1} \) and at an initial concentration \( C_0 = 147 \text{ mg L}^{-1} \). The single-pass conversion of PHE was about 11.9\% under the same conditions except the initial concentration was 505 \( \mu \text{g L}^{-1} \). The faster conversion rate of DCB was evident even though the initial concentration of DCB was much higher. The low conversion in both cases was a result of the inadequate use of the reactor volume as mentioned earlier since only 5 cm of the reactor was effective in light transmission from the fiber. If the entire reactor length (30 cm) were available for reaction, the actual conversion would be 69\% and 53\% for DCB and PHE respectively.

5.3.3 Effects of Feed Concentration

The initial concentration of the pollutant is always an important parameter in process water treatment through photocatalysis since the initial concentration affects the coverage on the catalyst surface. The kinetic expression is of the Langmuir type. When the initial concentration of the pollutant is high, the surface of the active catalyst will be saturated by the reactant. Thus the Langmuir-type kinetic rate expression reduces to a zero-order rate expression and the overall rate would not depend on external mass transfer, i.e., be kinetically limited. The concentration versus time will follow a linear relationship. On the other hand, when the initial concentration of the pollutant is very
low, the kinetic rate expression becomes a pseudo-first order. In this case, the overall rate would certainly depend on mass transfer and the initial concentration would not affect the conversion rate. Our previous paper [16] concluded that the saturation adsorption capacity for PAHs on TiO$_2$ was never reached since the solubility of PAHs in the aqueous solution is too small based on the experimental data in an annular continuous reactor. The effect of PHE concentration between 16.7 and 747 μg L$^{-1}$ upon fractional conversion is shown in Figure 5.5 at a fixed feed velocity of 2.87 cm min$^{-1}$ in the monolith reactor. The independence of the PHE fractional conversion on initial concentration was confirmed regardless of the different reactor configuration. This also suggested the necessity to improve the mass transfer behavior in the monolith reactor to get better overall degradation efficiency.

![Figure 5.5](image.png)

**Fig. 5.5.** The effect of initial feed PHE concentration on the removal efficiency. The flow velocity was 2.87 cm min$^{-1}$; the optic fibers were coated with 0.25 wt% TiO$_2$ slurry solution.
5.3.4 Effects of Mass Transfer

Organic compounds must diffuse from the bulk liquid through a boundary layer to reach the liquid-catalyst interface, i.e., external mass transfer. Organic compounds must then migrate through the catalyst layers (diffusion within the catalyst film) to find active surface sites where they adsorb and eventually react. The mass transfer process through the catalyst layer is similar to interparticle diffusion and is defined as an internal mass transfer process. It should be noted that TiO$_2$ catalyst particles are nonporous, and therefore intraparticle diffusion is absent. The internal mass transfer is an intrinsic property of the catalyst film, and is determined by the nature of the catalyst, coating porosity, and the thickness of the catalyst film. Internal mass transfer can be negligible if the catalyst film is very thin. On the other hand, increasing the flow velocity (Reynolds number) over the immobilized catalyst could reduce the external mass-transfer resistance. The extreme case is that the external mass transfer limitation is overcome at high flow velocity and the conversion is limited only by the intrinsic reaction rate, which is independent of flow velocity. For this we turn to Eq. (4-5), which represents the magnitude of external mass transfer and intrinsic reaction terms on the overall rate constant. Eq. (4-5) shows that the overall resistance to conversion (1/k*) is the sum of the mass transfer resistance (1/k$_{ma_v}$) and that due to intrinsic reaction (1/kK). The intrinsic reaction term is independent of feed velocity [15-18]. Increasing flow velocity decreases the boundary layer resistance in the liquid phase, and consequently decreases the term 1/k$_{ma_v}$, and increases the overall rate constant k*. The effect of the liquid flow velocity in the range 2.31 to 6.94 cm min$^{-1}$ on the overall removal efficiency and rate constant is shown in Figure 5.6b. As stated earlier the effective length of the column where light
transmission was occurring from the coated fiber in a channel was only 5 cm although the total fiber length was 30 cm. Thus the mass transfer coefficients are based on the 5 cm

**Fig. 5.6.** The effect of the liquid flow velocity on (a) the overall removal efficiency and (b) rate constant for DCB and PHE in the monolith reactor. The optic fibers were coated with 0.25 wt% TiO₂ slurry solution; dₐ = 0.4 mm.
effective length. Both PHE and DCB showed similar trends. The conversion decreased as flow velocity increased (Figure 5.6a). This is because increasing flow velocity decreases the residence time for a given reactor length and hence the overall conversion of PHE and DCB decrease. However, as shown in Figure 5.6b, the overall rate constant, k*, increased linearly with increasing flow velocity. This means the monolithic reactor was operated in the mass transfer control regime, which lowered the overall degradation efficiency.

5.3.5 Effects of Coating Thickness on Optical Fiber

In each channel of the monolith photocatalytic reactor, the catalyst can be immobilized either on the outer surface of the optical fiber or on the inner surface of the monolith channel. In the former case, the catalyst is illuminated by an immersion-type light source, which is the optical fiber quartz core. In the latter case, the optic fiber can be treated as an external-type light source, i.e., light has to travel through the absorbing liquid medium and then falls on the catalyst surface. Chen et al [19] depicted these two circumstances as substrate-catalyst (SC) and liquid-catalyst (LC) illumination, depending on whether the catalyst is activated from the substrate side or from the liquid side.

In the monolithic reactor, the surface area of the TiO$_2$ layer on the channel wall is much larger than that of the TiO$_2$ layer on the optical fiber (7.5 times larger considering the diameter of the optical fiber is 0.4 mm and that of the channel is 3 mm), thus ensuring that a strong enough UV light reaching the TiO$_2$ layer on the channel wall is the likely key to increase illuminated active catalyst surface area in a given reactor volume for the monolith reactor design. The direction of incident light and the diffusion of reactants onto the TiO$_2$ layer on optical fiber are opposite whereas the direction are same onto the TiO$_2$ layer on the wall of the channel. Based on the Beer’s law, the refracted light intensity is
exponentially extinguished when penetrating into the TiO$_2$ layer. The penetration depth was estimated to be 1.7-3.3 $\mu$m [8] or up to 5 $\mu$m [19], which depends on the characteristic of the catalyst and the porosity of the film. For LC illumination, incident light always penetrate from the outer layer of the TiO$_2$ film and the active catalysts are always close to the liquid-catalyst interface. Therefore internal mass transfer is not a problem in this case. However, SC illumination is much different. When the direction of the light penetration and the reactant diffusion are opposite, light cannot penetrate through the thick TiO$_2$ layer and thus the active catalyst is far away from the liquid-catalyst interface. Consequently, the reactants have to diffuse into the pores of the TiO$_2$ layer and then have a chance to contact the active catalyst. Thus internal mass transfer can be rate controlling, since the pores of the TiO$_2$ layer are very small. A thickness same as the penetration depth was claimed to be optimum for the OFR reactor [7]. However, in our reactor design, a thick TiO$_2$ layer on the optical fiber should be avoided in order to illuminate the catalyst surface on the channel wall. The desired thickness of the TiO$_2$ layer on an optical fiber is to be much less than the penetration depth.

As shown in Figure 5.7, the thickness of the TiO$_2$ film coated on the optical fiber affects the overall PHE rate constant using large optical fiber of 1 mm diameter and small optical fiber of 0.4 mm diameter. The effective reactor length is 10 cm and 5 cm for the reactor using large fibers and small fibers, respectively. Both the overall rate constants reach the highest value when the thickness of the optical fiber is around 0.4 $\mu$m, which is comparable to the wavelength of the UV-A light. The overall rate constants decreased dramatically for coating layers greater than 0.4 $\mu$m. When the TiO$_2$ coating thickness on optical fiber was 5 $\mu$m, almost all the refracted light was absorbed by the TiO$_2$ coating on
fiber and thus the TiO$_2$ coating on the channel wall was not illuminated due to lack of light. In this case, an OFMR becomes an OFR since the only reaction site is at the TiO$_2$ coating on the optical fiber. Figure 5.7 shows that the overall rate constant of the OFMR with optimum TiO$_2$ film thickness (in our finding, it was about 0.4 μm) is approximately 60% and 85% higher than that of the OFR using optical fibers with the diameter of 1 mm and 0.4 mm respectively under the same operation conditions. Note that if the thickness of a TiO$_2$ film is smaller than the wavelength, the film can barely absorb the light. Since the available catalyst surface on the channel wall is much larger than that on the optical fiber, decreasing the light intensity on the catalyst layer on the channel wall could decrease the overall reaction rate substantially.

![Graph](image)

**Fig. 5.7.** The effect of thickness of the TiO$_2$ film coated on the optical fiber upon the overall rate constant.

We observed from Figure 5.7 that even though the optical fibers were not coated with TiO$_2$ layer, some extent of photocatalytic degradation still existed, which contradicts
the assumption of the total reflection of UV light inside the bare quartz fiber core without TiO₂ film immersed in the aqueous solution. For small fibers, this is mainly because the surface of the bare optical fiber core was roughened by sandpaper treatment. The roughness of the interface between quartz and water can either increase or decrease the incidental angle. Thus the light rays whose incidental angles were larger than the critical angle leaked out of the fiber. The leaking light then penetrated the aqueous solution and illuminated the surface of the TiO₂ film on the monolith channel. And these illuminated active catalyst sites contributed to the photodegradation of the organic compounds. For large fibers which were not roughed, however, light escaped from the fiber tip end diffused through the bulk solution and illuminated the TiO₂ coating on the monolith channel wall, which in turn acted as reaction sites.

5.3.6 Comparison of Different Reactor Designs

Quantum efficiency (Φ), which is used to evaluate the efficiency of the photocatalytic reactor, is defined as the number of molecules \( N_{\text{mol}} \) undergoing an event (conversion of reactants or formation of products) relative to the number of quanta \( N_{\text{photon}} \) absorbed by the reactants or by the photocatalyst:

\[
\Phi \equiv \frac{N_{\text{mol}} \text{ (mol/s)}}{N_{\text{photon}} \text{ (einstein/s)}} = \frac{\text{rate of reaction}}{\text{rate of photon absorption}} \quad (5-1)
\]

However, the number of absorbed photons is hard to assess owing to the optical effects, such as reflection, scattering and transmission on the photocatalyst and support. Moreover, it is the total energy consumption, not just the absorbed optical energy, which would be an indicator of the operation cost to evaluate the economic efficiency of a
photocatalytic reactor. Therefore, the usage of the term apparent quantum efficiency referenced to incident photons in heterogeneous photocatalysis was proposed at 365 nm.

\[
\Phi_a = \frac{\text{rate of reaction}}{\text{flux of incident photons}} \approx \frac{k^*C_0V}{I_iA/U_{\lambda=365\text{nm}}} \tag{5-2}
\]

where \( V \) is the volume of treated water solution in the monolith reactor; \( A \) is the illuminated area of the fiber tips; \( U_{\lambda=365\text{nm}} = 3.28 \times 10^5 \text{ J Einstein}^{-1} \) is the energy of 1 molar photons at wavelength \( \lambda = 365 \text{ nm} \). All of the incident photons entering the upper fiber tips were treated as absorbed photons on TiO\(_2\) layers without attenuation. Obviously, the apparent quantum efficiency should be lower than the actual quantum efficiency.

Table 5.1 compares the optical fiber monolith reactor (OFMR) with the batch slurry reactor and the continuous annular reactor (CAR) in our previous study. Based on our calculation, we observed an increase of about an order of magnitude for the illuminated catalyst surface area per unit volume of liquid treated inside the OFMR when compared with the CAR or the OFR reactor. At the flow velocity range of 2 to 8 cm min\(^{-1}\) and an average initial concentration of 500 \( \mu \text{g L}^{-1} \) for PHE, the apparent quantum efficiency of the optical fiber monolithic reactor using small fiber with 0.4 mm diameter is much greater than that of the continuous annular reactor. For DCB at an initial concentration of 17 mg l\(^{-1}\) and at similar flow conditions, the apparent quantum efficiency is about 3 orders of magnitude greater compared with the annular reactor. When using large fibers with 1 mm diameter and fiber coating length of 10 cm, the apparent rate constant for PHE degradation is about ten times larger than that using small fibers, while the apparent quantum efficiency is comparable. All of these observations suggest the highly promising nature of the optical fiber monolith reactor in photocatalysis.
### Table 5.1. Comparison of photocatalytic reactors

<table>
<thead>
<tr>
<th></th>
<th>Slurry Reactor</th>
<th>Continuous Annular Reactor</th>
<th>Optical Fiber Monolith Reactor (d_f = 0.4 mm)</th>
<th>Optical Fiber Monolith Reactor (d_f = 1 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor volume, mL</td>
<td>5</td>
<td>8.1</td>
<td>21.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.94&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mode of reactor operation</td>
<td>Batch</td>
<td>Continuous</td>
<td>Continuous</td>
<td>Continuous</td>
</tr>
<tr>
<td>Illuminated catalyst surface area per unit volume of liquid treated inside the reactor /m² m⁻³</td>
<td>39,473&lt;sup&gt;c&lt;/sup&gt;</td>
<td>141</td>
<td>1,538</td>
<td>2,000</td>
</tr>
<tr>
<td>Apparent rate constant, k*/min⁻¹</td>
<td></td>
<td>DCB: 0.015–0.035</td>
<td>DCB: 4.0–4.5×10⁻²</td>
<td>PHE: 0.08–0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PHE: 0.10–0.17</td>
<td>PHE: 5.3–8.9×10⁻²</td>
<td></td>
</tr>
<tr>
<td>Apparent quantum efficiency</td>
<td>DCB: 7.2–52×10⁻⁵</td>
<td>DCB: 2.8–4.7×10⁻⁴</td>
<td>DCB: 0.045</td>
<td>PHE: 0.5–3.4×10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PHE: 3.7–27×10⁻⁵</td>
<td>PHE: 2.2–3.3×10⁻³</td>
<td></td>
</tr>
<tr>
<td>Scale-up possibility</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

<sup>a</sup> Based on an effective reactor length, which is 5 cm.
<sup>b</sup> Based on an effective reactor length, which is 10 cm.
<sup>c</sup> The value will be much lower than 39,473 m² m⁻³ as most of the suspended catalyst particles are not effectively illuminated.

### 5.4 CONCLUSIONS

A laboratory-scale optical fiber monolithic reactor was designed, constructed and tested with two model compounds (DCB and PHE) for overall performance evaluation. Experimental results showed two orders of magnitude higher apparent quantum efficiency compared with the continuous annular reactor, which suggested an appropriately designed optical fiber monolithic reactor could have potential in photocatalytic water treatment. The effects of initial feed concentration, flow velocity
(mass transfer), and the thickness of the TiO$_2$ layer on the optical fiber were investigated. The results showed mass transfer effects can’t be ignored due to the relatively low flow velocity in each cell of the monolith. Further research work should improve the mass transfer limitations either by increasing the Reynold’s number or changing the reactor column operation mode from the present fix-bed type to a trickle-bed type. Thin TiO$_2$ film on the optical fiber is required in this configuration to prevent the light from total reflection inside the fiber core and facilitating light penetration through the TiO$_2$ layer. The optimum thickness of the TiO$_2$ film on the optical fiber was about 0.4 μm in this study. Thick TiO$_2$ film was formed on the monolith channel wall to fully absorb the incident UV light. In the present study, the short light propagating length, which significantly limits the efficient use of optical fibers, should be overcome.

5.5 REFERENCES


CHAPTER VI
LIGHT TRANSMISSION AND DISTRIBUTION IN AN OPTICAL FIBER MONOLITH REACTOR

6.1 INTRODUCTION

The involvement of light radiation is the most important factor that distinguishes the photocatalytic reactor from the conventional thermally activated reactive processes. The UV light irradiation intensity controls the rate of light energy absorption, which in turn controls the photocatalytic reaction rate [1]. The operation of UV light source is usually considered to be the most expensive component for a photocatalytic oxidation system. Thus both the degradation efficiency and the operation cost for a photocatalytic system can be improved through the increase of the light utilization. The most common conventional fixed-bed photocatalytic reactors are annular or tubular reactors with slurry photocatalysts or immobilized photocatalysts coated on the walls of the reactor, on a support matrix, or around a tubular casing containing the light source [2-6]. In this type of photoreactor, a lamp is usually mounted in the center of the reactor. The emission of the light is assumed to be equal along the lamp. And the lamp is simplified as a line source if the length-to-radius ratio was large enough. The light transmission of the lamp is assumed to be diffuse, i.e., uniform in space and isotropic in directions, which leads to the line source with spherical emission (LSSE) model [7]. A simpler model, which is called line source with plane parallel emission model (LSPP), assumes each point of the line source emits radiation in parallel planes perpendicular to the axis of the lamp [8]. Based on the above simplifications and symmetry of the reactor configuration, the radiation field in the reactor is analyzed theoretically using the radiative transfer equation
that leads to various simplified or rigorous integro-differential mathematical models [1,11]. However, the efficiency of these configurations is comparably low since light-utilization is not effective due to absorption and scattering of the light by the reaction medium and the limited active surface area of photocatalyst. Optical fiber reactor (OFR) has been proven as a potential alternative to conventional photoreactors due to its unique configuration. The light transmitting characteristics within optical fibers in an OFR was reported by several research groups [10-21]. The TiO$_2$-coated quartz fiber transmits light in a specular fashion so that the individual beam of radiation within the fiber will not be diffuse. Therefore, theoretical analysis using RTE is difficult and thus the light transmission in OFR was mostly simulated from the experimental results.

In our study, a titania optical fiber monolith reactor (OFMR) with distributed TiO$_2$-coated optic fibers inside a TiO$_2$-coated ceramic monolithic multi-channel structure, which combined the advantages of the optical fiber reactor (OFR) and the monolith reactor, was constructed and tested to provide high photon utilization within a physically compact reactor system. The surface area of the TiO$_2$ coating layer on the monolith channel wall is larger than that of the TiO$_2$ thin film on the optical fiber. Thus it is likely to increase the illuminated active catalyst surface area in a given reactor volume if strong enough UV light reaches the TiO$_2$ layer on the channel wall for the monolith reactor design. To achieve this goal, it is necessary to determine the UV light transmittance in a single cell of the OFMR. Also an accurate description of the radiation field is the basis to successful modeling and subsequent optimization of the OFMR. In this chapter, we will present such a light transmission model within a single cell of the OFMR.
6.2 EXPERIMENTAL

6.2.1 TiO$_2$ Coating on Optical Fiber

Multimode quartz optic fibers (3M Power-Core FT-1.0-UMT and FT-400-UMT) with a diameter of 1 mm and 400 μm were purchased from Thorlab, Newton, NJ. The optic fiber wire was cut to multiple pieces with equal-length of 35 cm and both tip ends of an individual fiber were polished with super fine diamond sand paper. A section of the single fiber was then stripped for a desired length of 0, 2, 5, 10, 15, and 20 cm respectively. The stripping procedure is given in the previous chapter. A dip-coating method was used to immobilize TiO$_2$ particles on the outer surface of the quartz optic fiber. Detailed coating procedure is described in the last chapter. TiO$_2$ suspensions of 0.125, 0.25, 0.50, 1, and 5 wt % were used to coat the optical fibers.

6.2.2 Measurement of Light Intensity

The experimental assembly consists of a light source, a single stripped optical fiber, and a quartz tube with an inner diameter of 3 mm and a length of 40 cm which simulates the individual monolith cell. A 500 W Osram XBO 500W/H Xe short arc lamp was used as the UV radiation source. Light was delivered to the fiber from the UV light source, through a collimator, a reflecting mirror, a UV band pass filter (310-380 nm), a condenser lens and finally focused on the polished end of the fiber. Adjusting the relative position of the condenser lens and the reflecting mirror we can obtain desired incident angle. Here we set the incident angle at 85°.

The UV light intensity was measured by a UV radiometer (UVP UVX radiometer) coupled with a 365 nm sensor (UVX-36 long wave sensor). The incident light intensity was measured at the end of an unstripped optical fiber. At each fiber length
and for each coating TiO$_2$ sol concentration, total and tip flux measurements were made of the uncoated and coated fibers, respectively. The tip flux was also measured by masking the coated optical fiber with Teflon tape and aluminum foil. The difference between the masked and unmasked fiber tip flux measurements was taken to be the refracted radial light not absorbed by the TiO$_2$ coating. The sensor was attached to a movable control plate, which is used to produce motion up and down or back and forth (Figure 6.1). The light at different axial and radial position was collected by the sensor and the intensity was measured by the radiometer. To better simulate the aqueous photoreaction environment, before measurement the fiber coating was soaked in distilled water. To simulate the single monolith cell, the coated fiber was inserted into a quartz tube of inner diameter 3 mm, same as that of a monolith cell, filled with distilled water. The light intensity on the outer surface of the quartz tube approximated the intensity of light reaching the TiO$_2$ coating on the inner wall of the monolith cell.

**Fig. 6.1.** Schematic of experimental set up for measuring UV light intensity profile of a single optical fiber.
6.3 RESULTS AND DISCUSSION

6.3.1 Development of Light Transmission Model in OFMR

In each channel of the OFMR, the catalyst was immobilized both on the outer surface of the optical fiber and on the inner surface of the monolith channel. In the former case, the catalyst is illuminated by refracted light from the optical fiber quartz core. Light further travels through the absorbing liquid medium and then falls on the catalyst surface on the channel wall. The methods of light illumination on these two TiO$_2$ coating layers are quite different. We characterized these two circumstances as back-side and front-side illumination, respectively. For the back-side illumination, the direction of incident light...
and the diffusion of the reactants onto the TiO$_2$ layer are opposite, while they are the same for the front-side illumination. An optimum catalyst layer thickness exists for back-side illumination while rate increases monotonically to reach a saturation value with increasing coating thickness for front-side illumination [23,24]. This observation was confirmed by our study [22]. We coated the optical fibers to form the TiO$_2$ film thin enough to let light refract out while the monolith block is coated with a thick enough film to absorb all the refracted light out of the optical fiber. Figure 6.2 shows schematically the profiles of UV light in a single cell of the monolith with a coated optical fiber inserted.

Light in the form of a plane wave, which propagates in the quartz fiber core medium and impinges on an interface with an outer medium having a different refractive index, can be reflected and/or refracted according to Snell's law. When light falls on the smooth quartz interface, a part of it is reflected specularly in a specified direction and travels axially within the fiber and transmits from the bottom tip of optical fiber after multiple reflections, if applicable. The rest of light refracts into the outer medium. The reflection/refraction relationship follows Fresnel equation. The efficiency of light refraction to the TiO$_2$ coating in a single optical fiber depends on various parameters such as incidence angle, wavelength, refractive index, coverage of the coating, the coating thickness, the porosity of the coating layer, the fiber diameter and the fiber length [14,15]. In the present optical setup, the incident angle of light flux is near 90°, which was suggested by Peill and Hoffman [14] to enhance the axial light transmission. The axially propagating light loss contributes to the refractive light through the quartz-TiO$_2$ layer interface and the absorption of the fiber quartz core. Furthermore, the loss of
refractive light out of the optic fiber contributes to the absorption and scattering of the TiO$_2$ coating on the fiber. The absorption by the fiber quartz is negligible since quartz is almost fully transparent to UV light. Without the assumption of diffuse light transmission, it is difficult to set up a rigorous radiation transport equation to model the radiation field in the fiber. Marinangeli and Ollis [10] suggested that axial light intensity profile within a coated optical fiber could be represented by a simple exponential decay equation:

$$\frac{I_{\text{axial}}(z)}{I_{\text{input}}} = \exp(-\alpha z) \quad (6-1)$$

where $I_{\text{axial}}(z)$ is the light intensity in the fiber at axial position $z$, $I_{\text{input}}$ is the input light from the top end of the fiber where $z=0$, and $\alpha$ is a refractive loss coefficient that is obtained by fitting the experimental data. Choi et al. [18] revised the form of eq. (6-1) by introducing a new fitting parameter: $f_\theta$, a fraction of incident light with incident angle less than 90°:

$$\frac{I_{\text{axial}}(z)}{I_{\text{input}}} = (1 - f_\theta) + f_\theta \exp(-\alpha z) \quad (6-2)$$

$(1 - f_\theta)I_{\text{input}}$ represents near parallel incident light that is not absorbed by the TiO$_2$ coating. This is reasonable since (i) the interface is not perfectly smooth although light transmission cannot be considered as fully diffuse; (ii) the incident angle changes due to the curved geometry of the fiber interface. Thus there is still some portion of light that transmits out of the tip of a fiber even though the fiber is infinitely long if quartz absorbs no UV light. Compared with the TiO$_2$ film absorption, the absorption by the quartz core can be neglected. Then the refractive light intensity from the optical fiber at axial position...
z can be obtained from the axial light intensity through an energy balance over a segment of \( dz \):

\[
I_{\text{rad}}(z) = \left[-\frac{d_f}{4} \right] \frac{dI_{\text{axial}}(z)}{dz}
\]  

(6-3)

where \( I_{\text{rad}}(z) \) (mW/cm\(^2\)) is the amount of light refracted out of the interface of the fiber core at axial position \( z \); \( d_f \) is the diameter of the optical fiber. Substituting Eq. (6-2) into Eq. (6-3) we obtain the following:

\[
\frac{I_{\text{rad}}(z)}{I_{\text{input}}} = \frac{1}{4} \alpha d_f f_\theta \exp(-\alpha z)
\]  

(6-4)

The refractive light then penetrates the TiO\(_2\) thin layer deposited on the optical fiber. The depth of UV light penetration within the catalyst depends on the porosity of the catalyst layer and the thickness of the catalyst layer. The light intensity decreases with the depth of penetration due to the strong absorption and scattering of light by the TiO\(_2\) particles. The Beer’s law is stated to correlate the light attenuation and the thickness of the TiO\(_2\) film:

\[
I_{fc}(z) = I_{\text{rad}}(z) \exp(-\varepsilon l)
\]  

(6-5)

where \( I_{fc}(z) \) is the amount of penetrated light out of the TiO\(_2\) thin coating layer on the fiber at axial position \( z \), \( l \) is the light traveling distance inside the TiO\(_2\) thin layer on the fiber, which is dependent on the TiO\(_2\) film thickness and the refractive angle from quartz core to the TiO\(_2\) coating, and \( \varepsilon \) is the local attenuation coefficient of TiO\(_2\) thin layer whose value depends on the characteristics of the coating layer. Note that the actual photon traveling path inside the TiO\(_2\) film is more than the film thickness since light transmission is not fully directional in the porous film. However, for simplicity we used a film thickness \( \delta \) to approximate \( l \) and \( \varepsilon \) becomes the apparent attenuation coefficient.
Substituting eq (6-4) into (6-5), we can obtain the dimensionless light intensity on the outer surface of the coated fiber:

\[
\frac{I_{f_c}(z)}{I_{\text{input}}} = \frac{1}{4} \alpha d f \exp[-(\alpha z + \varepsilon \delta)]
\]

(6-6)

The penetrated UV light out of the TiO$_2$ film on the fiber then enters the bulk aqueous solution comprising the reaction medium. We assume the absorption by the bulk solution is negligible since the penetration distance of the aqueous solution is very small in the cell of the monolith. Assume the coated fiber is perfectly located in the center of the monolith channel. Since the distance between the fiber and the lamp is close, the light acceptance angle of the TiO$_2$ coating layer on the monolith channel wall is limited. Thus the Linear Source Spherical Emission (LSPP) radiation absorption model in the annular reactor [25] is introduced. The UV light intensity on the outer surface of the TiO$_2$ coating layer on the channel wall can be stated as:

\[
I_{mc} = \frac{R_f}{R_w} I_{f_c}(z)
\]

(6-7)

where $R_f$ is the radius of the optical fiber and $R_w$ is the radius of the monolith channel.

6.3.2 Light Transmission inside the Optical Fiber Core

The distribution of UV light intensity from the lower tip end with various stripping or coating lengths with and without TiO$_2$ coating was shown in Figure 6.3. As shown in Figure 6.3, without TiO$_2$ coating the tip light flux was not a function of the stripping length of the fiber, which implied there was no refracted light loss and absorption loss by the quartz medium. In other words, the light was totally reflected inside the fiber quartz core without refraction and absorption. Total reflection in a quartz fiber was observed by other researchers [14,17,18] and was explained according to the
Snell's law. The critical angle is given by \( \theta_C = \sin^{-1} \left( \frac{n_{\text{dense}}}{n_{\text{rare}}} \right) \) when light travels from denser to rarer medium, where \( n_{\text{dense}} \) and \( n_{\text{rare}} \) are the refractive indices of the denser and the rarer medium, respectively. In our case, the bare stripped optical fiber had a smooth surface without a TiO\(_2\) layer, the quartz core contacted water solution directly. The refractive index of quartz fiber is about 1.46 and that of pure water is about 1.33. Thus the critical angle \( \theta_C \) is about 66°. When \( n_1 > n_2 \) and \( \theta_1 \geq \theta_C \) (in our case, \( \theta_1 \approx 85° \gg \theta_C \)), the traveling light inside the optical fiber will be totally reflected which is undesirable.

The same authors also observed that the absorption of UV light by the quartz fiber was negligible. Wang and Ku [18] claimed that the intrinsic absorbance of a nude fiber could not be ignored and the attenuation coefficient was 0.0821 cm\(^{-1}\). The difference is probably due to the difference in fiber materials.

---

**Fig. 6.3.** Axial distribution of the cross-sectional light intensity along optical fiber with various TiO\(_2\) film thickness and TiO\(_2\)-coated monolith channel. \( I_{\text{input}} = 2.53 \) mW cm\(^{-2}\) as fiber diameter \( d_f = 1 \) mm; \( I_{\text{input}} = 1.89 \) mW cm\(^{-2}\) as fiber diameter \( d_f = 0.4 \) mm.
On the other hand, when \( n_1 < n_2 \), some degree of refraction at the interface will be always present irrespective of angle of incidence (0 to 90°) and total internal reflection will never happen. The refractive index of TiO\(_2\) film in terms of anatase crystalline phase on quartz fiber with sol-gel coating method was recently studied by Danion et al. [21] and Hou et al. [27], and the refractive indices of 2.3~2.35 were reported at 400 nm. The refractive indices of porous TiO\(_2\) thin film on glass were reported to between 2.4 and 2.8 at 400 nm [28]. The refractive index of the porous material is postulated to be a statistical composite of the refractive indices of the particles and the void material (water in our study). Thus increasing the porosity or the packing density of the TiO\(_2\) film decreases the refractive index. Choi et al. [18] estimated a porosity factor of 0.6 for the TiO\(_2\) film using dip-coating method. We can expect a similar refractive index value of 2.1 for the present dip-coated TiO\(_2\) film which is still higher than that of fused silica quartz (about 1.46) in the wavelength range of 300-400 nm. Thus when light from the quartz side falls on the quartz-titania interface, a part of it is reflected and travels axially and the rest is transmitted and emerges from the lateral surface. Figure 6.3 shows the TiO\(_2\)-coated fiber rapidly extinguished the transmitting light (I\(_{axial}\)) along the fiber, which can be well fitted by eq (2). Fitting the experimental data yielded an \( \alpha \) value of 0.386±0.056 cm\(^{-1}\) and an \( f_0 \) value of 0.762±0.033 for the large fiber with 1 mm diameter. For the small fiber with 0.4 mm diameter, the value of \( \alpha \) and \( f_0 \) was 0.777 cm\(^{-1}\) and 0.967, respectively. The attenuation coefficient was comparable with the results obtained by Peill and Hoffmann [14,15], Choi et al. [18] and Wang and Ku [20], who report values of 0.2-0.5 cm\(^{-1}\) with incidental angles of 71°~84°. The difference was attributed to the porosity and the roughness of the TiO\(_2\) coating. Figure 6.3 also shows the propagating light intensity.
within the fiber core decreased rapidly in the first 10 cm fiber length and then approached a plateau value. This observation agreed with the results of Choi et al. [18] and Danion et al. [21]. Based on the ray theory, two types of rays can propagate along an optical fiber. The first type is called meridional rays. Meridional rays are rays that pass through the axis of the optical fiber. The second type is skew rays that travel through an optical fiber without passing through its axis. At a given incident angle, the meridional rays tend to keep the directional path by following the Fresnel reflection/refraction rule. However, the skew rays travel more randomly and tend to have a smoothing effect on the distribution of the light as it is transmitted, giving a more uniform output. A portion of skew rays traveling near parallel the quartz-TiO$_2$ interface are not absorbed by the TiO$_2$ coating along the fiber. In our study, this portion of light took up about 24% of the input light, which is larger than the result of 11% reported by Choi et al. [18] but is less than 53% reported by Danion et al. [21]. The difference might result from the physical properties (porosity, coverage and roughness) of the TiO$_2$ film and the incident angle of light. Figure 6.3 also showed the effect of the coating thickness on the refractive loss was negligible. This suggests that the quartz-TiO$_2$ interface is uniformly covered irrespective of the TiO$_2$ coating thickness.

Figure 6.3 also compares the model-predicted light penetration through an empty TiO$_2$-coated monolithic circular channel with diameter of 3 mm with the light propagation within a TiO$_2$-coated optical fiber. The model was given by Hossain and Raupp [26] as:

$$\frac{I_{\text{e}}(X)}{I_{\text{input}}} = \left[1 + 2X^2 - 2X\sqrt{X^2 + 1}\right] + 0.4 \int_{0}^{\infty} \frac{I_{\text{e}}(X)}{I_{\text{input}}} \sqrt{X^2 + 1} \left[\left|X - X_0\right|^2 + 0.5\right] dX \quad (6-8)$$
where $I_{cs}(X)$ is cross-section intensity at a distance $X=z/d_c$ from the channel entrance; $d_c$ is the diameter of the circular channel. The radiation model described by eq. (6-8) assumes the light source is placed on the top of the monolith channel and the light is diffuse. The reflectivity of the titania coating on the channel inner wall is 0.4. As shown in Figure 6.3, the penetration length within the monolith channel is much shorter than that within the quartz fiber, which suggests that inserting the TiO$_2$-coated optical fiber as the light conductor in the monolith channel extends the light traveling distance and thus enhances the light utilization within the monolith cell.

6.3.3 Light Profile on Lateral Surface of the TiO$_2$ Thin Film on Optical Fiber

![Graph showing light profile on lateral surface](image)

**Fig. 6.4.** Absorbed, transmitted and unrefracted light distribution with a single TiO$_2$-coated optical fiber as a function of coating thickness. Fiber coating length $L = 5$ cm; Fiber diameter $d_f = 3$ mm.

The refracted light from the lateral surface of the fiber quartz core is either absorbed by TiO$_2$ layer or transmitted into the aqueous solution. The ratio of the absorbed and the transmitted light is an important parameter in OFMR design since the former
determines the photocatalytic activity of the TiO$_2$ coating on the fiber and the latter is the light source of the TiO$_2$ coating on the monolith channel wall. The absorbed and transmitted light distribution as a function of TiO$_2$ coating thickness at a fixed coating length of 5 cm is shown in Figure 6.4. As mentioned above, it is the surface coverage and roughness that determine the percentage of the unrefracted light. However, when the coating thickness is very thin (about 240 nm in this case), the ratio of the unrefracted light is obviously higher than that of a thicker coating layer, which indicates that the coverage of the thinnest film is not complete. The light ray hitting the uncovered interface will be totally reflected as we explained earlier.

On the other hand, the thickness strongly affects the percentage of the absorbed light. As shown in Figure 6.5, the percentage of the absorbed light exponentially increases as the TiO$_2$ film thickness increases, which can be fitted to the Beer’s law,

\[ \frac{I_{\text{abs}}}{I_{\text{input}}} = f(1-e^{-\varepsilon \delta}) \]

where $\varepsilon = 1.02 \times 10^{-3} \text{ nm}^{-1}$ and $f = 0.7622$.

![Graph showing the effect of TiO$_2$ film thickness on the absorbed refracted light out of quartz fiber core. Fiber coating length $L = 5$ cm; Fiber diameter $d_f = 3$ mm.]

Fig. 6.5. The effect of TiO$_2$ film thickness on the absorbed refracted light out of quartz fiber core. Fiber coating length $L = 5$ cm; Fiber diameter $d_f = 3$ mm.

On the other hand, the thickness strongly affects the percentage of the absorbed light. As shown in Figure 6.5, the percentage of the absorbed light exponentially increases as the TiO$_2$ film thickness increases, which can be fitted to the Beer’s law,
\[ \frac{I_{\text{abs}}}{I_{\text{input}}} = f_0(1-e^{-\delta \delta}). \]

is the ratio of refracted light to the total input light obtained above; \( \delta \) is the film thickness. The attenuation coefficient of TiO\(_2\) coating obtained by fitting the experimental data in Figure 6.5 is about 0.001 nm\(^{-1}\). This value is comparable with other reported values using quartz fiber with diameter of 1 mm: Aguado et al. \[29\] estimated average coefficients ranging from 0.0006 to 0.001 nm\(^{-1}\) for coatings comprised of nanosized crystallites; Peill and Hoffmann \[14\] found the apparent attenuation coefficient of P25 TiO\(_2\) layer by dip-coating was approximately 0.0003–0.0006 nm\(^{-1}\) for a film thickness of about 2–5 \(\mu\)m; Wang and Ku \[20\] estimated average coefficients ranging from 0.0003–0.001 nm\(^{-1}\) under various coating thickness of 1–18 \(\mu\)m; Danion et al. \[21\] determined the apparent extinction coefficient of the TiO\(_2\) coating prepared by sol-gel method to be 0.005 nm\(^{-1}\).

In the optical fiber reactor (OFR) design, the penetrated refractive light from the optical fiber should be avoided since the leaking light can not be utilized. Therefore, the previous authors usually used thick films and did little research on the lateral leaking light. However, since the direction of the light transmission is opposite to that of the reactant diffusion in OFR, thick TiO\(_2\) film retards the diffusion of reactants into the bottom layer where most of the refracted light is absorbed \[18\]. In the current OFMR design, the TiO\(_2\) film on the fiber is thin enough to let the light refract out and the distribution of the penetrated and absorbed refractive light should illuminate both TiO\(_2\) coating layers on fiber and on monolith channel. Hence, the choice of fiber film thickness represents a tradeoff between light absorption efficiencies by the two TiO\(_2\) coatings. As shown in Figure 6.3, with the TiO\(_2\) film thickness increasing, the percentage of the penetrated refracted light decreases. The optimum film thickness is around 400 nm since
the amount of total refracted light is close to the maximum value and ratio of the absorbed light to the penetrated light is appropriate, i.e., the illumination of the TiO₂ coating on a monolith channel is enhanced at the cost of decreasing an acceptable fraction of the absorbed light by the TiO₂ coating on an optical fiber. Since the surface area of the channel wall is three times larger than that of the optical fiber (the fiber diameter is 1 mm and the channel diameter is 3 mm), the total photoactive sites could increase if more refracted light penetrates the TiO₂ film on fiber.

![Graph](image-url)

**Fig. 6.6.** The effect of the tip light flux on the lateral light profile at the outer surface of a single optical fiber without TiO₂ coating. Stripped fiber length L = 5 cm; fiber diameter d_f = 1 mm; I_input=1507 μW cm⁻².

The profile of the lateral light on the outer surface of the bare optical fiber is shown in the Figure 6.6. The light intensity is almost zero along the bare fiber without TiO₂ coating due to total reflection. The exception takes place near the tip where light intensity sharply increases, which suggests the end effect can’t be ignored, especially for
large and short fibers. Similar to the eq. (5-4), we use the following equation to fit the experimental data:

$$\frac{I_{f}(z)}{I_{\text{tip}}} = \frac{1}{4} d_f \beta \exp[-\beta(L - z)]$$

(6-9)

where $\beta$ is the attenuation coefficient of the tip light flux. Light comes out of the fiber tip end is directional. However, the tip light tends to diffuse without confinement in quartz fiber. Therefore, the value of $\beta$ obtained by fitting experimental data in Figure 6.6 is 1.95 cm$^{-1}$, which is much higher than the value of $\alpha$ we obtained in Figure 6.3. With the larger value of $\beta$, the light intensity decreases more rapidly from the fiber tip end. We call the light transmission pattern from the fiber tip spread transmission, which has a dominant directional component that is partially diffused. Therefore, the inverse square law is not appropriate in the near tip region where the light is not fully diffuse and the distance to the light source is too close.

When the TiO$_2$ coating is applied on the stripped fiber, eq. (6-6) describing the penetrated refracted light intensity profile should be revised to include a component of eq. (6-9) if the end effect can not be ignored:

$$\frac{I_{fc}(z)}{I_{\text{input}}} = \frac{1}{4} \alpha d_f f_0 \exp[-(\alpha z + \varepsilon \delta)] + \frac{1}{4} d_f \beta \exp[-\beta(L - z)] [(1 - f_0) + f_\theta \exp(-\alpha L)]$$

(6-10)

The experimental results were compared with the model predicted results based on eq. (6-10) in Figure 6.7 when fiber coating length is 5 cm. As shown in Figure 6.7, the radially emanating light intensity is only between 4.7 and 18.8 $\mu$W cm$^{-2}$ when the input light intensity is 3140 $\mu$W cm$^{-2}$. The low value of radial intensity is due to two important factors. Firstly, the TiO$_2$ film, especially the thick film, absorbs a noticeable fraction of
input light, and secondly, there is a large difference in surface areas of inlet (polished end of the fiber) and outlet (outer surface of TiO$_2$ coating layer) regions (e.g. the ratio of the surface area of inlet to that of outlet is 0.005 for a fiber with diameter of 1 mm and coating length of 5 cm). Figure 6.7 also shows the effect of the TiO$_2$ film thickness on the profile of non-absorbed refracted light along the optical fiber. The non-absorbed refracted light intensity decreases with increasing film thickness towards the upper part of the coated fiber. However, the difference of light intensities with different film thickness is very close in the region near the lower fiber tip.

Figure 6.8 shows the effect of fiber diameter on the profile of non-absorbed refracted light intensity. Increasing the fiber diameter increases uniformity of the distribution of the light out of the TiO$_2$ film on fiber. Based on the expression of the number of reflections in a TiO$_2$-coated optical fiber given by the Abdelmalek et al. [30],

**Fig. 6.7.** The profile of the penetrated refracted light with various thickness of the TiO$_2$ film on the optical fiber. TiO$_2$-coated fiber length $L = 5$ cm; fiber diameter $d_f = 1$ mm; $I_{\text{input}} = 3140$ μW cm$^{-2}$. 

![Graph showing the profile of the penetrated refracted light with various thickness of the TiO$_2$ film on the optical fiber.](image-url)
NR, the number of reflections, is inverse to the fiber diameter, df. Therefore, as the fiber diameter is increased, photons undergo fewer reflections at the quartz core/TiO\textsubscript{2} interface for a given length. With a larger diameter fiber, the probability that a photon will be refracted out through the TiO\textsubscript{2} film is reduced and thus the light propagation down the fiber is extended. As shown in Figure 6.8, although the fiber length is 20 cm, only the upper 5 cm of the fiber is effectively illuminated for a small fiber with a diameter of 0.4 mm. For a large fiber with a diameter of 1 mm, however, the upper 10 cm and the lower 1.5 cm from the fiber tip is effectively illuminated.

6.3.4 Light Profile on the Surface of the TiO\textsubscript{2} Coating on Monolith Channel Inner Wall

The loss of light intensity in the bulk solution is mainly due to the absorption by the organic medium, which can be quantified with Beer’s law. Quickenden and Irvin [31]
measured the absorptivities of pure water and found that the apparent absorption coefficient was $(0.0100 \pm 0.0006) \text{ m}^{-1}$ at 320 nm. The UV light penetration depth of pure water is about 100 m and is far larger than that of TiO$_2$ coating, which is only a few micrometers. Since the distance between the fiber and the monolith channel wall is only 1~1.3 mm, we can safely neglect the light loss by water absorption without introducing large error. In the presence of a small amount of o-dichlorobenzene (DCB) or phenanthrene (PHE), the absorption coefficient of dilute aqueous solution can be larger by up to several orders of magnitude. We measured the absorption spectra of dilute DCB and PHE aqueous solution in the UV-A region using JASCO V570 spectrophotometer. The spectra showed less than 1% of incident light was absorbed by PHE solution at concentration of 100~1000 ppb and less than 10% of light was absorbed by DCB solution at concentration of 10~100 ppm. For simplicity, we assume the bulk aqueous solution is transparent for the UV light. This assumption will decouple the light transmission and mass transfer in the bulk solution which will greatly simplify the modeling of the OFMR photoreactor.

Figure 6.9 compares the light profiles on the surface of the TiO$_2$ coating layers on an optical fiber and a monolith channel wall. The intensity of the light impinging on the TiO$_2$ coating on the monolith wall is less than the intensity of light penetrated through the TiO$_2$ film on the optical fiber. The decrease in the light intensity is mainly due to the surface area difference of the fiber TiO$_2$ film and the monolith coating layer. For a fiber of diameter 1 mm and a channel diameter of 3 mm, the surface area of the channel is 3 times larger than that of the fiber. Light diffusing from a small trajectory area to a large area is similar to a dilution process. As shown in Fig. 8, the light profile on the monolith
coating layer is more uniform than that on the fiber TiO$_2$ film. The model result is obtained by substituting eq. (6-10) into eq. (6-7). Figure 6.9 shows that the experimental data agree well with the model, which validates the assumption of negligible light absorption in the aqueous solution.

### 6.4 CONCLUSIONS

The profile of the light intensity in a single cell of the optical fiber monolith reactor (OFMR) was measured and successfully modeled. The intensity of the transmitted light within a TiO$_2$-coated optical fiber was exponentially diminished along the fiber and then approached a plateau value. TiO$_2$ film thickness had no direct effect on the refracted light loss but strongly affected the ratio of absorbed refracted light to the penetrated non-absorbed refracted light. Light profile is more uniform as fiber diameter increases. The intensity of refracted light penetrating through the fiber TiO$_2$ film decreased

![Fig. 6.9. Profiles of the intensity of the light on the outer surface of the TiO$_2$ coating layer on the monolith channel wall and on the optical fiber. Fiber length L=10 cm; fiber diameter d$_f$=1 mm; I$_{input}$=19.54 mW/cm$^2$.](image)
exponentially along the fiber but increased rapidly near the fiber tip end. The absolute value of the light intensity on the optical fiber is much less than the input light due to the difference of the peripheral surface area with the cross-sectional area of an optical fiber and the TiO$_2$ film absorption. The ratio of the intensity of the light on the outer surface of the monolith channel wall to that on the optical fiber is in inverse proportion to the ratio of the radius of the monolith channel to that of the optical fiber. The light transmission model with the fitting parameters will be further used as a sub-model in the OFMR reactor model.

6.5 REFERENCES


CHAPTER VII

MODELING THE PHOTOCATALYTIC MULTI-CHANNEL OPTICAL FIBER MONOLITH REACTOR

7.1 INTRODUCTION

The design and modeling of photocatalytic reactors is essential for the successful commercialization of heterogeneous photocatalysis as an alternative method for wastewater treatment [1,2]. The rigorous modeling of photocatalytic reactors requires a complex analysis of the sub-models of the radiation field, the fluid dynamics and the reaction kinetics, which are cross-linked to the material and energy balances in the photoreactor [2-4], and results in integro-differential equations that require demanding numerical solutions. Therefore, these models are difficult to apply to large-scale photoreactors for wastewater treatment. Simpler models obtained by retaining the essential of elements of rigorous models are easier to use for scale-up and design purposes [5]. Thus the development of simple mathematical reactor models is especially important to assist the design, scale-up and optimization of the photocatalytic reactors on an industrial scale [3].

The most widely deployed photoreactor design is the annular flow configuration and modeling of this type of reactors has been extensively developed [5,6]. In our optical fiber monolith reactor design, a single channel with a fiber inserted is considered as an individual mini-annular reactor. The only exception is the reaction site(s). For a conventional immobilized annular reactor, either the reactor wall or the lamp casing is coated with the photocatalyst. Thus only one surface of the annuli is used as the reaction site. For a single channel of optical fiber monolith reactor, both the channel wall and the
fiber are coated with TiO$_2$ and function as reaction sites. In this chapter, we develop a simple model for the optical fiber monolith reactor by incorporating a semi-empirical sub-model of the radiation field which is decoupled with the concentration field of the substrates.

### 7.2 DEVELOPMENT OF THE MODEL

![Diagram of single monolith cell with TiO$_2$-coated optical fiber inserted](image)

**Fig. 7.1.** Schematic of a single monolith cell with a TiO$_2$-coated optical fiber inserted. The channel wall is also coated with TiO$_2$. At reactor inlet, $z=0$; at reactor outlet, $z=L$. $L$ is the coating length or the effective reactor length.

The monolith is composed of a large number of parallel channels whose conditions are presumed to be identical when assuming uniform distribution of variables such as flow flux and radiance flux at the monolith cell inlet and outlet. Figure 7.1 shows the schematic of a single monolith cell with TiO$_2$-coated optical fiber inserted. Under this hypothesis the simulation of the entire multi-channeled monolith reduces to the analysis of a single channel. We will set up a single channel monolith model incorporates a
representation of the developing flow field and simultaneous liquid-phase diffusion, and heterogeneous reaction. This model will also include the influence of the UV light radiance flux which is based on the light transmission sub-model in chapter 5. Except the assumption that all channels are identical, we make the following principal assumption to simplify the problem:

1. Steady state conditions;
2. Isothermal conditions along the monolith channel;
3. The channel is irradiated by a optical fiber placed in the center of the channel; and thus the channel is of annular symmetry;
4. Velocity field is fully developed laminar flow;
5. Dilute solution (dilute contaminants in water); the active sites on the surface of titania films are never saturated;
6. Heterogeneous reaction takes place only at the surface of titania layers on the optical fiber and the channel wall; internal diffusion of contaminants within titania films is neglected; homogeneous photolysis reactions in the bulk water phase are negligible;
7. The reaction is not limited by O₂ sorption or by competitive inhibition from reaction intermediates or other solution species. This assumption is made to simplify the model even though reaction intermediates might significantly affect the reaction rate of the parent compound;
8. Titania coatings on the optical fiber and the monolith channel wall are uniform and the surface is fully covered;
9. There is no deterioration of the photocatalysts, i.e., the activity of the photocatalyst remains same and there is no delamination of the photocatalyst film;

10. Incompressible Newtonian fluid with constant physical properties.

7.2.1 Fluid-Dynamic Model

Assuming steady-state, unidirectional, incompressible, continuous flow under a fully developed laminar regime in the annular channel, the velocity profile in a radial section of the annulus can be expressed as follows [7]:

\[ v_z(r) = \frac{2u}{(1+\eta^2)\ln(\eta)} \left[ 1 - \left( \frac{r}{R_w} \right)^2 + \left( \frac{\eta^2 - 1}{\ln(\eta)} \right) \ln \left( \frac{r}{R_w} \right) \right] \quad (7-1) \]

where \( r \) is an arbitrary radial position in the annulus, \( R_w \) is the radius of monolith channel or the external radius of annulus, and \( u \) is the superficial flow velocity through the annulus:

\[ u = \frac{Q}{\pi R_w^2 (1-\eta^2)} \quad (7-2) \]

where \( Q \) is the volumetric flow rate through the annulus and \( \eta \) is the ratio of the fiber radius to the monolith channel radius or the ratio of internal radius to external radius of annulus:

\[ \eta = R_f / R_w \quad (7-3) \]

where \( R_f \) is the radius of the fiber or the internal radius of annulus. Equation (7-1) is valid for laminar flow only which occurs when

\[ N_{Re} = \frac{2R_w(1-\eta)u \rho}{\mu} \leq 2000 \quad (7-4) \]
For dilute aqueous solution, we approximate the density and viscosity of the solution to those of pure water at room temperature. In this study, the Reynold’s number is between 1 and 11, thus equation (7-4) is satisfied.

7.2.2 Reaction Kinetics Model

The kinetic rate equation used in the present model is derived based on the following: (i) the rates of photocatalytic destruction of organic contaminants can be fitted by a Langmuir-Hinshelwood kinetic rate equation; (ii) the kinetic rate constant follows a power law expression of the total radiation absorbed in the TiO$_2$ coating layers on the outer surface of the optical fiber and the inner surface of the monolithic channel.

\[ KCkI_{\text{ln}} + 1 = C \]  
\[ (7-5) \]

where $K$ refers to the adsorption equilibrium constant; $n$ is the power law coefficient which varies between 0.5 and 1 depending on the light intensity (the suggested threshold value is 25 mW cm$^{-2}$ by Herrmann [8] or 6 mW cm$^{-2}$ by Peill and Hoffmann [9]); $C$ is the reactant concentration. The light intensity, $I$, at the illuminated TiO$_2$ surface inside a monolithic channel is low and $n$ is safely assumed to be 1 without introducing large error. $k$ is an observed rate constant that takes into account the major factors that affect the overall destruction rate: the intrinsic surface reaction rate, $k_s$, quantum yield of photodegradation of the contaminant, $\Phi$, TiO$_2$ film absorptivity for UV light, $\varepsilon$, and the concentration of total active reaction sites on the TiO$_2$ film, $C_a$.

\[ k = k_s \Phi \varepsilon C_a \]  
\[ (7-6) \]

The present kinetic rate equation does not include the effect of reaction intermediates since most of the applications of photocatalytic detoxification involve lightly
contaminated water in which the effect of the intermediates can often be neglected. For very dilute wastewater streams, KC << 1 and eq (7-5) is simplified to yield:

\[-r_{As} = k_T IC\]

where \( k_T \) is the total rate constant that takes into account all other major factors that affect the overall destruction except the concentration of the substrate.

\[k_T = k_s K\phi \sigma C_a\]  

(7-8)

### 7.2.3 Material Balance

With reference to Figure 1, the equation of convective diffusion in the annulus is:

\[v_z(r) \frac{\partial C_A}{\partial z} = D \frac{\partial}{r \partial r} \left( r \frac{\partial C_A}{\partial r} \right)\]

(7-9)

where \( v_z(r) \), \( C_A \) and \( D \) denote the axial velocity, concentration of species A, and diffusion coefficient, respectively. In this unit, the photocatalyst is deposited onto the inner surface of the channel. The stripped optic fiber is placed in the center of the channel and is used to conduct the UV light. The boundary conditions on the fiber titania coating and monolith coating are:

\[D \frac{\partial C_A}{\partial r} = r_{As} \quad r = R_f\]

(7-10)

\[D \frac{\partial C_A}{\partial r} = -r_{As} \quad r = R_w\]

(7-11)

At the reactor inlet,

\[C_A = C_{in} \quad z = 0\]

(7-12)

If the reactor is in the diffusion control region, the reactant A is quickly consumed on the titania surface and the boundary conditions at \( r = R_f \) and \( r = R_w \) become:

\[C_A = 0 \quad r = R_f\]

(7-13)
$C_A = 0 \quad r = R_w \quad (7-14)$

This is normally the case with certain photocatalytic reaction with high quantum yields and rapid kinetics. Therefore, the extent of conversion depends upon the rate of transport of target species to the titania surface from the bulk solution.

The equation of convective diffusion written in terms of species concentration and reactor length can be transformed into one in terms of conversion in a single pass, $x = 1 - \frac{C_{out}}{C_{in}}$, and time, $t$ by allowing $v(r) = \frac{\partial z}{\partial t}$, which implies the cross-sectional geometry of the reactor is constant and the diffusion in the main direction of the convective flow can be neglected. Also using dimensionless form of $\tilde{r} = r/R_w$, then eq (7-9) becomes:

$$\frac{\partial x}{\partial t} = \frac{D}{R_w^2} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial x}{\partial \tilde{r}} \right) \quad (7-15)$$

with the boundary conditions for reaction control:

$$D \frac{\partial x}{\partial \tilde{r}} = k_r I_f (1 - x) \quad \tilde{r} = \eta \quad (7-16)$$

$$-D \frac{\partial x}{\partial \tilde{r}} = k_r I_w (1 - x) \quad \tilde{r} = 1 \quad (7-17)$$

where $I_f$ and $I_w$ are the light intensity on the fiber coating and the monolith channel wall coating, respectively, which is obtained from eq. (5-10) and (5-7) in Chapter 5.

$$I_f = I_{input} \left\{ \frac{1}{4} \alpha d_f f_0 \exp[-(\alpha z + \varepsilon\delta)] + \frac{1}{4} d_f \beta \exp[-\beta(L-z)](1-f_0) + f_0 \exp(-\alpha L) \right\}$$

$$I_w = \eta I_f \quad (7-18)$$

$$I_{input} = \eta I_f \quad (7-19)$$
Here, per fiber $I_{\text{input}}$ equals the measured total incidental light intensity, $I_0$, divided by the total number of fibers within a fiber bundle, $N_f$. The total incidental light is collected by the polished fiber bundle tip end. Given the same cross-section area of the fiber bundle, for large fibers of 1 mm diameter, $N_f = 19$; and for small fibers of 0.4 mm diameter, $N_f = 61$. The boundary conditions for mass transfer control:

\begin{align*}
x &= 1 \quad \bar{\eta} = \eta \\
x &= 1 \quad \bar{\eta} = 1
\end{align*} 

(7-20) 

(7-21)

And the initial condition is:

\begin{align*}
x &= 1 \quad t = 0
\end{align*} 

(7-22)

The mean cup conversion is given by:

\[
x_m = \frac{2}{1 - \eta^2} \int_{\eta}^{1} xu_{dl} \bar{\eta} d\bar{\eta}
\]

(7-23)

where the bulk mean velocity $u_{dl}$ in the annuli:

\[
u_{dl} = \left[ \frac{2}{(1 + \eta^2) - \left( \frac{\eta^2 - 1}{\ln \eta} \right)} \right] \left[ 1 - \bar{\eta}^2 + \left( \frac{\eta^2 - 1}{\ln \eta} \right) \ln \bar{\eta} \right]
\]

(7-24)

7.2.4 Model Simulations

The model equations including the sub-model equations of radiation field in Chapter 5 constitute a system of nonlinear differential equations with complex nonlinear boundary conditions. FEMLAB is used to solve for the single pass conversion. For each value of $r$, with $r$ varying from $R_f$ to $R_w$, eq (7-23) was integrated numerically to obtain the average conversion of the substrate at the reactor outlet.

In a continuous reactor system in which all the flow emerging from the outlet of the photoreactor is recirculated back to the inlet passing through an ideal well-mixed
reservoir, which is assumed to be a continuous flow stirred tank reactor (CSTR), the number of passes \( N_p \) of the aqueous solution through the reactor in a given time \( t \) is:

\[
N_p = \frac{t}{\tau_{\text{reactor}}} = t \frac{Q}{V_{\text{reactor}}} \tag{7-25}
\]

where \( V_r \) and \( \tau \) are the volume and the space time of the reactor, respectively. The rigorous analysis of the present recirculation system requires solving the system of the time-dependent differential equations for the reactor and the reservoir. However, by assuming that the conversions per pass are small (valid when \( V_{\text{reactor}} \ll V_{\text{reservoir}} \)), which are conditions usually verified in most experimental recirculation photocatalytic reactor systems including ours, the differential form can be simplified in a discrete form. With the above assumption, it is sufficient to process the equivalent of one reactor volume of liquid in the time interval of \( \Delta t = \tau_{\text{reactor}} \). Eq (7-23) can be used to calculate the conversion of a single pass of one reactor volume of processed liquid. The new inlet concentration to the reactor after each pass is calculated by a material balance in the reservoir, which yields:

\[
C_{\text{in}}^\text{i}(t) = (1 - \lambda)C_{\text{in}}^\text{i}(t - \tau_{\text{reactor}}) + \lambda C_{\text{out}}^\text{i}(t) \tag{7-26}
\]

where \( \lambda \) is the ratio of the reactor volume to the reservoir volume:

\[
\lambda = \frac{V_{\text{reactor}}}{V_{\text{reservoir}}} \tag{7-27}
\]

The procedure is iterated for \( N_p \) number of passes to yield the final concentration, \( C_{\text{out}}^N_p(t) \), after a time \( t = N_p \tau_{\text{reactor}} \). The final conversion is therefore

\[
x_T(t) = 1 - \frac{C_{\text{out}}^{N_p}(t)}{C_0} \tag{7-28}
\]
where \( C_0 \) is the initial concentration of the substrate in the reservoir. In our previous finding [10], the conversion of each single pass is constant within a narrow range of inlet concentrations, i.e., the fraction removal is independent of the inlet concentration, thus iterating eq (7-26) yields the inlet concentration, \( C_{in}^{out}(t) \), and the outlet concentration, \( C_{out}^{out}(t) \), at \( t = N_p \tau_{reactor} \):

\[
C_{in}^{out}(t) = (1 - \lambda x)^{N_p} C_0 \quad (7-29)
\]

\[
C_{out}^{out}(t) = (1 - x)(1 - \lambda x)^{(N_p - 1)} C_0 \quad (7-30)
\]

**7.2.5 Estimation of Model Parameters**

The parameters and constants in the above reactor model are summarized in Table 7.1. Once these parameters have been estimated, the predicted reactor conversions can then be computed for given values of the inlet flow velocity, inlet substrate concentration and input light intensity. The geometrical and fluid dynamic parameters can be easily measured or calculated. The parameters of radiation field are given in Chapter 5. The diffusion coefficients of the substrates (PHE and DCB) in water are found in the literature [11,12]. The only adjustable parameters of the model, the specific rate constant \( k_T \), can be estimated by fitting the model to the experimental results under different operation conditions. Table 7.2 shows the summary of the estimated \( k_T \) for PHE degradation by fitting the model to the experimental results. Table 7.3 shows the summary of the estimated \( k_T \) for DCB degradation by fitting the model to the experimental results. By averaging the fitting values of \( k_T \), it is observed that \( k_T \) is a constant within a close range of variation. The operation variables include the intensity of total incidental light, the flow velocity, and the initial substrate concentration.
Table 7.1. Optical fiber monolith reactor model parameters

<table>
<thead>
<tr>
<th>Type</th>
<th>Model parameters</th>
<th>Values</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry</td>
<td>d_f</td>
<td>0.1; 0.04</td>
<td>cm</td>
</tr>
<tr>
<td></td>
<td>R_w</td>
<td>0.15</td>
<td>cm</td>
</tr>
<tr>
<td></td>
<td>R_f</td>
<td>0.05; 0.02</td>
<td>cm</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>5; 10; 20</td>
<td>cm</td>
</tr>
<tr>
<td></td>
<td>η</td>
<td>0.333&lt;sup&gt;a&lt;/sup&gt;; 0.133&lt;sup&gt;b&lt;/sup&gt;</td>
<td>dimensionless</td>
</tr>
<tr>
<td></td>
<td>δ</td>
<td>241; 390; 603; 1036; 1660; 4114</td>
<td>nm</td>
</tr>
<tr>
<td>Fluid dynamics</td>
<td>u</td>
<td>0.0386 ~ 0.1157&lt;sup&gt;a&lt;/sup&gt;; 0.1175 ~ 0.565&lt;sup&gt;b&lt;/sup&gt;</td>
<td>cm s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>N_Re</td>
<td>1.003 ~ 3.008&lt;sup&gt;a&lt;/sup&gt;; 2.35 ~ 11.3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Mass Transfer</td>
<td>D</td>
<td>PHE: 0.437 x 10&lt;sup&gt;-5&lt;/sup&gt;; DCB: 0.89 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>cm&lt;sup&gt;2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Radiation field</td>
<td>α</td>
<td>0.386&lt;sup&gt;a&lt;/sup&gt;; 0.777&lt;sup&gt;b&lt;/sup&gt;</td>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>f_0</td>
<td>0.762&lt;sup&gt;a&lt;/sup&gt;; 0.967&lt;sup&gt;b&lt;/sup&gt;</td>
<td>dimensionless</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>1.95</td>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>ε</td>
<td>0.00102</td>
<td>nm&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Kinetics</td>
<td>k_T</td>
<td>PHE: 1.575; DCB: 1.085</td>
<td>cm&lt;sup&gt;2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt; mW&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> using small fiber with diameter of 0.4 mm;  
<sup>b</sup> using large fiber with diameter of 1 mm;

Table 7.2. Estimation of model parameter, k_T. Substrate: PHE. Geometry: d_f = 1 mm; η = 1/3; L = 10 cm; δ = 390 nm; Experimental conditions: C<sub>0</sub> = 638.9 ppb; u = 33.9 cm s<sup>-1</sup>

<table>
<thead>
<tr>
<th>I&lt;sub&gt;input&lt;/sub&gt; (mW cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>x (%)</th>
<th>k_T (cm&lt;sup&gt;2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt; mW&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.08</td>
<td>0.01848</td>
<td>1.485</td>
</tr>
<tr>
<td>1.55</td>
<td>0.02530</td>
<td>1.616</td>
</tr>
<tr>
<td>2.22</td>
<td>0.02937</td>
<td>1.458</td>
</tr>
<tr>
<td>2.84</td>
<td>0.03634</td>
<td>1.709</td>
</tr>
<tr>
<td>3.14</td>
<td>0.03689</td>
<td>1.606</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>1.575</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>0.103</td>
</tr>
</tbody>
</table>

128
Table 7.3. Estimation of model parameter, $k_T$. Substrate: DCB. Geometry: $d_r = 1 \text{ mm}; \eta = 1/3; L = 10 \text{ cm}; \delta = 390 \text{ nm};$ Experimental conditions: $C_0 = 4.72 \text{ ppm}; u = 33.9 \text{ cm s}^{-1}$

<table>
<thead>
<tr>
<th>$I_{\text{input}}$ (mW cm$^{-2}$)</th>
<th>$\chi$ (%)</th>
<th>$k_T$ (cm$^2$ s$^{-1}$ mW$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.08</td>
<td>0.020525</td>
<td>1.001</td>
</tr>
<tr>
<td>1.55</td>
<td>0.026866</td>
<td>0.992</td>
</tr>
<tr>
<td>2.22</td>
<td>0.037035</td>
<td>1.076</td>
</tr>
<tr>
<td>2.84</td>
<td>0.045807</td>
<td>1.163</td>
</tr>
<tr>
<td>3.14</td>
<td>0.049919</td>
<td>1.195</td>
</tr>
</tbody>
</table>

Average: 1.085

Standard deviation: 0.092

As shown in Table 7.1-7.3, the diffusion coefficient of DCB is larger than that of PHE but the rate constant of DCB is smaller than that of PHE. This suggests that the extent of mass transfer effects of DCB is less than that of PHE.

7.3 RESULTS AND DISCUSSION

7.3.1 Comparison of Model with Experimental Results

Using the model parameters determined in the previous sections, the model simulations are compared to the experimental results under various experimental conditions. Eq (7-23) and (7-28) provide an estimation of the conversion of single pass and that of multiple passes, respectively. Figure 7.2a and 7.2b compare the predicted results of eq (7-28) to experimental multiple-pass data for PHE and DCB photooxidation. The experiments are operated in recycle continuous flow mode and the details are described in the previous chapter. Figure 7.3a and 7.3b depict the predictions of eq (7-23) for PHE and DCB degradation to experimental single-pass data at various flow rates. Figure 7.4a and 7.4b compare the model and experimental results under different intensities of the incident light. Overall, the model based on the assumption of reaction control is found to fit the experimental results satisfactorily within the ranges of the
Fig. 7.2. Overall conversion for photocatalytic oxidation of (a) PHE and (b) DCB in continuous recycling multipass runs in an OFMR. Geometry: $d_f = 1$ mm; $\eta = 1/3$; $L = 10$ cm; Experimental conditions: $C_{0,\text{PHE}} = 639$ ppb; $C_{0,\text{DCB}} = 180$ ppb; $u = 33.9$ cm s$^{-1}$, $I_0 = 3.14$ mW cm$^{-2}$.
Fig. 7.3. Single-pass conversion for photocatalytic oxidation of (a) PHE and (b) DCB at different flow velocities in an OFMR. Geometry: $d_f = 1$ mm; $\eta = 1/3$; Experimental conditions: $C_{0,PHE} = 562-711$ ppb; $C_{0,DCB} = 2113-2705$ ppb; $u = 33.9$ cm s$^{-1}$, $I_0 = 3.14$ mW cm$^{-2}$.
Fig. 7.4. Single-pass conversion for photocatalytic oxidation of (a) PHE and (b) DCB at different input light intensities in an OFMR. Geometry: $d_\text{f} = 1$ mm; $\eta = 1/3$; Experimental conditions: $C_{0,\text{PHE}} = 639$ ppb; $C_{0,\text{DCB}} = 4796$ ppb; $u = 33.9$ cm s$^{-1}$, $I_0 = 3.14$ mW cm$^{-2}$.
Fig. 7.5. Model simulation for photocatalytic oxidation of (a) PHE and (b) DCB in a single channel of OFMR. Radial profiles of the dimensionless concentration at different axial distances from the reactor inlet. Geometry: \( d_f = 1 \text{ mm}; \eta = 1/3; L = 10 \text{ cm}; \) Experimental conditions: \( C_{0,\text{PHE}} = 639 \text{ ppb}; C_{0,\text{DCB}} = 4796 \text{ ppb}; u = 33.9 \text{ cm s}^{-1}. \)
parameters investigated. The exception is that at low flow velocity (or low Reynold’s number) the model overestimates the conversion as shown in Figure 7.3a and 7.3b. This can be explained due to the limitation of mass transfer which lowers the overall removal efficiency at low Reynold’s number.

On the other hand, the model based on the assumption that diffusion of reactants to the catalyst surface is the rate limiting step, which implies extremely fast reaction rates, overestimates the conversion compared with the experimental data obtained, which suggests the surface reaction rates are not fast enough to create a complete mass-transport limited region. Figure 7.5a and 7.5b show the model predicted radial profile of the dimensionless concentration at different axial locations. The surface concentration decreases rapidly near the reactor inlet and outlet. The surface reaction rate is slow in the middle of the reactor. The surface concentration at the TiO$_2$ film on the monolith wall is always higher than that at the TiO$_2$ film on the optical fiber. The results are consistent with our previous findings of the light intensity profile, viz., the light intensity exponentially decays along the optical fiber from top to bottom but rapidly increases within a short distance when approaching the fiber tip end; the light intensity on the channel wall is always lower than that on the optical fiber. Thus slow reaction rates due to lack of photons suggest that it is not mass-transport limiting in the middle of the reactor. Conversely, in a portion of the reactor near the inlet and outlet where the light intensity is much higher, the mass transfer limitation becomes prominent. This highly non-uniform distribution of the light intensity along the reactor decreases the overall reactor efficiency and makes the optimizing the reactor more difficult.
7.3.2 Effects of Geometry

The ratio of fiber radius to monolith channel radius, \( \eta \), the fiber diameter, \( d_f \), and the coating length, \( L \), are important geometric parameters in the design and optimization of the OFMR. Compared to the conventional annular reactors, the light transmission and distribution inside a channel of the OFMR are more sensitive to the changes in these geometric parameters. Thus the overall removal efficiency of the substrate is further greatly affected by the geometric parameters in the OFMR.

Figure 7.6a to 7.6d depict the model predicted radial and axial profile of the dimensionless concentration, \( C_{\text{out}}/C_{\text{in}} \), in a single pass run of PHE photooxidation with different ratios of fiber radius to monolith channel radius, \( \eta \), which are 1/5, 1/3, 1/2, and 5/6, respectively. The fiber diameter is 1 mm and the coating length is set to 10 cm. The simulation results show higher conversion is achieved as the ratio of fiber radius to monolith channel radius, \( \eta \), increases. The improvement of the single-pass conversion through increase in the ratio, \( \eta \), can be attributed to: (i) less processing of liquid volume; (ii) higher light intensity on the TiO\(_2\) coating on the monolith channel wall; and (iii) shorter diffusion length of substrate from bulk solution to the surface of TiO\(_2\) coatings. Figure 7.6d shows that the concentration is low and the concentration gradient from the bulk solution to the catalyst surface is nearly flat near the reactor outlet, which suggests both reaction rate and mass transfer reach a high level, when the ratio is equal to 5/6. As is known for most types of annular reactors, the flow passage annulus determines the extent of radial mixing possible. Therefore, to minimize mass transfer intrusions, it becomes necessary to design for small flow passage annulus or large \( \eta \) and high flow Reynolds numbers. However, decreasing flow passage annulus by increasing the ratio of
Fig. 7.6. Model simulation for photocatalytic oxidation of PHE in a single channel of OFMR. Radial profiles of the dimensionless concentration along the axial direction from the reactor inlet. Geometry: \( d_f = 1 \text{ mm}; \eta = (a) \ 1/5; \) (b) 1/3; (c) 1/2; (d) 5/6; \( L = 10 \text{ cm}; \) Experimental conditions: \( C_0 = 639 \text{ ppb}; u = 33.9 \text{ cm} \cdot \text{s}^{-1}. \) Note: the scale of dimensionless radius is not same.
internal radius to external radius of the annulus reduces the volume of the processing liquid for a given reactor volume and increases pressure drop that is often unacceptable in most annular reactors. For a multiple-channel monolithic reactor, the adverse effect of increasing pressure drop in a single channel can be minimized to an acceptable level by increasing the number of channels. Choosing an optimal $\eta$ in OFMR design is a tradeoff of decreasing the effective reactor volume and increasing the reaction and diffusion rates. It should be noted that a large flow passage annulus does not necessarily increase the effective reactor volume. As shown in Figure 7.6a to 7.6c, as the ratio, $\eta$, is less than 1/2, the main body of the bulk solution in the middle of the annulus remains untreated.

The effects of fiber diameter in OFMR design are much more complex and should be considered comprehensively. Firstly, fiber diameter determines the ratio, $\eta$, for a given monolith channel radius, and thus affects the extent of mass transfer. Secondly, increasing fiber diameter provides larger TiO$_2$-coating surface area by increasing the outer surface area of the fiber and extending the light propagation length. Thirdly, fiber diameter greatly affects the fitting parameters in the radiation field, which is extensively discussed in the previous chapter. Finally, fiber diameter determines the fiber number density in a fiber bundle with a given cross-sectional area and thus the monolith channel number. It further affects the quantum efficiency with the given incidental light intensity [13] and the throughput of the reactor or the flow velocity. Figure 7.7 shows the overall conversion of PHE degradation in two reactors with fiber diameter of 1 mm and 0.4 mm, respectively. The TiO$_2$-coating length or the effective reactor length is 5 cm. The fiber coating thickness is 390 nm. The total incidental light intensity is 59.66 mW cm$^{-2}$. The number of fibers or channels is 19 for the large fiber and is 61 for the small fiber. The
The initial concentration of PHE is about 450 ppb. At a given input light flux and flow flux, the overall conversion of PHE in the OFMR with the large fiber is higher than that with the small fiber. Further investigation of the model predicted radial and axial profile of the dimensionless concentration, as shown in Figure 7.8, finds that when the small fiber of 0.4 mm diameter is used, the reaction on the surface of the monolith channel wall coating is very low due to lack of photons. Therefore, the illuminated TiO$_2$ surface area of the OFMR using small fibers is less than that of the OFMR using large fibers, though the total TiO$_2$ coating surface area of the OFMR with small fibers is much higher for the given effective reactor length since the number of channels is larger. Sufficient light illumination on the monolith channel wall coating must be obtained when using small fiber diameter in the OFMR design. When extremely high

**Fig. 7.7.** Effect of fiber diameter on the overall conversion of PHE in recycling flow mode in multi-channel OFMR. $L = 5$ cm; $e = 390$ nm; $C_0 = 450$ ppm; $Q = 14.83$ cm$^3$ min$^{-1}$; $I_0 = 59.66$ mW cm$^{-2}$. Flow rate is 14.82 cm$^3$ min$^{-1}$ and the flow velocities are 12.42 cm min$^{-1}$ and 3.5 cm min$^{-1}$, respectively.
light intensity is applied, using small fibers can minimize the negative light intensity effects on quantum yield while maintaining rapid overall degradation rates. In this case, the same input light flux can be divided by a larger number of fibers and distributed into more monolith channels. However, even though the incident light intensity is high enough, we cannot conclude that the performance of an OFMR using small fibers would be superior to that of an OFMR using large fibers since the above comparison is based on the same active catalyst coating length. Our previous findings show that as the fiber diameter is increased, the light propagation along the fiber is extended since photons
undergo fewer reflections at the quartz-titania interface for a fixed incident angle. The coating length or the effective reactor length is thus extended with a larger diameter fiber and the activated photocatalytic surface area is enhanced. Our measurements of the light intensity profile of a single fiber show that the effective light propagation length of the TiO$_2$-coated fiber of 0.4 mm diameter is only 5 cm. For the TiO$_2$-coated fiber of 1 mm diameter, the propagation length is extended to 20 cm. Therefore, the illuminated TiO$_2$ coating surface area is more than four times higher when using the fiber of 1 mm diameter than the 0.4 mm diameter in a single monolith channel.

**Fig. 7.9.** Model simulation for photocatalytic oxidation of PHE in a single-pass run in the OFMR. Effect of the reactor length on the single-pass conversion. Geometry: $R_w = 1.5$ mm; Experimental conditions: $Q = 33.9$ cm$^3$ min$^{-1}$, $I_0 = 59.66$ mW cm$^{-2}$.

Unlike the conventional photocatalytic reactors, the reactor length of an OFMR is not an independent design parameter. Instead, the reactor length is determined by the effective light propagation length along the TiO$_2$-coated fiber in an OFMR. The reactor length longer than the effective light propagation length is poorly utilized and is not cost-
efficient. With the assistance of the model, Figure 7.9 predicts the single-pass conversion for PHE degradation. As shown in Figure 7.9, when the reactor length is shorter than the effective light propagation length, the single-pass conversion increases linearly as the reactor length increase once the reactor length is larger than the effective light propagation length, only marginal enhancement of the conversion can be obtained. For an OFMR using a small fiber of diameter 0.4 mm, the single pass conversion only increases 0.39% when the reactor length increases from 5 cm to 100 cm.

7.4 CONCLUSIONS

A two-dimensional heterogeneous convective-diffusion-reaction model is developed to simulate the performance of a multi-channel optical fiber monolith reactor. With the assumption of identical channels, the multi-channel reactor model is reduced to a single-channel reactor model without losing the essential elements of the reactor. The reactor model incorporated an empirical radiation field sub-model, an annular flow dynamics model and a Langmuir-Hinshelwood kinetics sub-model. Reasonable agreement is found between the model-predicted and experimental photodegradation conversion data within the limits of experimental error, using the apparent rate constant as the only adjustable parameter.

Among the geometric parameters for OFMR design, fiber diameter not only affects the catalyst coating surface area but also affects the radiation field by changing the ratio of internal radius to external radius of the annulus and the effective light propagation length. The main bulk solution in the center of the annulus is untreated due to the limitation of mass transfer as the ratio of fiber radius to channel radius is less than
½. Reactor length is limited by the effective light propagation length along the titania-coated optical fiber.

7.5 REFERENCES


CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

The application of photocatalysis for wastewater treatment and purification on an industrial scale can be assisted by the development of new photoreactor designs. A good photoreactor design should meet the following challenges: high ratio of the illuminated catalyst area to the volume of the reactor; uniform light distribution; fast overall removal rate; high quantum efficiency; high throughput; low power consumption; and easy scale-up capability. Amongst these factors, how to yield high activated catalyst area within a compact reactor volume is of the most importance, especially for the design of fixed-bed reactor systems with immobilized photocatalyst.

In this work, a novel distributive-type multi-channel monolithic photocatalytic reactor, which employed optical fibers as light conductors, was designed. The distributive type has the inherent advantages of a fixed-bed design coupled with the reaction efficiencies of a slurry phase reactor. The distributive configuration enhances the uniformity and distribution of activated photocatalyst within a given reaction volume by subdividing the whole reactor into multiple individual small reaction units. It also reduces the mass transport limitations and allows for higher processing capacities at low pressure drop. Using optical fiber instead of lamp to deliver UV light can save reactor space and remotely control the reactor. Two model organic contaminants, DCB and PHE, which represent two major classes of organic pollutants, volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs), were chosen to evaluate the performance of the optical fiber monolith reactor.
Preliminary experiments were done to guide the reactor design and provide the comparison basis for the evaluation of the reactor in two simpler reactors including a slurry reactor and an annular continuous reactor. The slurry batch reactor was used to identify the intermediates of DCB and PHE by GC/MS analysis and postulated the reaction mechanisms. DCB is completely mineralized and do not produce other toxic products in our reactor whereas PHE photodegradation only shows partial mineralization which becomes a limitation of the heterogeneous photodegradation of PAHs. The continuous annular reactor using immobilized titania was used to evaluate the flow rate and mass transfer characteristics in a annular reactor configuration such as that to be used in a distributive monolithic reactor, the effects of radiant flux density and surface modification of titania, and the overall rate constants and apparent quantum efficiency for comparison basis with the degradation of DCB and PHE in the monolithic reactor.

A laboratory-scale optical fiber monolith reactor (OFMR) was then constructed and tested for overall performance evaluation. Experimental results showed two orders of magnitude higher apparent quantum efficiency and comparable overall rate constant compared with the continuous annular reactor, which suggested an appropriately designed OFMR could have potential in photocatalytic water treatment. The effects of initial feed concentration, flow velocity, and the thickness of the TiO$_2$ layer on the optical fiber were investigated. The results showed mass transfer effects could not be ignored due to the relatively low flow Reynolds number in each cell of the monolith. Thin TiO$_2$ film on the optical fiber is required in this configuration to prevent the light from total reflection inside the fiber core and facilitating light penetration through the TiO$_2$ layer.
The optimum thickness of the TiO$_2$ film on the optical fiber was found to be close to 0.4 $\mu$m in this study.

Theoretical analysis of the multi-channel OFMR was based on the assumption of identical channels. Thus the multi-channel reactor model was reduced to the single-channel reactor model. We first set up the two-dimensional UV radiation model in a single channel of the OFMR with four experimentally fitted parameters. The experimental measurements of UV flux at the outer surface of the TiO$_2$ films on both the optical fiber and the monolith wall were close agreement with model prediction. The validated radiation field model with the fitting parameters was then used as a sub-model in the development of a full heterogeneous OFMR reactor model.

The two-dimensional heterogeneous convective-diffusion-reaction steady-state model of a multi-channel OFMR was developed by incorporating an empirical radiation field sub-model, an annular flow dynamics model and a Langmuir-Hinshelwood kinetics sub-model. The model was simplified to a one-dimensional time-dependent model and then solved using finite element method. Reasonable agreement was found between the model-predicted and experimentally observed photodegradation conversion data within the limits of experimental error, using the total rate constant as the only adjustable parameter. The model was used to optimize the design parameters in an OFMR.

Among the geometric parameters for OFMR design, fiber diameter not only affects the catalyst coating surface area but also affects the radiation field by changing the ratio of internal radius to external radius of the annulus and the effective light propagation length. The main bulk solution in the center of the annulus was untreated due to the limitation of mass transfer as the ratio of fiber radius to channel radius was less
than ½. Reactor length was limited by the effective light propagation length along the titania-coated optical fiber. Optimization of the design parameters was the tradeoff between the removal efficiency and the throughput.

8.2 RECOMMENDATIONS

In the OFMR, the short light propagation length of the TiO$_2$-coated optical fiber and exponentially nonlinearity of the light distribution along the fiber, which significantly limited the efficient use of reactor volume, should be overcome. Increasing the fiber diameter can extend the light propagation length at the cost of decreasing the reactor throughput. Another option is to coat optical fibers with a macroporous TiO$_2$ thin film, which decreases the titania-quartz contact area and in turn decreases the ratio of the amount of the refracted light to that of the reflected light. High porous structures of titania can also provide high reactive surface area per unit reactor volume and good mass transfer characteristics. Template-directed syntheses can be applied to the creation of macroporous TiO$_2$ films [1-3]. Tapering a fiber to a point can improve the uniformity of the light distribution along the fiber. As the diameter of the fiber gradually decreases from the top of the fiber to the bottom, the number of light reflection/refraction at the TiO$_2$-quartz interface increases. Thus less refracted light comes out of the upper part of the fiber and more refracted light comes out of the lower part of the fiber compared to the fiber with fixed diameter.

Our experimental results shows the mass transfer limitations can not be neglected when the OFMR operated at low flow Reynolds number. However, increasing flow Reynolds number by increasing reactor throughput can result in a photon limited regime, i.e., availability of the light is limiting, and lead to reduced conversion. Also, as the flow
rate is increased, the entry zone extends further and further downstream and increases the possibility of the unreacted substrate solution by-passing the photocatalyst. The other option to improve mass transfer is to change the flow pattern from upflow mode to downflow mode. In downflow mode, the liquid film descends along the optical fiber and the monolith channel wall. Unlike the current reactor operated at low Reynolds number in upflow mode, the falling film reactor can be operated at a flow Reynolds number as high as 1500 to provide matching between fluid residence time and radiation field while maintaining a high liquid processing volume. The falling film reactor improves the mass transfer due to shorter diffusion distance and higher Reynolds number. However, the falling film reactor is not appropriate for the VOCs since these volatile compounds can easily escape from the falling film reactor.

One of the obstacles impeding the commercial use of the photocatalysis on waste water treatment is due to the high energy consumption of the artificial UV light source. Thus solar photocatalysis is a more promising process since use of sunlight is much more economical and clean. Cost-effective technological applications of photocatalysis would require the development of photocatalysts that can use the visible light (400 nm < \( \lambda \) < 700 nm), the main part of the solar spectrum. The visible-light-driven photocatalysis can be achieved through modifying the optical absorption of TiO\(_2\), i.e., extending the absorption of bulk TiO\(_2\) into visible region through narrowing the bandgap of TiO\(_2\) or introducing new absorption band. The bandgap of TiO\(_2\) can be narrowed by incorporating with anions such as F, C, N or S [4-8]. Among the anionic dopants, Nitrogen is not as difficult as the other anions to be incorporated into the TiO\(_2\) crystal due to its suitable ionic radius. Moreover, Nitrogen-doping was found to be particularly effective in
decreasing the band gap of anatase TiO$_2$, although there is controversy whether the oxygen sites were substituted by nitrogen or the nitrogen atoms were doped at the interstitial sites in the nitrogen-doped TiO$_2$. When N-doped TiO$_2$ is used in the OFMR, a sunlight collector, instead of the expensive short-arc light source, can be used to provide photons necessitating the photooxidation reactions.

8.3 REFERENCES


### APPENDIX A

**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Notation</th>
<th>Name</th>
<th>Units used</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>specific surface area</td>
<td>m² m⁻³</td>
</tr>
<tr>
<td>C</td>
<td>concentration</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>C₀</td>
<td>initial concentration</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>d</td>
<td>diameter</td>
<td>cm</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient</td>
<td>cm² s⁻¹</td>
</tr>
<tr>
<td>f₀</td>
<td>fraction of incident light with incident angle less than 90°</td>
<td>dimensionless</td>
</tr>
<tr>
<td>F</td>
<td>fractional removal</td>
<td>dimensionless</td>
</tr>
<tr>
<td>I</td>
<td>intensity</td>
<td>W m⁻²</td>
</tr>
<tr>
<td>k</td>
<td>reaction rate constant</td>
<td>mol m⁻³ s⁻¹</td>
</tr>
<tr>
<td>k星</td>
<td>overall rate constant</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>kₘ</td>
<td>mass transfer coefficient from liquid-to-catalyst surface</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>kₜ</td>
<td>observed total rate constant</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>k</td>
<td>adsorption equilibrium constant</td>
<td>m³ mol⁻¹</td>
</tr>
<tr>
<td>L</td>
<td>reactor length</td>
<td>m</td>
</tr>
<tr>
<td>m</td>
<td>power-law exponent</td>
<td>dimensionless</td>
</tr>
<tr>
<td>n</td>
<td>refractive index; power-law exponent</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Nₚ</td>
<td>Reynolds number</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Nₚ</td>
<td>number of passes</td>
<td>dimensionless</td>
</tr>
<tr>
<td>r</td>
<td>reaction rate; radial position</td>
<td>mol m⁻³ s⁻¹; cm</td>
</tr>
<tr>
<td>R</td>
<td>radius</td>
<td>cm</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>min</td>
</tr>
</tbody>
</table>
velocity \quad cm\ min^{-1}

bulk mean velocity \quad cm\ min^{-1}

velocity \quad cm\ min^{-1}

volume \quad ml

single-pass conversion; fraction removal \quad \text{dimensionless}

total multiple-pass conversion \quad \text{dimensionless}

axial position \quad cm

Greek letters

refractive loss coefficient \quad cm^{-1}

attenuation coefficient of the tip light flux \quad cm^{-1}

TiO\textsubscript{2} film thickness \quad nm

local attenuation coefficient of TiO\textsubscript{2} film \quad nm^{-1}

effectiveness factor; ratio of fiber radius to monolith channel radius \quad \text{dimensionless}

wavelength; ratio of reactor volume to reservoir volume \quad nm; \quad \text{dimensionless}

viscosity \quad N\ s\ m^{-2}

space time of reactor \quad \text{min}^{-1}

quantum efficiency \quad \text{dimensionless}

angle of incidence \quad ^\circ$

density \quad kg\ m^{-3}

Subscript and superscript

active sites

species A
abs  absorption
ads  adsorption
app  apparent
axial axial
c  critical
cat catalyst
diff dissociation
e  effective
f  optical fiber
fc  fiber coating
F  feed
in  inlet
input  input
LH  Langmuir-Hinshelwood
mc  monolith coating
out  outlet
rad  radial
R  reactor, reflectivity, rate
s  surface
T  total
w  monolith channel wall, water
APPENDIX B
LIST OF PUBLICATIONS AND PRESENTATIONS

PUBLICATIONS


PRESENTATIONS


APPENDIX C

LETTERS OF PERMISSION

7 July 2005

Our ref: HG/pr/july05.012

Hongfei Lin
Email: hlin3@lsu.edu

Dear Dr Lin


As per your letter dated 6 July 2005, we hereby grant you permission to reprint the aforementioned material at no charge in your thesis subject to the following conditions:

1. If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies.

2. Suitable acknowledgment to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

   “Reprinted from Publication title, Vol number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier”.

3. Reproduction of this material is confined to the purpose for which permission is hereby given.

4. This permission is granted for non-exclusive world English rights only. For other languages please reapply separately for each one required. Permission excludes use in an electronic form. Should you have a specific electronic project in mind please reapply for permission.

5. This includes permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

Yours sincerely

Helen Gainford
Rights Manager
Hongfei Lin  
Email: hlin3@lsu.edu

Dear Dr Lin


As per your letter dated 6 July 2005, we hereby grant you permission to reprint the aforementioned material at no charge in your thesis subject to the following conditions:

1. If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies.

2. Suitable acknowledgment to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
   “Reprinted from Publication title, Vol number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier”.

3. Reproduction of this material is confined to the purpose for which permission is hereby given.

4. This permission is granted for non-exclusive world English rights only. For other languages please reapply separately for each one required. Permission excludes use in an electronic form. Should you have a specific electronic project in mind please reapply for permission.

5. This includes permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

Yours sincerely

Helen Gainford  
Rights Manager
Dear Hongfei Lin,


With reference to your request (copy herewith) to re-use material on which Springer controls the copyright, our permission is granted free of charge, on the following conditions:

* it concerns original material which does not carry references to other sources,
* if material in question appears with credit to another source, authorization from and reference to that source is required as well and permission is also obtained from the author (address is given on the imprint page or with the article),
* allows you non-exclusive reproduction rights throughout the world,
* permission includes use in an electronic form, on the condition that content is
  - password protected,
  - at Intranet or
  - in CD-ROM/E-book,
* full credit (book/journal title, volume, year of publication, page, chapter/article title, name(s) of author(s), figure number(s), original copyright notice) is given to the publication in which the material was originally published by adding:
  With kind permission of Springer Science and Business Media.

Permission free of charge does not prejudice any rights we might have to charge for reproduction of our copyrighted material in the future.

With best regards,

Alice Essenpreis
Springer
Rights and Permissions

Tiergartenstrasse 17 | 69121 Heidelberg GERMANY
FAX: +49 6221 487 8223
Alice.Essenpreis@springer-sbm.com
www.springeronline.com/rights
VITA

Hongfei Lin was born in 1974 in the People’s Republic of China. He received his Bachelor of Science and Master of Science degrees from Tsinghua University in July 1996 and June 2000, both in chemical engineering. In August 2000, he came to Louisiana State University to pursue his doctoral degree in chemical engineering.