Visible Light Driven Photocatalysis for Degradation of Diclofenac

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Abstract

Diclofenac (DCF), a widely used non-steroidal anti-inflammatory drug (NSAID), is a commonly detected substance that readily accumulates in tissues of aquatic fish and poses a threat to wildlife and freshwater quality. Advanced Oxidation Processes (AOPs) have been explored as an alternative method for complete mineralization of DCF as conventional treatment methods are inadequate for treatment of trace contaminants.

This study employs a semi-batch, swirl-flow, monolithic type photocatalytic reactor to determine intrinsic kinetic parameters of DCF mineralization, in an immobilized system under both UV and visible radiation. The goal of this work to determine true kinetics of DCF, after correcting for external mass transfer resistance that exists when catalysts is immobilized, as a function of various operating parameters such as flow rate, catalyst loading, pH, light intensity, initial concentration, and photocatalyst type.

This study also utilized an innovative method of solar-activation of TiO$_2$ using Eosin-Y dye for the degradation of DCF. Furthermore, the study incorporated a central composite design (CCD) to optimize the dye concentration and estimated the cost for the present process. Optimized parameters for light intensity (750 mW/cm$^2$), Eosin-Y dye concentration (2 mg/L), TiO$_2$ loading (37.5 mg/cm$^2$) and DCF concentration (25 mg/L) were determined by means of a CCD study. A cost estimation for the materials used for the current process was also performed. It was determined that the additional cost of using 4 ppm instead of 2 ppm to achieve only 10% more DCF degradation is not warranted and would require additional treatment to remove subsequently formed halogenated compounds.

In the last part of this thesis, in order to determine mechanism of degradation of DCF, intermediate products were identified. 22 different intermediate products were found during the visible light photocatalytic degradation of DCF using EY-sensitized TiO$_2$ at the optimized conditions. Out of the 22 intermediates, 19 of the transformed products were identified. Toxicity analysis of the treated and untreated samples of DCF were also assessed. The treated samples indicated an increase in toxic effect to Daphnia magna compared to the untreated DCF solution.
The objective and significant contribution of this study lies in (1) obtaining true kinetic data independent of reactor types, (2) incorporation CCD to optimize the reaction operating parameters, (3) cost estimation of the present process, and (4) identification and toxicity analysis of DCF intermediates formed during the optimized process.

Keywords

Co-Authorship Statement

Chapter 2 is a work in progress for submission to Environmental Science and Technology journal.

Chapter 4 includes work that has been published in Industrial & Engineering Chemistry Research.

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Dedication

To my two wonderful sets of parents
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Chapter 1

1. Introduction

1.1 Background and Motivation

1.1.1 Water Pollution

Clean water is a precious resource. The world’s water supply is under considerable stress due to increasing industrialization, increasing demand, and a decreasing supply due to pollution. This threatens our health, environment and has become an issue of major social and economic concern. Water resources are becoming increasingly contaminated with toxic compounds. It is an immediate and important challenge in a world that is facing increasing pollution and decreasing energy resources. Water pollution reduces the already small 1% available amount of freshwater resources on the planet. The United Nations reported that two thirds of the world will experience fresh water scarcity by 2025.

The contaminants and waste from human activity are introduced into rivers, lakes, and groundwater, which all makes its way to the oceans. Thus, modifying the water quality and making it unsuitable for the environment, aquatic life and for human consumption. Water contaminates are but not limited to: herbicides, pesticide, textile dye, and inorganic compounds (such as heavy metals, mercury, cadmium, lead etc.). In addition, extensive use of emerging contaminants including endocrine disrupting compounds (EDCs), personal care products (PCPs) and pharmaceutical active compounds with mutagenic, genotoxic and carcinogenic effects are also of increasing prevalence in water resources. These organic and inorganic compounds of increasing concern. It is a threat to human and aquatic health, and are being considered by government regulators around the world. Many of these contaminates are reported to have toxic effects and compromise human health even at trace concentrations. The improper disposal of these contaminates in developing countries is aggravated due to the unreliability of conventional treatment methods adopted.

A significant portion of the pharmaceutical wastes in water sources are composed of pharmaceutical drugs with an estimated annual consumption of several hundred tons globally.
Diclofenac [2-(2,6-dichloranilino) phenylacetic acid], a common nonsteroidal anti-inflammatory drug (NSAID), heavily used all over the world is one of the most commonly detected compounds in wastewater. Research indicates that it has the potential to bio accumulate in the tissues of organisms. Other studies reported the presence of 1 ppb of Diclofenac (DCF) could damage liver and kidney cell functions in aquatic animals.

The conventional wastewater treatment is based on physical, mechanical, biological and chemical processes. After the removal of large particles, the primary treatment takes place. During primary treatment, particles in suspension are removed by filtration, then sent to a secondary treatment facility. In secondary treatment, pollutants are biologically eliminated. The conventional processes are unreliable for completely eliminating the mentioned contaminants because, filtration and adsorption of contaminated from wastewater improves the quality of water to certain extent but, it creates post process waste. Therefore, causing a new stream of waste that are pollutant rich, and need to be further treated. In addition, some of the pollutants found in water are non-biodegradable, for which a tertiary treatment is required.

Stringent regulations set by the United States Environmental Protection Agency (USEPA) to eliminate these potentially harmful compounds. As a result, advanced oxidation processes (AOPs) have been introduced. AOPs can be a potential tertiary treatment for the mentioned contaminants in wastewater. They are well known processes and extensive research around the world has been performed in improving these technologies.

There are several types of AOPs, such as O$_3$, O$_3$/H$_2$O$_2$/UV, photocatalysis, and O$_3$/H$_2$O$_2$/photocatalysis. Among these, TiO$_2$ is proven to be a promising technology.

1.1.2 Heterogeneous Photocatalysis

The details of the mechanism for heterogeneous photocatalysis is ongoing and uncertain. In general in photocatalytic reactions and all advanced oxidation processes utilize hydroxyl radical (HO$^-$) formation. These radicals are strong enough to convert water pollutants to carbon dioxide, water and stable mineral acids. Photocatalytic treatment is not limited to water purification, the
process can be used to in air purification, self-cleaning surface, hydrogen generation, and other applications.\textsuperscript{20}

Heterogeneous photocatalysis uses semiconductors as a photocatalyst. There are different photocatalysts utilized in this process, among them TiO\textsubscript{2} has been shown to have the highest effectiveness in removing harmful compounds.\textsuperscript{2, 16, 17, 18} In addition, TiO\textsubscript{2} is commercially available in various crystalline forms with a wide range of particle characteristics. It is nontoxic and photo-chemically stable and can be reused for long period of time. The catalyst photo-activation can be achieved with a low-energy UV-A (300nm < \lambda < 390nm) light source. In addition, the surface of TiO\textsubscript{2} can be modified to make the catalyst active under lower energy light, such as the solar light.\textsuperscript{8, 21, 22, 23}

Heterogeneous photo-stimulated catalysis presents a possibility in degrading toxic organic pollutants for environmental cleanup. There are numerous advantages of this technology compared to other AOPs and the conventional methods. They are but not limited to\textsuperscript{2, 24} 1) a complete mineralization of the organic contaminants without any pH adjustments or the use of harmful compounds such as O\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} are possible, 2) the process can be carried out under the ambient conditions, 3) only require sufficient dissolved oxygen (or air) for continuing the redox reaction by scavenging electrons, 4) The photocatalyst TiO\textsubscript{2} is chemically stable, can be reused and it can be modified to make it the catalyst active under lower energy light.

1.1.3 Problem Statement

In accordance with the principles of green chemistry, it is desirable to utilize processes that minimize energy consumption and minimize the use and generation of hazardous substances. Conventional water treatment does not meet this objective, since it involves high-energy consumption, uses hazardous chemicals such as chlorine (Cl\textsubscript{2}), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and ozone (O\textsubscript{3}), and generates waste streams. Catalytic technologies present an opportunity to improve the environmental sustainability of water treatment, particularly for treating chemical contaminants in water. By employing catalytic technologies whereby toxic contaminants adsorb on the catalyst surface and are transformed in situ (at the site) to non-toxic or substantially less
toxic compounds within the reactor. Since the reactions occur on surfaces through the interaction of adsorbed species, the reactions can be carried out with high yield and with greater control of the product distribution through the careful molecular design of the catalytic materials. This is particularly significant in water treatment, where contaminants may be found in trace amounts (parts per billion or parts per trillion level) resulting in very low reaction rates and a very low utilization of the photonic energy. These contaminants may be substantially concentrated as adsorbed species on catalytic surfaces resulting in higher reaction rates, far greater chemical conversions and improved process efficiencies. Consequently, there is great incentive to explore the potential for catalytic technologies for water treatment.

Treatment processes for the removal of diclofenac and other mentioned contaminate from wastewater streams have been reported, together with their corresponding degradation rates alone in a mixture. However, all these studies are not in depth investigations. More precisely, they deal with the effects of only a limited number of parameters such as initial concentration and catalyst loading. In addition, most data reported are overall rates and do not correspond to true intrinsic kinetics for these contaminants, meaning the reaction rate does not consider the mass transfer effect. For production of large industrial reactors for wastewater treatment the values reported are meaningless. Therefore, a fundamental experimental data investigated under conditions independent of a reactor type and design is necessary are missing.

Catalytic technologies create the opportunity to reduce or eliminate the need for the addition of chemical reagents and improve the efficiencies of water treatment processes. If the water treatment process is catalytic, toxic waste is neither generated nor sequestered for further processing. It is of particular interest to generate the reactants (such as hydroxyl radical for example) in situ or to utilize the redox property of photocatalyst directly to avert the need for the addition of chemical reagents and to mitigate the requirement of downstream processing.
1.2 Thesis Overview

This PhD dissertation follows the “the integrated article” format. The aims is to fill out the knowledge gap by proposing solutions by series experimental studies. A brief description of the content of the chapters are as follows:

**Chapter 2**, provides a critical review on water pollution and treatment processes available. **Chapter 3**, outlines the main, and specific objectives of this research. **Chapter 4**, is a research article entitled “Intrinsic Kinetic Study for Photocatalytic Degradation of Diclofenac under UV and Visible Light” describes the experimental study performed to determine true kinetic rate of DCF. **Chapter 5**, is a research article entitled “Solar Degradation of Diclofenac using Eosin Y Activated TiO₂: Cost analysis, Process Optimization and Parameter Interaction Study” describes the incorporation of a central composite design (CCD) to optimize the integrated factors, specifically dye concentration used to activate TiO₂ under visible light source. In addition, a cost estimation of the present process was also proposed in this chapter. **Chapter 6**, is another research study entitled “Solar Degradation of Diclofenac using Eosin Y Activated TiO₂: Identification of DCF intermediates and toxicity analysis”. The chapter describes and proposes transformation pathways for DCF degradation under solar visible light, with eosin Y -TiO₂ as catalyst. **Chapter 7**, summarizes the key conclusions and suggests directions future work based on this study.
Chapter 2

2 Literature Review

2.1 Water Pollution

An immediate problem facing humanity is the lack of clean and accessible water. About 70% of the earth’s surface is covered in water, however only 1% is accessible for human consumption. Increasing industrialization, urbanization, global pollution, growth and climate change have increased the demand for potable water, and are contributing to the water crisis. Water crisis threatens our health and environment, therefore becoming a major social, economic, and political concern. In a world that faces increasing pollution and decrease in energy supplies, water pollution is an immediate and important challenge.

Common water pollutants include organic and inorganic compounds, such as pharmaceuticals, personal care products, textile dyes, herbicides, pesticides and heavy metals (such as mercury, cadmium, silver, nickel, lead; noxious gases). These organic and inorganic contaminants can be found in the ground, wells, and surface waters.

2.1 Diclofenac

Diclofenac (DCF) [2-(2,6-dichloranilino) phenylacetic acid] is ingested as a pharmaceutical active to reduce inflammation in patients, and is one of the most heavily used non-steroidal anti-inflammatory drugs (NSAIDs) around the world. In water sources, the main contamination pathways are identified to be through domestic use. Concentrations as high as 0.42 μg l⁻¹ and 5.45 μg L⁻¹ are detected in surface water and the effluent streams of wastewater treatment plants (WWTPs) respectively. DCF was believed to be the cause of the catastrophic decline of vulture populations in Western Asia (ng/l levels was reported to be able to inhibit cell proliferation by affecting their physiology and morphology). Recent research reported that sub-chronic exposure to diclofenac at ng/l levels could interfere with biochemical functions and cause tissue damage in fish. It presents the highest acute aquatic toxicity. Therefore, it increases the potential to harm organisms at a cellular level. The presence of 1 μg l⁻¹ of DCF has been reported to damage
liver and kidney cell functions in aquatic animals. Furthermore, ingestion of DCF by birds results in death shortly after exposure to the contaminated source. Its physical, chemical, and aquatic toxicity parameters are listed in Table 2-1.

Table 2-1 Physical, chemical and aquatic toxicity parameters of DCF

<table>
<thead>
<tr>
<th>Drug</th>
<th>Mol.Weight (g/mol)</th>
<th>Vap.P (mmHg)</th>
<th>Sol. (mgL⁻¹)</th>
<th>pKa (20°C)</th>
<th>LogKow</th>
<th>Henrys Const. (at m³/mol)</th>
<th>EC₅₀ Daphnia</th>
<th>EC₅₀ Algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCF</td>
<td>296.2</td>
<td>6.14 x10⁻⁸</td>
<td>2.37</td>
<td>4.1-4.5</td>
<td>1.9-4.5</td>
<td>4.7 x10⁻¹²</td>
<td>22-68</td>
<td>72</td>
</tr>
</tbody>
</table>

Chemical Structure of DCF

![Chemical Structure of DCF]

The potency or half maximal effective concentration (EC50) for DCF reported in the literature is considered to be very toxic to bacteria (EC50<1mg/L) and algae (EC50 =1-10mg/L). As a result of significant risk it poses to the aquatic life, DCF is placed in the EU priority list of water contaminants.

During the photodegradation of DCF, new compounds form and are known as the intermediates or transformation compounds (TPs). It is important to study this transformation pathways because the TPs might be more toxic to the environment compared to the model compound. Understanding and analyzing this pathway is an essential step for their environmental fate. As a result, extensive effort has been made by several authors to find effective solutions for elimination of DCF from water. The type of processes and the effectiveness of are listed in Table 2.2 below.
Table 2-2 DCF removal efficiency in conventional and advanced processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Removal (%)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Settling</td>
<td>-</td>
<td>Tanaka et al. 39</td>
</tr>
<tr>
<td>Coagulation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe2(SO4)3</td>
<td>66</td>
<td>Tuhkanen et al. 40</td>
</tr>
<tr>
<td>Al(SO4)3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sand filtration</td>
<td>10</td>
<td>Vieno et al. 41</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>39</td>
<td>Vieno et al. 42/Westeroff et al. 43</td>
</tr>
<tr>
<td>Disinfection</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl2(up to 3.8mg/L)</td>
<td>80-95</td>
<td>Benotti et al. 44</td>
</tr>
<tr>
<td>O3 (up to 1.5mg/L)</td>
<td>&gt;99</td>
<td>Vieno et al. 42/Ternes et al. 45</td>
</tr>
<tr>
<td>AOPs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photolysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solar</td>
<td>4</td>
<td>Tanaka et al. 39/Canonica et al. 46</td>
</tr>
<tr>
<td>UV (254nm)</td>
<td>90-100</td>
<td>Yamashita et al. 47</td>
</tr>
<tr>
<td>UV/H2O2</td>
<td>&gt;90</td>
<td></td>
</tr>
<tr>
<td>Photocatalysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO2/UV</td>
<td>100</td>
<td>Pe´rez-Estrada et al. 16</td>
</tr>
<tr>
<td>Fenton</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO2/UV</td>
<td>100</td>
<td>Pe´rez-Estrada et al. 16</td>
</tr>
<tr>
<td>Sonocatalysis</td>
<td>35</td>
<td>Naddeo et al. 48</td>
</tr>
</tbody>
</table>

2.2 Advanced Oxidation Processes (AOPs) as a Treatment Method

Nanofiltration technologies, ultraviolet (UV) radiation, and advanced oxidation processes (AOPs) are known methods for removing contaminants in water.9 The use of membranes and filters trap contaminants removed from water, however the disposal process of these membranes and filters pose risks to the environment.49 50 In this regard, and AOPs are more reliable in the sense that the contaminants are converted into stable, harmless inorganic compounds such as carbon dioxide, water and mineral salts. There are several types of AOPs, such as ozone/hydroxide ion (O3/OH−), ozone/hydrogen peroxide (O3/H2O2), hydrogen peroxide/UV radiation (UV/H2O2), ozone/UV radiation (O3/ UV), ozone/heterogeneous catalysts (HCO), and heterogeneous photocatalysis (UV/TiO2).49 Among these, heterogeneous photocatalysis, using a semiconductor catalyst, particularly TiO2 is an emerging technology.23 50 51 Photocatalysis presents different advantages
when compared to conventional methods. Advantages include 1) complete mineralization of the organic pollutants to CO$_2$, H$_2$O and mineral acids;\textsuperscript{23} 2) the process can be achieved without any pH adjustments or the use of toxic compounds such as O$_3$ and H$_2$O$_2$ as it requires only dissolved oxygen (air);\textsuperscript{16} 3) TiO$_2$ is inexpensive and it is commercially available in various crystalline forms with a wide range of particle characteristics. In addition, it is non-toxic, photo chemically stable and can be reused; 4) TiO$_2$ can also be modified to further enhance its photo-catalytic activity; 5) a low-energy light source such as the UV-A is sufficient to promote catalyst activation; solar visible, full spectrum and UV-LED light could also be used as alternative sources of energy when the catalyst is suitably modified.\textsuperscript{2,3,21}

2.2.1 Fundamentals of Heterogeneous Photocatalysis and its Mechanism

Illumination of a semiconductor or a photocatalyst by light (UV light, $\lambda < 380$ nm for example) results in the generation of electron/hole (e-/h+) pairs as a primary step in the photo-degradation process, Equation 1 (Refer to Figure 2.1 for schematic). As a result, oxidation-reduction reactions occur at the semiconductor surface. The majority of these e-/h+ pairs tend to recombine with the liberation of heat; however, in the presence of dissolved oxygen, the photo-generated conduction band electrons are trapped, resulting in the formation of a superoxide ion (O$_2^-$) as shown in Equation 2.

$$\text{Photocatalyst } \xrightarrow{\lambda < 380 \text{ nm}} \text{Photocatalyst } (e^- + h^+) \quad (2.1)$$

$$O_2 + e^- \rightarrow O_2^- \quad (2.2)$$

Similarly, the photocatalyst surface-active $HO^-$ group (electron donor), formed by the ionization of water molecule scavenges the valence band holes resulting in the formation of hydroxide radicals.

$$h^+ + OH^- \rightarrow HO_{ad}^- \quad (2.3)$$

Or
\[ h^+ + H_2O_{ad} \rightarrow HO^*_{ad} + H^+ \]  

(2.4)

Figure 2.1 UV Light Activated Photocatalytic Mechanism (TiO\(_2\) as the semiconductor)

These reactions moderate the recombination rates and in turn enhance the photo-degradation rate. The organic molecules present in water react with the hydroxyl radicals formed, and are eventually oxidized to carbon dioxide, water and mineral acids, as depicted below (equation 2.5):

\[
\text{Organics} + \text{photocatalyst} + h\nu \xrightarrow{HO^*} \text{Intermediates} \rightarrow \text{MineralAcid} \rightarrow H_2O + CO_2
\]  

(2.5)

2.2.2 Application of Semiconductor TiO\(_2\) Photocatalysis

TiO\(_2\) is a very well known and most utilized semiconductor studied around the globe because of its multidisciplinary nature. The diverse application of this material, and the principle of photocatalytic process taking place on the surface of TiO\(_2\) make it applicable to a wide range of technologies such a water purification for degradation of organic and inorganic pollutants in water bodies, such as for self-cleaning surfaces; materials coated on the surface of window blinds, titles, kitchen or bathroom.\(^{19} 52 53 54 55\)
2.3 Green Detoxification of Environmental Pollutants

Photocatalytic treatment of pollutant under UV light has been proven effective. In addition, it has made great progress since its start with the pioneer work of Fujishim and Honda photocatalytic water splitting. Despite its effectiveness, UV light photocatalysis has its limitations. The UV light has a narrow wavelength which covers only 4% of the solar spectrum. This means only 4% of the solar spectrum could be used as a source of energy for any application, and it will be a challenge in industrial applications. In comparison, solar visible light includes 46% of the solar spectrum. In addition, visible light source has a higher wavelength. As per Planck’s law \( E = h \frac{c}{\lambda} \); with the use of higher wavelength the energy (larger wavelengths) is no longer sufficient to overcome the band-gap energy requirement for most semiconductors. Therefore, electron/hole (e-/h+) pair formation are not promoted. Therefore, two approaches can address this issue and improve response of TiO\(_2\) in the visible light region. The first involves an addition of dopants (cations/anions), coupling with other semiconductors.\(^{21,22,56,49}\) The second strategy involves dye-sensitization. It has attracted industrial interests in the fields of photography, photolithography, as well in solar cell for producing electricity.

2.3.1 Selection of Semiconductors and Dyes

The energy requirement for activation of a semiconductor depends on its characteristics. The minimum energy (light) wavelength \( (\lambda_{\text{min}}) \) required to photo excite a catalysts depends on its bandgap energy. Table 2-3 gives band gap energies, as well as minimum wavelength for semiconductors extensively studied.
Table 2-3 Bandgap energy and $\lambda_{\text{min}}$ for various photocatalysts

<table>
<thead>
<tr>
<th>Photocatalyst(s)</th>
<th>Bandgap (eV)</th>
<th>$\lambda_{\text{min}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (rutile)</td>
<td>3.0</td>
<td>413</td>
</tr>
<tr>
<td>TiO$_2$ (Anatase)</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>Si</td>
<td>1.1</td>
<td>1127</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.2</td>
<td>564</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>3.5</td>
<td>354</td>
</tr>
<tr>
<td>CdS</td>
<td>2.4</td>
<td>517</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.7</td>
<td>335</td>
</tr>
</tbody>
</table>

High stability and performance of TiO$_2$ has been proven. It is widely availability, low cost and it is nontoxic in nature. In that regard, the photocatalytic activity of TiO$_2$ for a variety of organic and inorganic compounds found in water has been documented in the literature. The semiconductors shown above are studied with different dyes. Thionine, eosin Y, rhodamine B, methylene blue, Nile blue A and Safranine O are different dyes studied with TiO$_2$ catalyst for the degradation of pollutants under visible light. Natural extracted dyes from mulberry, blue pea, java palm, pomegranate seeds, cabbage, and rosella fruits are also studied and utilized in dye-sensitization process. In addition, successful application of dye-sensitized TiO$_2$ in solar cell, and visible light induced detoxification of pollutants are reported in the literature. Regardless of the type of dyes used, the semiconductor surface morphology and its particle size ultimately affect the electron/hole (e-/h$^+$) recombination and photocatalytic activity. In the decades to follow, more TiO$_2$ catalyst modification will be forthcoming. In this research the focus is intended to utilize a dye in order to generate hydroxyl radicals with visible radiation.
2.3.2 Dye-sensitization

2.3.2.1 Theory

Dye-sensitization is the process by which a dye (organic or inorganic) is used to activate a large band gap semiconductor at a molecular level, under the visible light spectrum. Tennakone et al. performed the first experimental work utilizing dye sensitization technique. They used SnO2 electrodes with Ru metal-based polypyrrole complex dye. In step one, the adsorption of photon by the dye molecule resulting in formation of the excited states (equation 2.6). The second step was the injection of the electron into the conduction band of the semiconductor (equation 2.7). Therefore, the photon formed by the irritated light drives the electron through the semiconductor, and then through an external circuit. For the oxidized dye (dye*), an electron donor can be used to reduce it to its ground state (dye). An electron donor can be a molecule or redox couple in a regenerative cell. Their experiments demonstrated the dye sensitization mechanism of an n-type semiconductor electrode, such as TiO2. The process is known as anodic sensitization. A process is anodic when the dye molecule is adsorbed chemically on to a photocatalyst surface, where the adsorbed dye molecule acts as spectral sensitizer. Here the illuminated dye (with a visible light) can inject an electron into the conduction band of the semiconductor. Cathodic processes, on the other hand, occur when the adsorbed dye molecule injects holes into the valence band of a semiconductor.

\[ \text{Dye} + h\nu (\lambda > 400nm) \rightarrow \text{dye}^* \]  
(2.6)

\[ \text{dye}^* \rightarrow \text{dye}^* + e^-_{CB} (\text{dye} C) \]  
(2.7)

The efficiency of the sensitization process depends on three factors. The nature of the dye molecule

1. Type of semiconductor and the electrode interface
2. Mediating redox electrolyte

In the dye sensitization process, different binding of dye molecules to the surface of semiconductor TiO2 is proposed by Galoppini et al. They are all based on interaction mode of TiO2 surface and
–COOH group. Other interaction and bindings include –P(O)(OH)$_2$, COOR, -COX, COOM etc. Here R represents alkyl group. X, inorganic molecule such as Cl, Br etc. M can be Na, K etc.\textsuperscript{75} In last three decades, there have been several approaches in attaching dye molecule onto a semiconductor. Esterification or Si-CH$_2$-CH$_2$-NH-CO-dye linkages of xanthene dye molecule were proposed Matsumura et al.\textsuperscript{76} Another study by Houlding et al.\textsuperscript{77} proposed colloidal TiO$_2$ by eight hydroquinone for generating hydrogen from water under the visible light. In all these methods, the efficiency of the process depends on the band position of the semiconductor and the energy level of the dye.

In recent studies it was reported that in the process of dye-TiO$_2$ sensitization, the excited electron from the dye surface was not trapped on to the surface of the semiconductor, and was found to enter the bulk solution. Several authors explained the electron injection/excitation process that takes place during dye-sensitization mechanism, including the study performed by Willig’s group\textsuperscript{78,79}

### 2.3.2.2 Mechanism of Dye-sensitization

In dye sensitization process, the dye molecule is known to adsorb on the semiconductor surface, forming a thin layer of film. This film then adsorbs visible light, and illumination excites the electrons in the dye as a first step; these electrons from the excited dye are then directly injected into the conduction band of the semiconductor, if and only if the energy requirement is met. Figure 2.2 shows a schematic of the process.

In general practice, the semiconductor is dipped into the dye solution in the dark. The semiconductor and the dye are then separated by simply washing it with alcohol or water. This step is necessary for the removal of unbound dye molecules. The semiconductor can then be dried in an oven or at room temperature. There are different variations of the process as reported throughout literatures. Variations include the use of different pH level of solutions to concentration of dye, and or incorporation of other compounds as an electron donor, all being important parameters for an efficient dye –sensitization process.
2.3.3 Degradation of Dye

Self-sensitized degradation mechanism\textsuperscript{61} is a process where the sensitized dye degrade in the process of other non-sensitizing dyes (such as acid blue1 (AB1)), or other compounds. In recent studies dyes such as AB1, methylene blue, thionine, and eosin Y were used to destroy non-sensitizing dyes found in polluted water.\textsuperscript{61, 80, 81, 82, 83} The efficiency of the process and the rate of degradation are influenced but not limited to the pH of the solution, catalyst loading, and type of semiconductor. The pH of the solution is specifically important because it influences the surface charge of the solutions. Thus, the adsorption behavior of the pollutants on to the semiconductor surface will depend on this parameter. In literature Degussa P25 were reported to have the highest efficiency.\textsuperscript{81, 82} A study performed by Jiang et al.\textsuperscript{84}, where they synthesized a dye modified TiO\textsubscript{2} catalyst that show much higher activity than TiO\textsubscript{2} alone as catalyst. It was reported that in the dye-sensitized TiO\textsubscript{2} photocatalyst, the dye particles adsorbed on to TiO\textsubscript{2} surface and forms no stable bonds. Therefore, this could lead to a decrease in photocatalytic activity since the bonds formed could easily be desorbed from the TiO\textsubscript{2} surface. Nonetheless, by dye-sensitizing, a semiconductor extend its activity on the solar visible region. In addition, some authors also utilized natural dyes.
as an alternative source for sensitization. These dyes found in plants and fruits are but not limited to mulberry, cabbage, rosella, blue pea, chaste tree fruit, and pomegranate seeds.

2.3.4 Application of dye degradation

Recent studies reported many effective dye-sensitized degradation of compounds.

Table 2-4 lists some of the main studies and their promising results.

<table>
<thead>
<tr>
<th>Type</th>
<th>Compound</th>
<th>Conc.</th>
<th>Sensitizer/Photocatalyst</th>
<th>Light source/time</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compounds</td>
<td>CCl₄</td>
<td>3-4 mM</td>
<td>Silylated [RuII(pypzH)₃]²⁺/TiO₂</td>
<td>Tungsten lamp/30 min</td>
<td>Fung et al. 88</td>
</tr>
<tr>
<td></td>
<td>Trichloro-acetate (TCA)</td>
<td>1 mM</td>
<td>ruthenium (II)complex</td>
<td>Xe lamp/UV cut off filter/2hrs</td>
<td>Bae &amp; Choi 89</td>
</tr>
<tr>
<td></td>
<td>Trichloro-ethylene (TCE)</td>
<td>2-500 ppm</td>
<td>Natural anthocyanine dye-TiO₂</td>
<td>Xe lamp/15-1440 min</td>
<td>Alexander &amp; Rosentreter 90</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Bromacil (BR)</td>
<td>30-100 ppm</td>
<td>Methylene blue, Red</td>
<td>UV and Sunlight</td>
<td>Muszkat et al.</td>
</tr>
<tr>
<td>Phenol</td>
<td></td>
<td>100 ppm</td>
<td>Zn (II) and Co(II) tetracarboxphthalocyanine/Pt/TiO₂</td>
<td>Halogen lamp/60min</td>
<td>Granados O et al. 92</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td></td>
<td></td>
<td>Riboflavin, Safranine O, Methyl red, Eosin Methylene blue/TiO₂ P25</td>
<td>Sunlight/75min</td>
<td>Hussein et al. 93</td>
</tr>
<tr>
<td>Hydrazine</td>
<td></td>
<td>1 mmol</td>
<td>Ru(III)(EDTA)(H₂O)/Pt/TiO₂ P25</td>
<td>Xe lamp/8h</td>
<td>Chatterjee et al. 94</td>
</tr>
<tr>
<td>Dyes</td>
<td>Acid blue (AB1)</td>
<td>25 ppm</td>
<td>Eosin Y, Thionine/TiO₂</td>
<td>Xe Lamp/5h</td>
<td>Chatterjee et al. 61 95</td>
</tr>
<tr>
<td></td>
<td>Chrysoidine Y</td>
<td>0.25 mM</td>
<td>Chrysoidine Y/TiO₂ P25</td>
<td>Hg lamp/120min</td>
<td>Qamar et al. 81</td>
</tr>
<tr>
<td></td>
<td>Methylene blue</td>
<td>50 ppm</td>
<td>Chrysoidine G/TiO₂ P25</td>
<td>Metal halide lamp/12h</td>
<td>Jiang et al. 84</td>
</tr>
</tbody>
</table>
2.4 Photocatalytic Reactors

The first step in any photocatalytic treatment is the activation of the semiconductor where the rate of initiation of the process is directly proportional to the radiation intensity of the energy source. Therefore, it is important to have a well-illuminated reactor in order to prevent dark zones. This ensures that the light distribution inside a photocatalytic reactor is not limiting the rate determining step of the reaction.

Design of an efficient photocatalytic reactor is the most challenging goal in photocatalytic process. It is of great technical importance to develop and design water and air treatment systems. It is of great value, however difficult task to design, an efficient reactor for large scale industrial and commercial applications. A photocatalytic reactor must provide good flow channeling to reduce the dead volume and high mixing, to minimize mass transfer resistance of pollutants to reach the activated catalyst surface. In that regard, optimization of photoreactor geometry, type of semiconductor, light source and operating conditions are all important considerations to reactor design.

2.4.1 Photoreactor configuration

For water treatment applications, a photocatalytic reactor must have the following characteristics:

1. The photoreactor must be able to utilize UV or solar radiation.
2. The light source can be external to the system or distributed by reflectors inside the reactor.\textsuperscript{96}
3. The semiconductor can in suspended form or immobilized on a surface.\textsuperscript{3, 97}
4. The reactor must provide good flow channeling to reduce the dead volume
5. Provide high mixing in order to minimize mass transfer resistance of pollutant to reach the activated catalyst surface.

When a catalyst is suspended in the system, it provides larger photocatalytic activity as opposed to a reactor with an immobilized catalyst.\textsuperscript{96} As a result, a great extent of reactors patented are slurry reactors, as well as classical annular form.\textsuperscript{100} Therefore, most of the kinetic studies presented
in the literature deal only with experimental data produced in slurry photoreactors. A slurry system can provide uniform catalyst distribution with low pressure drop through the reactor. In addition to a high photocatalytic surface area to reactor volume with minimum mass transfer limitation. However, the disadvantages of such a system is its requirement for post process treatment, and in some cases it can be difficult to assess light scattering in the suspended medium.

Immobilization of the catalyst generally reduces the overall performance of the photo reactor due to the mass transfer limitations and less catalyst irradiated area. However, there are some advantages to this type of system. It provides a continuous process, without the need for catalyst separation and post treatment. If a suitable support is provided, such as fiberglass sheets for the immobilization of the photocatalyst, the mass transfer limitation can be improved greatly.

In recent years, the effectiveness of reactors utilizing solar irradiation have given considerable attention. However, most photocatalytic reactors using solar irradiations are slurry type processes.

2.4.2 Operating Conditions

In a photocatalytic process, the degradation of organic pollutants depends on but is not limited to intensity of the light source, catalyst loading, pH, temperature, and amount of dissolved oxygen. The specific reasons for such dependence are explained as follows below.

2.4.2.1 Light Intensity

The electron/hole formation in a catalytic process need sufficient UV, or visible light. At high radiation intensities, a zero order dependency of the rate of degradation of the pollutant to light source can be observed. However, in general, one can expect a linear trend which changes to a square root dependency of the photocatalytic reaction rate to the radiant flux at certain thresholds depending on the system. The activation threshold for TiO$_2$ is reported to be at 388nm.
Meaning UV light less than 388nm is required to activate TiO$_2$. For Eosin Y dye a visible light source of at least 512nm is required for its activation.  

2.4.2.2 Photoreactor Geometry

The geometry of a photoreactor is also very important. It must provide a good flow channeling to reduce the dead volume, high mixing, and should be able to minimize mass transfer resistance of pollutant to reach the activated catalyst surface.  

2.4.2.3 Catalyst Loading

The amount of the photocatalyst is proportional to the overall photocatalytic reaction rate. This parameter also depends on reactor geometry, as well as type of catalyst in the system (immobilized or suspended particles).  

2.4.2.4 pH

Depending on the pH of the system, the adsorption of the pollutant on to the catalyst surface varies. Therefore, it is important to know the surface charge or the isoelectric point of the photocatalyst. The point zero charge for TiO$_2$ is found in the pH range of 4.5-7.0.  

2.4.2.5 Temperature

Below a temperature of 80°C in a photocatalytic system, a high adsorption of organic pollutants to the surface of TiO$_2$ was reported. However, above 80°C temperature the rate of electron and hole recombination is increased in the systems, therefore, decreasing the rate of degradation.
2.4.2.6 Oxygen

The amount of dissolved oxygen in a photocatalytic process prevents the electron/hole recombination. Meaning oxygen is an electron scavenger. Therefore, excess dissolved oxygen in the system ensures the recombination process and therefore is an important parameter to take into consideration. 50 51

2.4.2.7 Initial Concentration of Pollutants

In a photocatalytic process, the initial concentration of pollutant being treated is significant. For instance, the concentration of pollutants should not be excessive to prevent even saturation on the photocatalyst surface. This could saturate the catalyst surface and could prevent the activation by the light source, which is the essential part of a photocatalytic process. 3 49 106

2.5 Conclusions

Water has become increasingly contaminated with toxic compounds, making water pollution an immediate and important challenge in the world. Water pollution reduces available amount of freshwater resources and earth will experience fresh water scarcity in the near future.

Treatment processes for most water pollution, and for DCF from wastewater streams have been reported. However, the studies are not in depth investigations, meaning the reaction rate report for most of these pollutants (including DCF) does not consider the mass transfer effect. Apparent rates are reported as opposed to true kinetics. Thus, for design and development of large scale reactor, true kinetic rate values that is independent of reactor geometry is significantly important. Obtaining a detailed systematic study (considering all operation parameters, such as flow rate, pH, etc.) and investigation of true kinetic of the photocatalytic degradation process under UV and visible radiation is needed.

TiO₂ photocatalysis can be an alternative green solution for water and wastewater treatment. In addition, this technology can be applied to other applications, such as hydrogen production and
self-cleaners. Application of TiO$_2$ photocatalysis for a variety of organic and inorganic compounds has been well documented and proven effective in the literature. The limitation with using TiO$_2$ (in both forms) as a photocatalyst is the wide band gap energy requirement. This means only 4% of solar spectrum could be used as a source of energy for any application, making a challenge in industrial application. A shift to solar base photocatalysis, such as dye-sensitization could create economic and social benefits. Although, there are advantages when a photocatalyst are used in suspension in photocatalytic process as mentioned in this literature review. As an alternative, immobilizing the catalyst on a suitable support makes this process economically feasible without requiring a subsequent post process treatment. Despite it creating certain limitations such as mass transfer resistance. However, finding a suitable support media for immobilization of the photocatalyst could eliminate some of the limitations.
2.6 Nomenclature

DCF  Diclofenac, a model compound for this kinetic study
EC₅₀  Median Effective Concentration (required to induce a 50% effect)
e⁻  Electron
h⁺  Hole
H₂Oₐd  Adsorbed water molecule
LogKₐw  Kₐw = concentration in octanol phase /concentration in aqueous phase
OHₐd  Adsorbed hydroxide radical
pzc  point zero charge of a catalyst
PCPs  Pharmaceutical and personal care products
EDCs  Endocrine disruptive compounds

Greek Letters

λ  Wavelength of incident light, nm
2.7 References


26. Rizzo, L., Meric, S., Guida, M., Kassinos, D. & Belgiorno, V. Heterogenous


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139. Qi, S. *et al.* Toxicity assessments with Daphnia magna of Guadipyr, a new neonicotinoid

Chapter 3

3 Research Objectives

3.1 Main Objectives

This PhD dissertation investigates the efficiency of a photocatalytic reactor and a reliable photocatalytic treatment processes for the purpose of facilitating chemical transformations in aqueous medium. To understand this specific objectives flow charts for this study are shown in Figure 3.1.

3.1.1 Model Compound

DCF was chosen as the model compound for the reasons mentioned in literature review section of this report. Treatment processes for the removal of DCF from wastewater streams have been reported, together with their corresponding degradation rates of DCF alone or as a mixture with other pharmaceuticals. However, all these studies are not in depth investigations, meaning the reaction rate report for DCF does not consider the mass transfer effect, and it is not true kinetics.

3.1.2 Support media for Immobilization of Semiconductor

Studies have been carried out earlier, using the semiconductor (photocatalyst) in slurry form. There are advantages in slurry system. Almost no mass transfer limitation exists because the diffusion distance is very small. In addition, high ration of illuminated catalyst surface area to the effective reactor volume is possible. However, suspended TiO$_2$ presents certain disadvantages when it comes to scaling up the process; it requires a post process treatment to separate the suspended solid from the reacting solution. Installation and operation of liquid and solid separator will add on the cost of the overall processes because separation of the ultrafine catalyst particles is a slow and expensive process.
As an alternative, immobilizing the catalyst on a support system is economically feasible without requiring a subsequent post process treatment. The advantages include elimination of post process and providing a continuous operation. However, catalyst immobilization presents certain limitations: its efficiency is largely determined by the nature of the support media used; further, it does not provide an equivalently large surface area as that of the slurry systems, apart from the mass transfer resistance caused by the immobilization. Nonetheless, these issues are not as significant if proper catalyst supports are chosen. Based on extensive literate review, porous fiberglass sheets and Pyrex glass plates were chosen for this study.

3.1.3 Light Source

Comparing the nobility of the two light sources under consideration in the chart, while a solar visible light source is of lower energy and more abundant against the narrow range of UV-A and hence preferable, it is offset by the high cost and large area requirements for the corresponding reactor installations and the fact that the reactor efficiency is dictated by the direction intensity and solar light availability \(^{13, 111-115}\); visible and full spectrum, making itself easily available from the sun could probably resolve the cost issues of filtering out the UV involved with a solar visible light source but it has the disadvantage that its intensities vary throughout a year and hence the reaction conditions would have to be constantly modified to achieve a particular extent of degradation.
3.2 Specific objectives

Figure 3.2 shows a schematic of the specific study. It is divided into three parts and a brief description of the section is listed below.

3.2.1 Intrinsic Kinetic Study for Photocatalytic Degradation of Diclofenac under UV and Visible Light

The first study will be on determining the true kinetic of DCF, utilizing a modified swirl flow reactor. The novelty of this study lies in performance of a detailed multi-parametric study to determine the true kinetic rate constants and adsorption equilibrium rate constants. The following tasks were performed and accomplished.

1. A suitable support system for the immobilization of various photocatalyst were tested and determined.
2. Obtained a detailed systematic investigation of true kinetics of the photocatalytic degradation process under UV and visible radiation. The influence of all major operational parameters, such as flow rate, catalyst loading, pH, light intensity, DCF initial concentration, and photocatalyst type on degradation rate were investigated.

3. An overall rate expression that describing the degradation kinetics of DCF were determined.

3.2.2 Solar Degradation of Diclofenac using Eosin Y Activated TiO$_2$: Cost Estimation, Process Optimization and Parameter Interaction Study

In this study, the aim was to find an innovative solution for the activation of TiO$_2$ in DCF degradation under the visible light using Eosin Y dye. The originality of this study lies in


2. An incorporation of a central composite design (CCD) to optimize the integrated factors, specifically dye concentration, as well as the interaction of all the operating parameters.

3. A cost estimation of the process.

3.2.3 Solar Degradation of Diclofenac using Eosin Y Activated TiO$_2$: Identification of DCF intermediates and toxicity analysis

DCF intermediate products formed during the visible light photocatalytic treatment at the optimized parameters found in Section 3.2.2. The originality of this study lies in

1. Utilization of HPLC/Ms-orbitrap to identify DCF intermediate products formed during the visible light photocatalytic degradation of DCF using EY-sensitized TiO$_2$.

2. Toxicity analysis of the treated and untreated samples of DCF were assessment.
Figure 3.2 Photocatalytic mechanism under visible light
Chapter 4

4 Material and Methods

4.1 Materials

TiO\(_2\) (Degussa P25) (80:20 anatase/rutile) from Evonik Degussa Corporation was used as the catalyst, with and without modification. Eosin Y dye (99.0\%) used as the sensitizer for TiO\(_2\) for dye-sensitized studies, diclofenac sodium salt of 99.5\% purity (CAS No. 15307-79-6), and Methanol HPLC grade with 99.93\% purity (CAS No. 75-05-08) were all purchased from Sigma-Aldrich Canada Ltd.; a proprietary doped-TiO\(_2\) catalyst (VN-TiO\(_2\) (Doped-TiO\(_2\))) was provided by a Canadian company. DAPHTOXKIT F\textsuperscript{TM} was purchased from MicroBioTests Inc. Milli-Q water by Millipore system was used for the preparation of the standard solution. Glass fiber sheets (1/8” thickness, 16” width, and 10’ length) and Pyrex glass plates (4 1/2” OD \times 1/8”) were purchased from McMaster-Carr and GreatGlas Inc. Scientific Glassware, respectively.

4.2 Immobilization of Photocatalyst

4.2.1 Glass Plate Supports

A Pyrex glass was used because of its transparency to UV up to 320 nm. Pyrex glass also cuts off any light below 320 nm, thus eliminating any direct photolysis reaction. Prior to catalyst immobilization, the Pyrex glass was roughened by sandblasting to enhance catalyst fixation strength, sanitized with 5\% HNO\(_3\) solution overnight, rinsed with water, and dried at 400 K. A 20\% aqueous suspension of the photocatalysts (TiO\(_2\), dye-sensitized TiO\(_2\), and doped-TiO\(_2\)) was prepared with Milli-Q water. An ultrasonic cleaner (Fisher Scientific; model F560) was used to uniformly disperse the catalyst particles within the suspension. As opposed to the doped-TiO\(_2\) catalyst, an aqueous solution was available and, hence, used as such. The Pyrex glass was then coated with the catalyst by inserting it into the suspension or solution (depending upon the catalyst) and pulling it out slowly by a dip-coating technique.\(^{27}\) The catalyst coating was dried at 373 K for 3600 s and then calcined for 5400 s in a furnace (Thermo Scientific; model no. F30430CM) at 575 K with a temperature ramp of ca. 0.15 K/s to avoid cracking of the film. After
calcinations, the catalyst was gradually cooled to room temperature using the same temperature ramp. The above procedure could be repeated a few times depending on the desired catalyst loading (catalyst layer thickness). The calcination temperature has a significant effect on the catalyst activity as it can affect the physical properties of the catalyst, such as porosity, surface area, and crystal size. An optimal temperature of ca. 575 K was chosen as the calcinations’ temperature. As a final step, the plates were flushed with Millipore water to remove the loosely bound catalyst. The total amount of catalyst loaded was measured by weighing the glass pre- and post-coating and was dependent on the amount of dipping.

4.2.2 Fiberglass Sheet Supports

When the photocatalyst was immobilized on the surface of the fiberglass, the plates were cut into circular shapes with 0.05 m diameters and placed in a furnace (Thermo Scientific; model no. F30430CM) at 573 K for 1800 s to remove the polymer-coated surface and soften them. After this step, the fiberglass was ready to be coated, and the remainder of the procedure was exactly the same as that of the Pyrex glass support system. Dye-sensitized catalyst was loaded onto the TiO$_2$ coated fiberglass sheets by a dip-coating technique, with known concentrations of Eosin-Y dye. The sheets were then dried at 373 K prior to use.

4.3 Experimental Setup

A semibatch swirl-flow monolithic-type reactor (Figure 4.1 Schematic drawing of the photoreactor (A: Pyrex glass plate, B: fiberglass sheet, C: stainless steel/Aluminum casing)) was used to study the kinetics of photocatalytic reactions. The reactor setup consisted of a circular glass plate (A), and a circular fiber glass sheet or glass plate (B), each with a diameter of 0.05 m. The plate and sheet were placed between soft padding housed within stainless steel and aluminum casings separated by 0.01 m (C). The catalyst was deposited on top of the fiberglass sheet or glass plate, depending on which catalyst support was used. The reactor provides a high catalyst surface-to-volume ratio and allows for high flow rates with a small pressure drop. In addition, the reactor provides the flexibility to work with a supported or suspended catalyst and to determine true kinetic
rate constants as a function of various parameters, such as flow rates, catalyst loading, light intensity, and so forth.

Figure 4.1 Schematic drawing of the photoreactor (A: Pyrex glass plate, B: fiberglass sheet, C: stainless steel/Aluminum casing)

The aqueous solution was introduced tangentially through two inlets aligned in different directions into the reactor by a peristaltic pump from a tank and exited from the center of the top plate (Figure 4.1). The effluent tubing was also connected to the tank for a continuous treatment. The tangential inflow of liquid through two inlets aligned in different directions creates a swirl flow, reducing flow channeling (liquid bypass) and dead volume and at the same time increasing mixing and, thereby, minimizing mass transfer resistance of pollutants to reach the catalyst surface. The use of two inlets, in contrast two just one inlet, is the modification of the reactor made in this study compared to our earlier studies. In order to optimize the reactor with respect to the flow distribution inside the reactor, the flow pattern was visualized by solving momentum equations using commercial software package, FLUENT. Flow patterns inside the reactor were visualized by tracking fluid particles released from a plane perpendicular to the top and the bottom circular plates. In Figure 4.3, particle trajectory is shown for inlet flow rate and reactor dimensions used in this study for three inlet configurations—one inlet (Figure 4.3a) as well as two inlets in the same direction (Figure 4.3b) and in the opposite directions (Figure 4.3b). The figures clearly shows that tangential introduction of fluid indeed creates swirl-flow inside the reactor but reveals the presence
of dead zone(s) and bypassing of fluids. Figure 3a reveals the presence of a dead zone in the upper right corner and bypassing of a fraction of the fluid demonstrated by the shorter path lines which originate from the middle portion of the reactor and terminating at the outlet that is located at the center. As a result, attempts were made to push the re-circulatory dead zone by introducing another tangential jet in the same direction at the diagonally opposite peripheral point of the reactor. Flow patterns for this case (Figure 4.3b) reveals that instead of reducing the existing dead zone region it introduced another dead zone placed symmetrically on the other side. Though impingement of two oppositely directed jet does create highly turbulent region and introduces good mixing, it also directs the fluid particles toward to the outlet by giving them the way between the two dead zones. This configuration, thus, was not realized as the optimum arrangement of the inlets with respect to the reactor body. Apart from creating a swirl flow inside the reactor, presence of a tangential jet through a narrow inlet also creates a low-pressure zone near the entrance, which draws path lines from the lower part of the reactor toward the inlet as shown in Figure 4.3a. This feature was realized as an advantage for dragging the trapped fluid particles out of the recirculatory zone. Subsequently, another jet inlet directing in the opposite direction was introduced at the other end of the reactor. This not only removed the dead zone but also forced the bypassing fluid particles into a swirl, and thereby increased the average residence time (see Figure 4.3c).

![Figure 4.2 Schematic diagram of the experimental setup. Light source: UV and visible light](image-url)
Figure 4.3 FLUENT flow pattern inside the swirl-flow kinetic reactor. (a) one inlet showing dead zone and fluid bypass, (b) two inlet in the same direction showing dead zone and significant fluid bypass, and (c) two inlet in opposite direction (used in this study).

Figure 4.3 Flow pattern inside the swirl-flow kinetic reactor. (a) one inlet showing dead zone and fluid bypass, (b) two inlet in the same direction showing dead zone and significant fluid bypass, and (c) two inlet in opposite direction (used in this study).

A UV-A lamp (Sylvania–Mercury Vapor Lamp: 175 W) was used as the light source and placed underneath the bottom glass plate on a holder that could be moved to adjust the incidence angle of light on the catalyst plate. The lamp was kept from overheating by cooling with a fan. A wooden box was used to house the lamp and the reactor to prevent stray light from entering into the reactor. A UVX radiometer was used to measure the light intensity (UVX digital radiometer E29091). An HPLC (Agilent technologies 1200 series) was used to measure the concentration of degraded DCF.
The pH was measured with a pH meter (Metrohm 780). A solar simulator (model SS1KW, ScienceTech, Ontario, Canada, with 1000W Xe arc lamp and an AM 1.5G filter) providing visible light could also be used with modified TiO₂. High-pressure liquid chromatography (HPLC) (Agilent Technologies, 1200 series) was used to monitor the concentration of DCF in the photo degradation experiments. The HPLC was equipped with a ZORBAX Eclipse XDB C-18 column (ID 5 μm, 4.6 × 150 mm). The mobile phase is composed of methanol and water (50:50 v/v). A volume of 5 μL of DCF sample was injected in to the C18 column. Mobile phase was kept at the rate of 0.5 mL/min. Concentration of DCF was reported by means of a UV detector at an absorbance of 228 nm, and the retention time for DCF samples were found to be at 5.76 min.

4.4 Analytical Methods

4.4.1 Quantification of DCF by HPLC
A high pressure light chromatography (HPLC) (Agilent Technologies 1200 series) unit was used to measure the concentration of degraded DCF. The HPLC was equipped with a ZORBAX Eclipse XDB C-18 column (ID 5 μm, 4.6 × 150 mm). The mobile phase is composed of methanol and water (70:30 v/v). A volume of 5 μL of DCF sample was injected into the C18 column. Mobile phase was kept at the rate of 0.5 mL/min. Concentration of DCF was reported by means of a UV detector at an absorbance of 228 nm and 270 nm. The retention time for DCF samples were found to be 5.76 min.

4.4.2 Identification of DCF by HPLC/MS-orbitrap
The DCF intermediate products formed were monitored using high performance liquid chromatography- mass spectrometry (LTQ Orbitrap Discovery MS 2.5.5) instrument provided by
Thermo Scientific. The process was operated at room temperature and the instrument was equipped with an auto-sampler (Accela AS 2.2.1), a pump (model number: 1.04.05.), and a syncronis C18 (50mm length, 2.1 I.D., and 1.7m particle size).

The mobile phase was composed of two solvents, A and B. Solvent A contained AcN acidified with 0.1 vol% of formic acid. Solvent B was composed of water acidified with 0.1 vol% of formic acid. The flow rate of the mobile phase was 0.2mL/min and a gradient technique was used to implement the flow. The gradient was run according to the following program reported by Undri et al.9 10 Solvent A 2 vol%, increased to 10 vol% at 2 min, increased to 25 vol% at 6 min, increased to 50 vol% at 10 min, increased to 75 vol% at 14 min, increased to 95 vol% at 18 min, decreased to 2 vol% at 20 min, followed by 2 min of isocratic elution with 2% of solvent A (total elution time 22 min).

The mass spectrum was equipped with an ESI (+/-) source ionization modes. In this study an ESI positive ionization mode was used. The operating parameter was set in accordance with a method formed by Undri et al.9 as follows: sheath gas flow rate of 8abu (an arbitrary unity), auxiliary gas flow rate of 1abu, electrospray voltage of 3.1 kV, capillary temperature of 270 °C, capillary voltage set to 49.00 V, and tube lens offset at −148.43 V. The mass resolution power of the mass analyzer was set to 30,000 (m/m) at m/z 400. The resulting mass spectra are shown either in molecule + or – 1 hydrogen atom ( [M + H] + or [M − H] − ). Nitrogen gas (purity 99.95%) was used for the sheath gas, auxiliary gas, as well as used in HCD cell in C-trap as the collision gas. The identified mass spectrums was viewed and analyzed using the software Xcalibur provided by Thermo Scientific.

4.5 Toxicity Analysis

Toxicity analysis was performed using DAPHTOXKIT F™ (MicroBioTests Inc.). The 24-48h test is based on immobility of freshwater organisms with respect to calculation of the EC50 and LC50. It is based on the observation of species Daphnia magna mortality rate. The test observes D. magna after exposure at 24 and 48 hrs.
For the analysis, water samples were aerated for two hours prior to mixing it with CaCl₂, NaHCO₃, KCl, and MgSO₄. This step ensures the saturation of oxygen and complete dissolution of the mixture. The sample is then left for 24 hours prior to using the diluted solution for hatching organisms (*ephippia*). The pH of the sample was kept at 7.0 by adjusting using 1M NaOH or 1M HCl, and the organisms were grown under the exposure of illuminated light (6000 lux) at approximately 21°C.

The experiments were performed on test plates containing the dilutions. Five *D. magna* organisms were transferred into each cell and covered. The cells were then placed in the dark and incubated at 20°C. Each sample was tested 5 times for statistical evaluation. The samples were then observed at 24 and 48 hours of exposure and the mortality rate of the organisms were recorded. This test was used to compare the intermediates formed at different stages of the photocatalytic treatment to the original solution containing only DCF (solution prior to treatment).
4.6 References


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139. Qi, S. et al. Toxicity assessments with Daphnia magna of Guadipyr, a new neonicotinoid

Chapter 5

5  Intrinsic Kinetic Study for Photocatalytic Degradation of Diclofenac under UV and Visible Light

5.1 Introduction

Clean water is a precious resource upon which every life on the planet is dependent. Over 70% of Earth’s surface is covered by water; however, less than 1% of all fresh water is accessible for human use. Global population growth, increasing industrialization and urbanization, and decreasing supply due to pollution and changing climate patterns have increased the demand of potable water. Wastewater reuse and value recovery from wastewater have resulted in market growths for sustainable technologies in water and wastewater treatment. However, water pollution threatens our health and environment and has become an issue of major social and economic concern. Water resources are becoming increasingly contaminated with toxic compounds and it is of immediate important challenge in the world that faces increasing pollution and decreasing energy resources. These emerging contaminants are of increasing concern as a threat to human and aquatic health and are being considered by government regulators around the world.

Contaminated water results from improper disposal of household drugs, industrial effluents, agricultural run-offs, and human and animal consumptions in developed as well as in developing countries. The problem aggravates due to the unreliability of conventional treatment methods. Extensive use of emerging contaminants including endocrine disrupting compounds (EDCs), personal care products (PCPs), and pharmaceutically active compounds with mutagenic, genotoxic, and carcinogenic effects are also of increasing prevalence in water resources.

A significant portion of the pharmaceutical wastes in wastewater is composed of anti-inflammatory and analgesic drugs with an estimated annual consumption of several hundred tons around globally. Diclofenac [2-(2,6-dichloranilino) phenylacetic acid], a common nonsteroidal anti-inflammatory drug (NSAID), is also heavily used all over the world to reduce inflammation and as an analgesic and dysmenorrheal in reducing acute and chronic aches and pains (such as those due to arthritis) as well as fever associated with common infections. It is one of the most commonly detected compounds, even though it can be degraded partially by photolysis under normal environmental condition. Concentrations as high as 3 and 2.5 ppb are detected in the
influent and effluent streams of wastewater treatment plants (WWTPs), respectively, with 1.2 ppb in surface waters and 0.25–50ppt in drinking water. Its physical, chemical and aquatic toxicity parameters are listed in Table 5-1.

Table 5-1 Physical, Chemical, and Aquatic Toxicity Parameters of DCF

<table>
<thead>
<tr>
<th>Drug</th>
<th>MW (g/mol)</th>
<th>Pv (mm Hg)</th>
<th>S (mg/L)</th>
<th>pKa</th>
<th>log Kow</th>
<th>H (m^3/mol)</th>
<th>EC50 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCF</td>
<td>296.2</td>
<td>6.14 x10^-8</td>
<td>2.37</td>
<td>4.16</td>
<td>1.9 - 4.5</td>
<td>4.7 x 10^-12</td>
<td>22 - 68</td>
</tr>
</tbody>
</table>

Research indicates that the toxic effect of DCF in combination with other pharmaceutical compounds present in water samples can increase with time even if it is present at very low concentrations as it has the potential to bio accumulate in the tissues of organisms. Other studies reported that the presence of 1ppb of DCF could damage liver and kidney cell functions in aquatic animals. It is also the cause of the catastrophic decline of vulture populations in Western Asia, as even parts-per-thousand levels may inhibit cell proliferation. Recent research reported that sub-chronic exposure to DCF at milligrams-per-liter levels could interfere with the biochemical functions and cause tissue damage in fish. Furthermore, ingestion of DCF by birds results in death shortly after exposure to the contaminated source.

There are many advanced treatment options are available in removing DCF from water: nano-filtration technologies, ultraviolet (UV) radiation, and advanced oxidation processes (AOPs), among others. As for the use of membranes and filters, the trapped contaminants, although removed from water, pose risks to the environment in the process of their disposal. In this regard, AOPs are more reliable because the contaminants are converted into stable, harmless inorganic compounds such as carbon dioxide, water, and mineral salts. There are different AOPs, such as O₃, H₂O₂, O₃/H₂O₂/UV photocatalysis, and O₃/H₂O₂/photocatalysis. Among these semiconductor photocatalyst, particularly TiO₂ is a promising technology. In heterogeneous photocatalysis, when TiO₂ is illuminated by UV-A light (λ < 380 nm) electron–hole (e^-/h^+) pairs are generated as a primary step in the photodegradation process. As a result, oxidation–reduction reactions occur at the semiconductor surface. The hole forms a hydroxyl/peroxyl radical while the electron in the presence of dissolved oxygen forms a superoxide
ion. However, the majority of these $e^-/h^+$ pairs tend to recombine with the liberation of heat. The organic molecules present in water (DCF in the present study) react with hydroxyl/peroxyl radicals, which eventually oxidized the parent toxic compounds to mineral acids and CO$_2$. Heterogeneous photostimulated catalysis presents a possibility in degrading toxic organic pollutants for environmental cleanup. Numerous advantages of this technology is well documented when compared to conventional methods; namely, complete mineralization of the organic contaminants at times without any pH adjustments or the use of harmful compounds such as O$_3$ and H$_2$O$_2$ as dissolved oxygen (or air) is sufficient in continuing the redox reaction by scavenging electrons; conventional catalytic material, TiO$_2$, is cheap and is commercially available in various crystalline forms with a wide range of particle characteristics. In addition, TiO$_2$ is nontoxic and photochemically stable and can be reused for long period of time, and catalyst photoactivation can be achieved with a low-energy UV-A light source.$^{16,22,23}$ However, the key challenge with this technology is the requirement of an artificial UV lamp due to large band gap energy for commonly used photocatalytic materials. Because of the ubiquity of sunlight, the commercial success of this technology depends on engineering of electronic bands of the photocatalyst for paradigm-shift to solar-based photocatalysis that could create significant economic and social benefits. As per Planck’s law ($E = h\nu/\lambda$), with the use of higher wavelength visible light ($\lambda > 400$ nm) as compared to UV ($100 < \lambda$ (nm) < $400$), the energy associated with larger wavelength light is not sufficient to overcome the TiO$_2$ band gap (ca. 3.2 eV requiring $\lambda < 380$ nm). Hence, $e^-/h^+$ pairs formation may not take place. Two approaches address this issue. The first involves reducing the band gap through addition of dopants,$^{22,23}$ thereby allowing light absorption in the visible part of the spectrum. The second strategy involves dye-sensitization. The quintessence of dye-sensitization is the electron injection from the excited dye to the conduction band (CB) of TiO$_2$ and the subsequent interfacial electron transfer. Once the interfacial electron transfer is achieved, the remaining oxidation–reduction steps are the same as before. Hence, successful synthesis of chemically modified photocatalyst through molecular band engineering will enable sun-powered remediation of environmental pollutants.

In this study a semibatch, swirl-flow, monolithic photocatalytic reactor was used. Monoliths are unique catalyst supports that provide a high surface to volume ratio and allows operation at high flow rates with low pressure drop. The kinetic reactor used in this study is a modified design from
that used in our earlier studies. The new reactor uses two inlets in opposite direction contrary to only one inlet to reduce dead zones and fluid bypass, thereby improving residence time distribution of reactants inside the reactor. The novelty of this study lies in (a) use of the modified reactor that provides improved fluid mixing, (b) a suitable support system (fiberglass sheet and glass plate) for the immobilization of various photocatalysts. Immobilization of the photocatalysts eliminates the need for post process separation, (c) evaluating the efficiency of the three types of photocatalysts (Degussa P25, doped-TiO$_2$ and dye-sensitized TiO$_2$) in degradation of an anti-inflammatory and analgesic drugs, diclofenac (DCF), (d) obtaining a detailed systematic investigation of true kinetics of the photocatalytic degradation process under UV and visible radiation, (e) the influence of all major operational parameters, such as flow rate, catalyst loading, pH, light intensity, DCF initial concentration, and photocatalyst type on degradation rate, and (f) an overall rate expression that describes degradation kinetics of DCF. A detailed multiparametric study is reported in order to understand the complex interplay of various process parameters. True kinetic rate constants and adsorption equilibrium rate constants were determined and reported after correcting for mass transfer limitation. For design and development of large-scale (high-rate) reactor, true kinetic rate values are important, that is, independent of reactor geometries. To our knowledge, true kinetic rate constants for DCF are not reported in literature.

5.2 Results and Discussion

Degradation of DCF in the presence of light and catalyst reported in this work is ensured that it is entirely due to photocatalysis. Prior to the photocatalytic reaction studies, an investigation was performed to see whether direct photolysis occurs. It was observed that no direct photolysis occurs for DCF. When dark reactions (adsorption, absence of light, presence of catalyst) were performed, there was a small decrease in DCF concentration due to adsorption, which reached equilibrium within 1800 s. Therefore, prior to turning the light on, it was always ensured that adsorption equilibrium has reached.
5.2.1 Photocatalyst Support

In previous studies performed by our group, using swirl flow reactor, Pyrex glass plates were used as the support system for immobilization of the photocatalytic degradation of various organic and inorganic water pollutants.\textsuperscript{26,28,29} Although glass plates are excellent support systems, they do not provide enough reaction surface area. After carefully investigating the various support systems available,\textsuperscript{25} two different supports, fiberglass sheet and glass plate were selected to immobilize the photocatalysts for the photo degradation of DCF (Figure 5.1). SEM and EDX analysis were performed to understand which support provides better surface area. Figure 5.2 show the surface properties of the fiberglass and glass plates. Comparing Figure 5.2a and b with Figure 5.2c and d, fiberglass sheet is visibly more porous and, hence, provides greater surface area to accommodate a higher catalyst loading. To further verify the effectiveness of fiberglass sheets, the two catalyst supports were loaded with TiO$_2$, and the rates of degradation of DCF were obtained. A maximum stable loading of 50 \times 10^{-3} \text{ kg/m}^2 was found for fiberglass as opposed to 23 \times 10^{-3} \text{ kg/m}^2 for the glass plates. At this maximum loading the overall reaction rates were observed to be much higher when fiberglass was used as a support. The experimental results are shown in Figure 5.3.

Figure 5.1 (a) Pyrex glass plate coated with TiO$_2$, (b) fiberglass sheet coated with TiO$_2$, (c) fiberglass sheet coated with dye-sensitized TiO$_2$
Figure 5.2 (a) SEM images of glass plate coated with TiO$_2$, (b) left at 1K 30 μm and right at 10K 3 μm, (c) SEM images of fiberglass coated with TiO$_2$, (d) left at 2K 15 μm and right at 10K 3μm.

Figure 5.3 Effect of TiO$_2$ dosage on degradation of DCF for different support systems. Experimental conditions: $Q = 1.15 \times 10^{-5} \text{ m}^3/\text{s}$, $V_L = 4 \times 10^{-4} \text{ m}^3$, $I = 45 \text{ W/m}^2$, $[\text{DCF}]_o = 25 \text{ ppm}$, pH = neutral, $T = 298 \text{ K}$, O$_2$ saturated.

Stability analysis was also performed to ensure the immobilized catalyst was stable on the surface of the fiberglass support via two methods: (1) blank experiment and (2) differences in mass pre-
and post-treatment. In the blank experiment, immobilized TiO$_2$ on fiberglass was run in the reactor with distilled water. ICP was used to measure leaching of the TiO$_2$ samples, which were collected every 1800 s for 24 h. No leaching was observed. The difference in loaded catalyst mass was measured by weighing the fiberglass sheet pre- and post-treatment. A decrease in mass was used as an indicator for catalyst leaching. No difference in mass was observed.

### 5.2.2 Rate Expression

Numerous researchers working on heterogeneous photocatalysis reported degradations of model compounds that follow Langmuir–Hinshelwood type kinetics. The intrinsic reaction rate, $r_{rxn}$, could be defined as

$$
r_{rxn} = \frac{V_L}{V_R} \left[ -\frac{dC_b}{dt} \right] = \frac{k_rK C_s}{1+K C_s} \tag{5.1}
$$

where $V_R$ and $V_L$ are volume of the reactor and liquid volume treated, respectively; $dC_b/dt$ is the experimentally measured rate (mol/m$^3$/s), $k_r$ and $K$ are the reaction rate constant (mol/m$^3$/s) and adsorption–desorption equilibrium constant (m$^3$/mol), respectively; and $C_s$ is the reactant concentration on the catalyst surface (mol/m$^3$) in equilibrium with the bulk concentration. It is difficult to measure the precise value of the catalyst surface area effectively participating in photocatalytic reactions. In slurry system, it is not possible to enumerate the active surface area due to lack of measured data on the light penetration depth, average catalyst particle size (and its distribution) due to particle agglomeration, as well as fluid hydrodynamics inside the reactor. In immobilized (fixed) system, it is also not easy to ascertain the active catalyst surface area because of lack of detailed information on the structure, morphology, porosity (pore distributions), and catalyst layer thickness. Hence, it is not sensible to calculate reaction rates based on the catalyst surface area for both slurry as well as immobilized systems.
5.2.3 Determination of Intrinsic Reaction Rate Constant

When photocatalyst is immobilized on a support, it is apparent that mixing of fluid within the reactor will be an important factor as transport of pollutant from the bulk solution to the catalyst surface will dictate the overall reaction rate. Hence, to find out the intrinsic kinetic rates, it is essential to undertake the effect of mass transfer resistance. In order to determine the reaction rate from equation 1 one needs to know the concentration of the pollutant on the surface of the catalyst \( C_s \). There are two ways, one can determine reaction rate constant from equation 2. When the initial concentration of the pollutant is high \( (KC_s \gg 1) \), the Langmuir-type kinetic rate expression of equation 1 turn into a zero-order rate expression, and the overall rate would be independent of external mass transfer resistance. Figure 5.4 and 8a show experimental results for concentration with time for five different initial concentration values of DCF. The figures clearly show that the \( C-t \) plot follow a linear relationship particularly for high initial concentration of DCF \( ([DCF]_o = 0.154 \text{mM}) \) and thin catalyst layer thickness (negligible internal mass-transfer resistance). The true kinetic rate \( (k_r) \) can be determined from the slope of the linear concentration versus time plot and is obtained as \( 6.163 \times 10^{-5} \text{mM/s} \).

![Figure 5.4 Effect of initial concentration of DCF. Experimental conditions: } Q = 1.15 \times 10^{-5} \text{ m}^3/\text{s}, \ V_L = 4 \times 10^{-4} \text{ m}^3, \ I = 45 \text{ W/m}^2, \ \text{pH = neutral, } T = 298 \text{ K, O}_2 \text{ saturated}](image)

Figure 5.4 Effect of initial concentration of DCF. Experimental conditions: \( Q = 1.15 \times 10^{-5} \text{ m}^3/\text{s}, \ V_L = 4 \times 10^{-4} \text{ m}^3, \ I = 45 \text{ W/m}^2, \ \text{pH = neutral, } T = 298 \text{ K, O}_2 \text{ saturated} \)
Another way to determine the reaction rate constant is to analyze the results when the initial concentration of the pollutant is very low ($K_{Cs} \ll 1$). In this case, the kinetic rate expression of equation 1 becomes a first-order rate expression, and the overall rate would indeed depend on mass transfer limitation (Figure 5.5b). For estimation of the true intrinsic kinetic parameters, it would be required to account for mass-transfer resistance. At steady state, the conversion rate follows

$$r_o = \left[ \frac{V_L}{V_R} \right] \left[ -\frac{dC_b}{dt} \right] = k_o C_b = k_{m,ext} \kappa (C_b \pm C_s) = \frac{k_o K_{Cs}}{1 + K_{Cs}}$$  \hspace{1cm} (5.2)$$

where $k_o$ ($s^{-1}$) is the first-order observed rate constant, $k_m$ (m/s) is the mass-transfer rate, and $\kappa$ (m$^{-1}$) is the specific surface area ($\equiv A/V_R$). When $K_{Cs} \ll 1$, from equation 4.2 have

$$r_o = k_{m,ext} \kappa (C_b \pm C_s) = k_r K_{Cs} = k_r' C_s$$  \hspace{1cm} (5.3)$$
where $k_r'$ is the pseudo-first-order reaction rate constant ($s^{-1}$). Solving for the unknown concentration, $C_s$, as

$$C_s = \left[ \frac{k_{m,ext}}{k_{m,ext} + k_r'} \right] C_b$$  \hspace{1cm} (5.4)

the rate expressions results can be obtained as

$$r_o = k_o C_b = \left[ \frac{k_r' k_{m,ext}}{k_{m,ext} + k_r'} \right] C_b = \left[ \frac{1}{k_{r'} + \frac{1}{k_{m,ext}}} \right]$$  \hspace{1cm} (5.5)

Accordingly, the various rates (observed, kinetic, and mass-transfer rates) are related as

$$\frac{1}{k_o} = \frac{1}{k_r'} + \frac{1}{k_{m,ext}} = \frac{1}{k_{r'} k} + \frac{1}{k_{m,ext} k}$$  \hspace{1cm} (5.6)

Besides the external mass-transfer resistance, when a catalyst is immobilized on a surface, the role of internal mass-transfer resistance becomes important, particularly for a thick layered film. The internal mass-transfer resistance results from the diffusion of pollutant molecules within the porous catalyst layers. When catalyst is present as a layered film, the whole catalyst surface is not reachable to the reactant because the reactant must diffuse through the layers of the catalyst film. In that case, the connection among the various rates, observed degradation rate, the external and internal mass-transfer rates, and the intrinsic kinetic reaction rate is given by the following relation:

$$\frac{1}{k_o} = \frac{1}{k_r'} + \frac{1}{k_{m,int}} + \frac{1}{k_{m,ext}}$$  \hspace{1cm} (5.7)

Therefore, to estimate intrinsic kinetic parameters, it is essential to find out the mass-transfer rates.

### 5.2.4 Effect of External Mass Transfer

When external mass transfer resistance exists, the observed reaction rate depends on fluid mixing intensity or the circulation flow rate, particularly if the circulation flow rate is low. External mass transfer resistance can be decreased to a minimum by enhancing the mixing intensity of the fluid elements through stirring or increasing the circulation flow rate (Reynolds number) of the reaction.
fluid. In this study, the fluid mixing was enhanced through tangential introduction of fluids through two inlets oriented in different directions. The existence of external mass-transport limitation can be determined from experimental studies of photocatalytic degradation rate of DCF at different circulation flow rates. Figure 5.6 shows existence of external mass-transfer limitation when the catalyst is fixed (immobilized) on a surface. It is apparent that $1.15 \times 10^{-5}\text{m}^3/\text{s}$ is the optimal circulation flow rate for our experimental system where external mass transfer limitation is at a minimum although even at this optimal flow rate, the mass-transfer limitation still exists.

Figure 5.6 Effect of flow rate. Experimental conditions: $V_L = 4 \times 10^{-4}\text{m}^3$, $I = 45\text{ W/m}^2$, $[\text{DCF}]_o = 25\text{ ppm}$, pH = neutral, $T = 298\text{ K}$, $\text{O}_2$ saturated

5.2.5 Determination of the External Mass Transfer

Quantitative value of external mass transfer resistance depends on hydrodynamics or dynamics of fluids inside the reactor. Hence, external mass transfer rate depends on reactor geometry, fluid flow rate and fluid properties. The external mass-transfer coefficient, $k_{m,ext}$, was determined experimentally for this modified reactor (in which two inlets oriented in opposite direction) using procedure similar to described in our earlier studies. The inside surface of the bottom glass plate
was coated with sparingly water-soluble benzoic acid, and the dissolution rate) at different flow rates at 303 K was experimentally measured using a UV-Spectrophotometer.

The dissolution rate of benzoic acid can be described by equation 4.8 When the experimental results are plotted as a function of Reynolds number (Re), the best fit can be expressed as given by equation 4.9.

\[
V_L \frac{dC_b}{dt} = -k_{m,ext} A (C_b \pm C_s)
\]  

(5.8)

\[
k_{m,ext} (m/s) = 9.5 \times 10^{-7} Re^{0.77}
\]  

(5.9)

In the expression for Reynolds number, the gap size between the two plates were used as the characteristic length and the inlet velocity (volumetric flow rate divided by the cross-sectional area of the two inlets) was used as the characteristic velocity. It is apparent that at high circulation flow rate, the external mass-transfer resistance will be least. However, physical limitation of the reactor used in this study would limit the use of a very high circulation flow rate due to bubble formation, leading to large experimental error. This is noticeable in the experimental results shown Figure 5.6 at high flow rate. Hence, all subsequent experiments were performed at a circulation flow rate of \(1.15 \times 10^{-5} \text{ m}^3/\text{s}\), which is equivalent to a Reynolds number of 208.

The true rate constant \(k_r\) calculated from Figure 5.5a (when \(KC_s \gg 1\)) is \(6.163 \times 10^{-5} \text{ mM/s}\), and the observed pseudo first-order rate constant, \(k'_r (\equiv k_rK)\), obtained from Figure 5.5b (when \(KC_s \ll 1\)) is \(1.424 \times 10^{-3} \text{ mM/s}\). Using the value of \(k_{m,ext} (8.06 \times 10^{-5} \text{ m/s})\) calculated using equation 4.9 for value for \(Re = 208\), and \(\kappa (\equiv A/V_R)\) as \(59.7 \text{ m}^{-1}\), the value of \(K\) from equation 4.6 can be determined as \(33.98 \text{ mM}^{-1}\). Martinez et al. \(32\) reported a value of \(38.01 \text{ mM}^{-1}\) for \(K\). For the above calculation, we assumed the effect of internal mass transfer was negligible. This is because all of our experiments were conducted at a low catalyst loading of \(50 \times 10^{-3} \text{ kg/m}^2\). The internal mass transfer is an intrinsic property of the catalyst film layers, which depends on the nature of the catalyst, coating techniques, pre- and post-treatment of catalyst films, and so forth.
5.2.6 Effect of Internal Mass Transfer

The influence of the internal mass transfer resistance on the observed photocatalytic reaction rate can be determined by the magnitude of the Thiele modulus. When the catalyst film is thin porous slab, for the first-order reaction, the Thiele modulus (Φ_H) is given by

\[ \Phi_H = H \frac{k_r'}{D_e} \]  

(5.10)

where \( H \) is the thickness of the catalyst film, \( k_r' \) is the first-order kinetic rate constant, and \( D_e \) is the effective diffusivity of the pollutant within the catalyst film. An effective diffusivity value of \( 1 \times 10^{-10} \text{ m}^2/\text{s} \) for benzoic acid was experimentally determined previously for the same system.\(^{27}\) Using the rate constant (\( k_r \)) value obtained earlier as \( 6.163 \times 10^{-5} \text{ mM/s} \), \( K \) value as 33.98 \( \text{mM}^{-1} \) and a film thickness ranging between 2 and 5 μm, the Thiele modulus value found was between 0.0091 and 0.0229, which is significantly less than 1. Therefore, the internal mass transfer limitation is insignificant, as assumed earlier.

5.2.7 Effect of pH

If the photodegradation takes place on a catalyst surface, then pH plays a major role in heterogeneous photocatalysis. The point of zero charge (pzc) for \( \text{TiO}_2 \) lies between 5.5 and 6.8 \(^{22}\) \(^{30}\) making the catalyst surface positively charged at more acidic pH values (pH < 5.5) and negatively charged at pH values above 6.5. As a result, the adsorption–desorption property at the catalyst’s surface is influenced by the pH, which in turn has a direct implication on the photo degradation rate of DCF

\[ \text{Ti}^{IV} + \text{OH}^- + \text{OH}^- \rightarrow \text{Ti}^{IV} + \text{O}^- + \text{H}_2\text{O} \]

\[ \text{Ti}^{IV} + \text{OH}^- + \text{H}^+ \rightarrow \text{Ti}^{IV} + \text{OH}_2^- \]

Our experiments were limited to a pH range of 2 to 9 due to the specifications of the HPLC column used to analyze the samples. In addition, at pH below 2.8, DCF has very low solubility (\( pK_a = 4.15 \)), \(^{31}\)^{32} and hence, the degradation of DCF was evaluated at 3 different pH values (5.1, 7.2, and 8.4). When the experiments were performed at neutral pH value, pH drops from 7.2 to 6.5
during a 1800 s reaction time, and the color of the solution changed from clear to light brown. The pH drop indicates formation of acidic intermediate compounds and dechlorination of DCF during the reaction. Leonidas et al.\textsuperscript{12} and Perez-Esterda et al.\textsuperscript{19} studied possible intermediates formation by Photo-Fenton and solar driven photocatalysis respectively for DCF. In addition, a study performed by Mantzavinos et al.\textsuperscript{33} noted that acidic intermediates seem to be more difficult compounds to mineralize. Photodegradation rate of DCF at acidic solutions were observed to be high compared to neutral pH and basic solution, indicating that pH has a significant effect. At similar experimental conditions, the percent degradation rate for 1800 s reaction time were found to be 89, 75, and 47 at acidic, basic, and neutral pH levels, respectively. Similar results were obtained in photolysis of DCF.\textsuperscript{34} Table 5-2 summarizes the percent degradation values as well as observed reaction rate constants at three different pH levels when experiments were conducted at $Q = 1.15 \times 10^{-5} \text{ m}^3/\text{s}$, $V_L = 4 \times 10^{-4} \text{ m}^3$, $I = 45 \text{ W/m}^2$, $[\text{DCF}]_0 = 25 \text{ ppm}$, $T = 298 \text{ K}$, and $\text{O}_2$ saturated.

<table>
<thead>
<tr>
<th>pH</th>
<th>$k_o \times 10^3$, s$^{-1}$</th>
<th>% degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>1.15</td>
<td>89</td>
</tr>
<tr>
<td>7.2</td>
<td>0.54</td>
<td>75</td>
</tr>
<tr>
<td>8.4</td>
<td>0.32</td>
<td>47</td>
</tr>
</tbody>
</table>

Although the best pH for degradation of DCF appears to be 5.1, however, photocatalytic treatment of DCF degradation at neutral pH level provides advantageous for the environment and one can avoid the need for pH adjustment before discharge into the environment, or to biological treatment if necessary. Therefore, when the reasonable degradation at the neutral pH is considered, all the experiments were carried out at the neutral pH.
5.2.8 Effect of Light Intensity

To the best of our knowledge, there is no evidence of a true kinetic study of photocatalytic degradation of DCF with respect to the light intensity. Therefore, a thorough investigation of the rates corresponding to a varied radiant flux in the range of 14–45 W/m² was investigated. Figure 5.7 shows these results. The kinetic constant can be related to the light intensity according to the following expression:

\[ k_r = \alpha(I)^{\beta} \]  

(4.11)

Figure 5.7 Effect of light intensity on degradation rate of DCF. Experimental conditions: \( Q = 1.15 \times 10^{-5} \text{ m}^3/\text{s}, V_L = 4 \times 10^{-4} \text{ m}^3, [\text{DCF}]_0 = 25 \text{ ppm}, T = 298 \text{ K}, \text{O}_2 \) saturated

For our experiments, a value of 0.53 was found for \( \beta \) and 0.9243 for \( \alpha \). Previous studies on semiconductor photocatalysis of organic compounds with respect to light intensity indicated that the reaction rate increases with the square root of light intensity at high intensity level. On the other hand, at low levels of illumination, degradation rate was observed to be first-order with
respect to intensity. In this study, however, a behavior close to a square root relationship was observed.

5.2.9 Effect of Photocatalysts

The effect of visible light using dye-sensitized TiO$_2$ and UV light using Degussa P25 TiO$_2$ and a proprietary doped-TiO$_2$ catalyst, was studied at the optimum conditions (TiO$_2$ on fiberglass sheet 50 $\times$ 10$^{-3}$ kg/m$^2$, $Q = 1.15 \times 10^{-5}$ m$^3$/s, [DCF]$_o$ = 25 ppm, $T = 298$ K, O$_2$ saturated). As shown in Figure 5.8, a very small (1.5–2.2%) decrease in the concentration of DCF was observed in the absence of either the light source or the photocatalyst. However, a considerable degradation rate was observed with the use of an illuminated photocatalyst, the extents differing with the type of photocatalyst employed. The pH of the solution decreased from 7.2 to 6.5 during the course of 1800 s reaction. This can be attributed to dechlorination and to the formation of mineral acids during the photoreaction. Figure 5.8 shows dye-sensitized TiO$_2$ is the most efficient photocatalyst with a maximum degradation of DCF as compared with the other catalysts used under similar experimental conditions adjusting the light intensity for UV and visible light at same wattage, flow rate, and catalyst loading. Furthermore, dye-sensitized TiO$_2$ makes use of visible light that is available in significant fraction of the solar spectrum—the most abundant and economic light source possible—and can, thus, be easily exploited. This benefit is offset by the band gap limitation of TiO$_2$ with a lower energy light source such as visible light. However, considering the dye-sensitization technique, an electron is easily injected into the conduction band of TiO$_2$ from the excited dye without having to overcome its considerable band gap of 3.2 eV.
Figure 5.8 Effect of photocatalyst on degradation rate of DCF. Experimental conditions: $Q = 1.15 \times 10^{-5}$ m$^3$/s, $V_L = 4 \times 10^{-4}$ m$^3$, $I = 45$ W/m$^2$, $[DCF]_0 = 25$ ppm, $T = 298$ K, O$_2$ saturated

5.3 Conclusions

An in-depth analysis on the photodegradation kinetics of diclofenac (DCF) was performed. The following conclusions can be made: (a) The modified swirl flow monolithic type reactor used in this study provides better residence time distribution of fluid by reducing dead zone and fluid bypass, (b) the reactor is unique for extracting true kinetic parameters in photocatalysis, as a function of catalyst layer thickness, light intensity, and pH, (c) fiberglass sheets were found to be the better catalyst support compared to glass plates, as it provides more surface area with an optimal catalyst loading of $50 \times 10^{-3}$ kg/m$^2$, (d) external mass transfer resistance exists even for the modified reactor configuration; however, true kinetic rates can be calculated from the observed reaction rates after correcting for mass transfer resistance, (e) adsorption equilibrium rate constant for DCF was found to be 33.98 mM$^{-1}$, (f) optimum pH, catalyst layer thickness, effect internal mass transfer resistance, and dependence of light intensity on reaction rate were determined experimentally, and (g) dye-sensitized TiO$_2$ was proven to be a more efficient by facilitating considerably high DCF degradation rates at visible wavelength compared to Degussa P25 and
doped TiO\textsubscript{2} photocatalyst. The initial concentration of DCF significantly influences the photodegradation kinetics. Within the experimental concentration range, pseudo-first order kinetics was observed for concentrations below 88 mmol/m\textsuperscript{3} and zero-order for concentration above 120 mmol/m\textsuperscript{3}. The photocatalytic rates reported can be described by the following equation:

\[ r = k_m k (C_b - C_s) = \frac{k_r(I)KC_s}{1 + KC_s} \]

where,

\[ k_{m,ext} \left( \frac{m}{s} \right) = 9.5 \times 10^{-7} Re^{0.77} \quad \text{for } Re \leq 208 \]

\[ k_r (I) = \alpha (I)^\beta \quad \text{for } 14 \leq I (W/m^2) \leq 45 \quad \text{and } \alpha=0.9243, \beta=0.53 \]

\[ W_{cat} = 50 \times 10^{-3} \text{Kg/m}^2 \]

\[ k \left( = \frac{A}{V_R} \right) = 59.7 \text{m}^{-1} \quad \text{for } K = 33.98 mM^{-1} \]
5.4 Nomenclature

A  Surface area of benzoic acid film
Cb  Concentration in the bulk
Cs  Concentration at the catalyst surface
DCF  Diclofenac, a model compound for this kinetic study
De  effective diffusivity of the pollutant within the catalyst film
EC50  Median Effective Concentration (required to induce a 50% effect)
EDCs  Endocrine Disrupting Compounds
e-  Electron
h+  Hole
H2Oad  Adsorbed water molecule
HPLC  High pressure liquid chromatography
I  Light intensity, mWcm^-2
ITC  Isothermal Titration Calorimetry
K  Adsorption equilibrium constant, mM^-1
kr  True kinetic reaction rate constants, ms^-1
ko  Observed reaction rate constant, ms^-1
km,ext  External mass transfer coefficient, ms^-1
km,int  Internal mass transfer coefficient, ms^-1
k  Effective diffusivity constant, (=A/V_R)
V_R  Volume of reactor (m^3)
W_cat  Weight of catalyst on the surface of a support (Kg/m^2)
LogK_ow  K_ow = concentration in octanol phase /concentration in aqueous phase
OHad  Adsorbed hydroxide radical
pzc  point zero charge of a catalyst
PCPs Pharmaceutical and personal care products
EDCs Endocrine disruptive compounds
Re Reynolds number

Greek Letters

<table>
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<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( \lambda )</td>
<td>Wavelength of incident light, nm</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>A constant</td>
</tr>
<tr>
<td>( \beta )</td>
<td>A constant</td>
</tr>
<tr>
<td>( \phi_H )</td>
<td>Thiele Modulus</td>
</tr>
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</table>
5.5 References

Chapter 6


6.1 Introduction

Water pollution is an ever-increasing problem in a world that faces declining water and energy sources. Population growth, industrialization, urbanization and shifting climate patterns are increasing the demand for potable water, which is becoming increasingly scarce.\(^3\) Anthropocentric factors are also contributing to pollution in freshwater sources, of which pharmaceuticals and personal care products (PCPs) make up a substantial portion. One of the most commonly detected and heavily used pharmaceuticals is Diclofenac [2-(2,6-dichloranilino) phenylacetic acid] a non-steroidal anti-inflammatory drug (NSAID).\(^{12,116,42}\) While DCF is found at low concentrations (ng/L to μg/L), it possesses a bio-accumulative risk due to its steady input into recipient waters.\(^{116,42}\) The compound has been found in concentrations greater than 1 μg/L and is readily metabolized in fish.\(^{116}\) It has toxic effects on cell function of aquatic animals and is known to be the cause of vulture population decline in Western Asia.\(^{11,9,12,13}\) DCF has recently been added to the Water Framework Directive (WFD) watch list of priority substances under the European Union as of 2013.\(^{117}\) The mean measured concentrations in municipal water vary between 0.11 and 2.3 μg/L depending on the municipality and country. The yearly consumption of DCF is between 195 and 940 mg per inhabitant in different countries.\(^ {42}\) DCF also has the eighth highest average mass load in the secondary effluent of municipal wastewater treatment plants out of 73 reviewed pharmaceuticals.\(^{42}\)

Conventional wastewater treatment methods require high-energy inputs and the use of chemicals such as chlorine, hydrogen peroxide and ozone. These methods are costly or harmful due to formation of harmful by-products, while being ineffective at eliminating a multitude of organic and inorganic compounds.\(^3\)\(^,\)\(^{118}\) DCF elimination is not achieved using conventional wastewater treatment methods and the need for effective tertiary treatment is required. Advanced Oxidation Processes (AOPs) have emerged to address this issue while complying with environmental regulations. Among the current AOPs, heterogeneous photocatalytic oxidation, in which light energy is used to excite a semiconductor material producing electron/hole pair that eventually
involves in the detoxification of pollutants, has attracted a great deal of scholarly attention and is a promising solution for the treatment of industrial wastewater. The commonly used photocatalyst is titanium dioxide (TiO₂), a nontoxic, photo-chemically stable and reusable compound. Catalyst photo-activation can be achieved with a UV-A light source. One of the challenges in utilizing this catalyst is the requirement for an artificial UV lamp due to the large band-gap of TiO₂. According to Planck’s law (E = hc /λ), the use of higher wavelength visible light (λ > 400 nm) compared to UV light (100 < λ (nm) < 400), does not grant sufficient energy to overcome the TiO₂ band-gap of 3.2 eV. Hence, sufficient e-/h+ pair formation does not occur.

The high energy requirement for TiO₂ poses limitations on its usage. One concern is when the process has to be scaled-up since the installation and operation of a UV chamber may not always be economically viable. However, TiO₂ itself can be manipulated to utilize a higher range of the solar spectrum by modifying its surface with noble or transition metals, non-metals, and dye sensitization. In recent year, photocatalysis has been widely studied using chemically modified doped nanoparticles as new photocatalytic materials for visible light activation of the catalyst. Although doping allows catalyst activation in the visible range, it doesn’t solve the enigma of low efficiency of the process that occurs due to recombination of generated e-/h+ pair. Dye sensitization, which has been widely studied in the development of solar cell technology, is a simpler method for activation photocatalyst, but has been hardly been studied for photocatalytic water treatment. A dye is chemically adsorbed onto the semiconductor surface and the chemisorbed dye molecules play the role of spectral sensitizer which upon excitation with visible light either inject an electron into the conduction band (anodic sensitization) or a hole into the valence band (cathodic sensitization) of the semiconductor depending on the energy levels, band position, ground state redox potential and the presence of surface anchoring groups in the dye molecule. Hence, dye sensitization addresses both the aforesaid challenges as catalyst can be activated with full solar spectrum and either electron or hole is created not both at the same time, thus the question of e-/h+ pair recombination doesn’t even arise. In anodic sensitization, the injected electron travels through the semiconductor and participates in redox reaction. The electron either on reaction with dissolved O₂ in water forms super oxide (O₂⁻), which oxidizes toxic pollutants. The oxidized dye is subsequently reduced to ground state by an electron donor. Dye sensitization of TiO₂ is one of the
most cost-effective techniques and it has been applied to a multitude of water pollutant detoxifications. One way of activating TiO$_2$ catalyst under a visible light source is by an electron donor, such as through the addition of a dye (such as Rhodamine B, Methylene blue, Safranine O, Eosin Y). Recent studies on dye-sensitized phenol degradation and H$_2$ production with an artificial dye (Eosin Y), a co-catalyst (Pt) and an electron donor, it was possible to achieve quantum efficiency greater than 12%. It was observed that use of the co-catalyst allows higher interfacial electron flow from semiconductor surface to metal/semiconductor junction due to reduced Schottky barrier height and about 93% degradation of phenol was achieved within 90mins using Eosin Y-TiO$_2$/Pt photocatalyst at optimum conditions. In both studies it was observed that the presence of minute amount of co-catalyst and electron donor is necessary but otherwise it has a negative effect. Hence, dye-sensitization offers a transformative technology addressing all the existing challenges.

In a photocatalytic process, the TiO$_2$ catalyst is utilized either as a suspended or as an immobilized form. Studies indicate that when TiO$_2$ is immobilized onto a surface it is not as effective due to mass transfer limitation. However, Hashim et al. 2014 determined that TiO$_2$ is just as effective in its immobilized form when it’s applied onto a suitable support that would compensate for its lack of surface area. The advantage of immobilizing the catalyst is the elimination of the post processing treatment, thereby saving time and costs. Different substrates have been used to immobilize the photocatalyst in other studies. These include, mesoporous clays, nanostructures (nanofibers, nanowires or nanorods) and membranes among others. In this study fibreglass sheets are used to immobilize the TiO$_2$ catalyst due to its high surface area.

This study seeks to find an innovative solution for the activation of TiO$_2$ in DCF degradation under the visible light using Eosin Y dye. The originality of this study lies in (a) dye-sensitized photocatalysis - the modification of TiO$_2$ using Eosin-Y dye as an electron donor. To the best of our knowledge there is no studies using TiO$_2$ in the visible range of the solar spectrum to degrade DCF, (b) the incorporation of a central composite design (CCD) to optimize the integrated factors, specifically dye concentration, (c) the interaction of all the operating parameters, and (d) a cost estimation of the present process.
6.2 Reaction Mechanism and Kinetic Rate Expression

In the dye sensitization process, the dye acts as an electron donor, making its activation an essential part of the process. Once dye activation is achieved, the electron ejected from the excited dye is transferred to the conduction band (CB) of TiO₂. The subsequent interfacial electron transfer and the oxidation-reduction steps are as follows:¹³⁰ ⁷⁵ ⁷⁹ ³⁹

\[
\text{TiO}_2 - (\text{Dye})_s^{hv\leq520\text{nm}} \rightarrow \text{TiO}_2 - (\text{Dye}^*)_s
\]

\[
\text{TiO}_2 - (\text{Dye})_s \rightarrow \text{TiO}_2 - (\text{Dye} + e_{CB^-})_s
\]

\[
\text{TiO}_2 - (\text{Dye} + e_{CB^-})_s + \text{organic pollutant} \rightarrow \text{TiO}_2 - (\text{Dye} + e_{CB^-})_s + \text{organic pollutant}^*
\]

\[
\text{TiO}_2 - (\text{Dye} + e_{CB^-})_s + \text{O}_2 \rightarrow \text{TiO}_2 - (\text{Dye})_s + \text{O}_2^-
\]

\[
\text{O}_2^- + H^+ \rightarrow \text{HO}_2^- \rightarrow \text{OH}^-
\]

\[
\text{OH}^- + \text{organic pollutant} \rightarrow \text{intermediates} + \text{CO}_2
\]

\[
\text{OH}^- + \text{intermediates} \rightarrow \text{H}_2\text{O} + \text{CO}_2
\]

6.3 Experimental Design

A central composite design (CCD) with four factors was selected using the software, Design-Expert 9.0.5. Each numeric factor was set to five levels: plus and minus alpha (axial points), plus and minus 1 (factorial points) and the center point. A rotatable design was employed with eight center points and two blocks, with a total of 30 experimental runs. The four selected factors were; (a) light intensity (mW/cm²), (b) DCF concentration (mg/L), (c) dye concentration (mg/L), and (4) TiO₂ loading (mg/cm²). The factors were selected based on a previous study dealing with photocatalytic degradation of DCF, and varied by randomly generated design matrix as shown in Table 6-1.³
The percentage degradation of DCF after 5 minute reaction time was taken as the response. The effect of the selected factors on the response was tested using CCD and response surface methodology (RSM). All kinetic experiments were conducted in the same conditions presented in the design matrix. The temperature, pH of the solutions, and oxygen concentrations were kept constant throughout the experiments to minimize variations due to environmental factors.
Table 6-1 CCD summary with values in coded and un-coded forms

<table>
<thead>
<tr>
<th>Factors</th>
<th>-α</th>
<th>Low (-1)</th>
<th>Middle (0)</th>
<th>High (+1)</th>
<th>+ α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity (mW/cm²)</td>
<td>0</td>
<td>250</td>
<td>500</td>
<td>750</td>
<td>1000</td>
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<tr>
<td>DCF (mg/L)</td>
<td>20</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>Dye (mg/L)</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>TiO₂ (mg/cm²)</td>
<td>0</td>
<td>37.5</td>
<td>75</td>
<td>112.5</td>
<td>150</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>A: Intensity (mW/cm²)</th>
<th>B: [DCF] (mg/L)</th>
<th>C: [Dye] (mg/L)</th>
<th>D: [TiO₂] (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
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<td>-1</td>
<td>1</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>4</td>
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<td>-1</td>
<td>1</td>
<td>-1</td>
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<td>0</td>
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<tr>
<td>24</td>
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<td>27</td>
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<td>28</td>
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<td>0</td>
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<td>30</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</table>

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6.4 Results and Discussion

6.4.1 Experimental data sets and response

Model fit summary for photocatalytic degradation of DCF is listed in Table 6-2. A Logit transformation was applied to the response due to the high ratio of the maximum to minimum response. The fit summary table suggests a quadratic model, whereas the cubic model is aliased. To determine the appropriateness of the quadratic model as a fit for the experimental data, a detailed analysis of variance (ANOVA) was performed. The results are discussed below.

Table 6-2 Model fit summary for photocatalytic degradation of DCF

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob &gt; F</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>2.88</td>
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<td>2.88</td>
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<td></td>
</tr>
<tr>
<td>Block</td>
<td>4.81</td>
<td>1</td>
<td>4.81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear</td>
<td>52.97</td>
<td>4</td>
<td>13.24</td>
<td>14.18</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>2FI</td>
<td>3.50</td>
<td>6</td>
<td>0.58</td>
<td>0.56</td>
<td>0.7599</td>
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</tr>
<tr>
<td>Quadratic</td>
<td>15.09</td>
<td>4</td>
<td>3.77</td>
<td>13.79</td>
<td>&lt; 0.0001</td>
<td>Suggested</td>
</tr>
<tr>
<td>Cubic</td>
<td>3.59</td>
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<td>0.45</td>
<td>11.49</td>
<td>0.0040</td>
<td>Aliased</td>
</tr>
<tr>
<td>Residual</td>
<td>0.23</td>
<td>6</td>
<td>0.04</td>
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<tr>
<td>Total</td>
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<td>30</td>
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</table>

Lack of Fit Tests

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<tr>
<th>Source</th>
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<th>Mean Square</th>
<th>F Value</th>
<th>Prob &gt; F</th>
<th>Remarks</th>
</tr>
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<tr>
<td>Linear</td>
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<td>14</td>
<td>1.34</td>
<td>55.89</td>
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<td>Quadratic</td>
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<td>10</td>
<td>0.37</td>
<td>15.52</td>
<td>0.0089</td>
<td>Suggested</td>
</tr>
<tr>
<td>Cubic</td>
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<td>2</td>
<td>0.07</td>
<td>2.88</td>
<td>0.1681</td>
<td>Aliased</td>
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<td>Pure Error</td>
<td>0.10</td>
<td>4</td>
<td>0.02</td>
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</table>

Model Summary Statistics

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<thead>
<tr>
<th>Source</th>
<th>Std. Dev.</th>
<th>R²</th>
<th>Adj. R²</th>
<th>Pre. R²</th>
<th>PRESS</th>
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</thead>
<tbody>
<tr>
<td>Linear</td>
<td>0.97</td>
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<td>0.57</td>
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<td>2FI</td>
<td>1.03</td>
<td>0.75</td>
<td>0.61</td>
<td>0.42</td>
<td>43.71</td>
</tr>
<tr>
<td>Quadratic</td>
<td>0.52</td>
<td>0.95</td>
<td>0.90</td>
<td>0.65</td>
<td>26.60</td>
</tr>
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</table>
6.4.2 ANOVA

The ANOVA for response surface reduced cubic model of DCF photocatalytic degradation is shown in Table 6-3. An ANOVA fitting the quadratic model to the experimental data revealed a significant lack of fit (LOF). Other models also failed to fit the experimental data. The best fit for the experimental data is a cubic model, which was determined via backward selection, outlined in Table 6-3, where the aliased terms were removed by backward elimination. An F-value of 93.98 was determined, implying that the model effectively captures the variability of the experimental data. There is only 0.01% chance that an F-value this large could occur due to noise. Additionally, the LOF F-value for the model is not significant relative to pure error. A non-significant LOF indicates that the cubic model is the best fit.

Values of “Prob>F” less than 0.05 indicate that the model terms are significant. Table 6-3 shows light intensity, dye concentration, and TiO$_2$ loading are the significant terms, whereas the concentration of the pollutant (DCF) is not significant. The interactions between these parameters are also shown in Table 6-3.

Table 6-3 ANOVA for response surface reduced cubic model of DCF photocatalytic degradation
A: Intensity, B: [DCF], C: [Dye], D: [TiO$_2$]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Df</th>
<th>Mean Square</th>
<th>F-Value</th>
<th>Prob &gt; F</th>
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</thead>
<tbody>
<tr>
<td>Block</td>
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<td>4.81</td>
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</tr>
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<td>Model</td>
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<td>4.16</td>
<td>93.98</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>A</td>
<td>8.66</td>
<td>1</td>
<td>8.66</td>
<td>195.52</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>B</td>
<td>0.01</td>
<td>1</td>
<td>0.01</td>
<td>0.20</td>
<td>0.6643</td>
</tr>
<tr>
<td>C</td>
<td>0.56</td>
<td>1</td>
<td>0.56</td>
<td>12.63</td>
<td>0.0052</td>
</tr>
<tr>
<td>D</td>
<td>4.48</td>
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<td>4.48</td>
<td>101.04</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>A2</td>
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<td>7.44</td>
<td>167.96</td>
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</tr>
<tr>
<td>B2</td>
<td>1.33</td>
<td>1</td>
<td>1.33</td>
<td>29.96</td>
<td>0.0003</td>
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<tr>
<td>C2</td>
<td>8.41</td>
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<td>8.41</td>
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<tr>
<td>D2</td>
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<td>3.00</td>
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</tr>
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<td>AB</td>
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<td>0.05</td>
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</tr>
<tr>
<td>AC</td>
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<td>0.73</td>
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<td>AD</td>
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<td>1</td>
<td>0.65</td>
<td>14.76</td>
<td>0.0033</td>
</tr>
</tbody>
</table>
Table 6-4 shows that the regression coefficient of 0.9941 indicates the model fit the data. The predicted $R^2$ value of 0.8658 is in reasonable agreement with the adj-$R^2$ value of 0.9835. The signal to noise ratio for this model is 45.178, which is well above the ratio limit of 4. This was measured using Adeq Precision.

Table 6-4 Regression analysis coefficients and model equation

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std. Dev.</td>
<td>0.21</td>
</tr>
<tr>
<td>Mean</td>
<td>0.31</td>
</tr>
<tr>
<td>C.V.</td>
<td>67.95</td>
</tr>
<tr>
<td>PRESS</td>
<td>10.12</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99</td>
</tr>
<tr>
<td>Adj. $R^2$</td>
<td>0.98</td>
</tr>
<tr>
<td>Pre. $R^2$</td>
<td>0.87</td>
</tr>
<tr>
<td>Adeq. Precision</td>
<td>45.18</td>
</tr>
</tbody>
</table>

Equation 1 shows the predicted model equation. This model equation can be used to predict given levels of each factor within the experimental design limits.
\[ \text{Logit(\% degradation)} = \ln \left[ \frac{\% \text{ degradation} + 2.72}{52.33 - \% \text{ degradation}} \right] \]

\[
= -15 + 0.022 \times I + 0.457[D\text{CF}] + 1.83[D\text{ye}] + 0.0546[T\text{iO}_2] - 1.9 \times 10^{-5} I^2 - 0.0088[D\text{CF}]^2 - 0.43[D\text{ye}]^2 - 2.35 \times 10^{-4}[T\text{iO}_2]^2 - 1.5 \times I[D\text{CF}] - 4.32 \times 10^{-4}I[D\text{ye}] - 1.03 \times 10^{-4}I[T\text{iO}_2] + 0.0184[D\text{CF}][D\text{ye}] - 2.84 \times 10^{-4}[D\text{CF}][T\text{iO}_2] - 2.52 \times [D\text{ye}][T\text{iO}_2] + 7.1 \times 10^{-9}I^3 + 0.0243 [D\text{ye}]^3 + 2.63 \times 10^{-6}I[D\text{CF}][T\text{iO}_2] + 1.15 \times 10^{-5}I[D\text{ye}][T\text{iO}_2] \] (6.1)

### 6.4.3 Model Diagnosis

#### 6.4.3.1 Effect of one factor on the response

The effects of one factor at a time on the response are discussed as follows: Figure 6.1 shows the effect of intensity on the percent degradation of DCF. The percentage degradation increases from approximately 9 to 40% on increasing the intensity from 250 to 750 mW/cm² at minimum dye concentrations (2 mg/L).

![Figure 6.1 Effect of intensity on the percent degradation of DCF. Experimental condition: Q = 1.15 x 10⁻³ m³/s, V₅₇ = 4 x 10⁻⁴ m³, pH = neutral; T = 298 K, O₂ saturated.](image)

Figure 6.1 Effect of intensity on the percent degradation of DCF. Experimental condition: Q = 1.15 x 10⁻³ m³/s, V₅₇ = 4 x 10⁻⁴ m³, pH = neutral; T = 298 K, O₂ saturated.
Figure 6.2 shows the effect of increasing the dye concentration from 2 to 6 mg/L on the percentage degradation of DCF. At all DCF concentrations, TiO$_2$ loading and light intensity, the increase in the dye concentration increases the percentage degradation about 40%, from which point the rate increase stabilizes. This indicates that the maximum dye concentration is 4 mg/L, after which further addition of dye does not contribute to the increase in DCF degradation.

![Figure 6.2 Effect of increasing dye concentration on the percentage degradation of DCF.](image)

Figure 6.2 Effect of increasing dye concentration on the percentage degradation of DCF. Experimental condition: Q = 1.15 x 10$^{-5}$ m$^3$/s, V$_L$ = 4 x 10$^{-4}$ m$^3$, pH = neutral; T = 298 K, O$_2$ saturated.

Figure 6.3 shows the effect of TiO$_2$ loading on the degradation of DCF. The figure shows that increasing the TiO$_2$ loading does not have a considerable effect on the percentage degradation, remaining constant at a range of 32 to 39%. There are two reasons for TiO$_2$ being selected as a significant parameter by the model. First, photocatalytic treatment requires a catalyst for the process. However, we are limited by the fact that we are using TiO$_2$, which is a catalyst that
requires high-energy inputs such as UV light for its activation. Sakkas et al.\textsuperscript{11} utilized UV and H\textsubscript{2}O\textsubscript{2} for photocatalytic degradation of DCF using TiO\textsubscript{2}, where the most significant factors in degradation were TiO\textsubscript{2} concentration (684 mg/L). The difference between this study and Sakkas et al.\textsuperscript{11} study is that the solar visible portion of light was used in this study. TiO\textsubscript{2} activation is normally prohibited without an external source of activation, which is addressed in this study using dye. Furthermore, TiO\textsubscript{2} interacts with all other factors affecting the response, granting it importance in the degradation of DCF. Hence, three factors were found to be significant, and they are: Intensity (A), dye concentration (C), and TiO\textsubscript{2} concentration (D).

![Figure 6.3 Effect of TiO\textsubscript{2} loading on the percentage degradation of DCF. Experimental condition: Q = 1.15 x 10\textsuperscript{-5} m\textsuperscript{3}/s, V\textsubscript{L} = 4 x 10\textsuperscript{-4} m\textsuperscript{3}, pH = neutral; T = 298 K, O\textsubscript{2} saturated.](image)

6.4.3.2 Effect of factor interactions on the response
The effect of significant factors and their interactions on the response is listed in
Table 6-5. All the interactions at different levels of factors were significant. However, the effects of some interactions did not follow the usual trend. This is discussed below.

Intensity (A) and Dye concentration (C) interactions at low DCF concentration (B-) and TiO$_2$ loading (D-): The percent degradation at the lowest and highest intensity values was equal at both low and high dye concentrations. However, as the intensity increased, the percentage degradation for a high dye concentration was considerably higher than for low dye concentration. Figure 6.4 shows a 3D contour representation of this interaction.

Figure 6.4 Effect of interaction of intensity (A) and dye concentration (C) on DCF degradation. Experimental condition: Q = 1.15 x 10$^{-5}$ m$^3$/s, $V_L$ = 4 x 10$^{-4}$ m$^3$, pH = neutral; T = 298 K, O$_2$ saturated, at [DCF] = 25 ppm, [TiO$_2$] = 37.50 mg/cm$^2$. 

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DCF concentration (B) and TiO$_2$ loading (D) interactions at high intensity (A+) and low dye concentration (C-): The percent degradation was high at a low DCF concentration and low TiO$_2$ loading, but after DCF concentration of 27 mg/L, the response reversed. The percentage degradation was greater at high TiO$_2$ loading than at low TiO$_2$ loading at the minimum dye concentration, the percentage degradation was higher at low TiO$_2$ loading and low DCF concentration. This situation is advantageous because this study seeks to minimize the dye concentration without significantly affecting the percentage degradation. A graphical representation of this interaction is presented in Figure 6.5.

![Interaction Graph](image)

Figure 6.5 Effect of DCF concentration (B) and TiO$_2$ loading (C) on the degradation of DCF. Q = 1.15 x 10$^{-5}$ m$^3$/s, V$_L$ = 4 x 10$^{-4}$ m$^3$, pH = neutral; T = 298 K, O$_2$ saturated

Dye concentration (C) and TiO$_2$ loading (D) interactions at high intensity (A+) and low DCF concentration (B-): At low dye concentrations, the percentage degradation was higher for low TiO$_2$ loading up to a dye concentration of 2.62 mg/L. After this dye concentration, the effect
reversed. This indicates that low TiO$_2$ loading achieves a high degradation even at the lowest dye concentration (2 mg/L). If a photocatalytic process runs with a low loading of TiO$_2$, small additions of dye can significantly increase the degradation of DCF. A graphical representation of this interaction is presented in Figure 6.6.

![Graph showing the interaction of Dye and TiO$_2$ loading on the DCF degradation.](image)

Figure 6.6 Effect of interaction of Dye and TiO$_2$ loading on the DCF degradation. Experimental conditions: $Q = 1.15 \times 10^{-5}$ m$^3$/s, $V_L = 4 \times 10^{-4}$ m$^3$, pH = neutral; $T = 298$ K, O$_2$ saturated
Table 6-5 Effect of interactions between significant Factors on the Response: A = Light intensity, B = [DCF], C = [Dye], D = [TiO$_2$], subscript +, -, and * indicates the high, low, and mid values of the respective factors.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Combinations</th>
<th>Conclusions</th>
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<tbody>
<tr>
<td>AB</td>
<td>C-, D-</td>
<td>% Degradation increase with intensity for both high and low concentration of DCF, the increase being at low [DCF]</td>
</tr>
<tr>
<td>C-, D+</td>
<td>Low Intensity: % degradation is more at low [DCF]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High intensity: % degradation is more at high [DCF]</td>
<td></td>
</tr>
<tr>
<td>C*, D*</td>
<td>The increase of % degradation with intensity is unaltered by [DCF]</td>
<td></td>
</tr>
<tr>
<td>C+, D-</td>
<td>Low Intensity: % degradation is more at high [DCF]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High intensity: % degradation is more at low [DCF], however the changes is marginal for both [DCF]</td>
<td></td>
</tr>
<tr>
<td>C+, D+</td>
<td>At low and high Intensity: % degradation is more at high [DCF], however, the changes are considerable for [DCF]</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>B-, D-</td>
<td>At low and highest values of intensity the % degradation of DCF is the same for both low and high [Dye] respectively. But as we increase the intensity % degradation for high value of dye is considerable higher than of low [dye]</td>
</tr>
<tr>
<td>B-, D+</td>
<td>At low intensity the % degradation for both high and low [dye] is the same. However, as we increase the intensity the % degradation is much higher at high [dye], compare to that low [dye], the changes being considerable</td>
<td></td>
</tr>
<tr>
<td>B*, D*</td>
<td>At all value of intensity the % degradation is significantly higher for high [dye] compare to the low [dye]</td>
<td></td>
</tr>
<tr>
<td>B+, D-</td>
<td>Same as B*, D*</td>
<td></td>
</tr>
<tr>
<td>B+, D+</td>
<td>Same as B*, D*</td>
<td></td>
</tr>
<tr>
<td>AD</td>
<td>B-, C-</td>
<td>At low intensity the % degradation is more for high loading of TiO$_2$, but this effect is reversed on increasing the intensity beyond 500 mW/cm$^2$</td>
</tr>
<tr>
<td>B-, C+</td>
<td>% degradation is higher for higher TiO$_2$ loading at all intensities. The changes being considerable at high and low TiO$_2$ loadings.</td>
<td></td>
</tr>
<tr>
<td>B*, C*</td>
<td>Same as B-, C+</td>
<td></td>
</tr>
<tr>
<td>B+, C-</td>
<td>Same as B-, C+</td>
<td></td>
</tr>
<tr>
<td>B+, C+</td>
<td>Same as B-, C+ , however the rate of % degradation is much higher</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>A-, D-</td>
<td>Lowest value of DCF the % degradation is same irrespective of [Dye], but as we increase the [DCF] the % degradation is higher at high [Dye]</td>
</tr>
<tr>
<td>A-, D+</td>
<td>Same as A-, D-</td>
<td></td>
</tr>
<tr>
<td>A*, D*</td>
<td>The % degradation is significantly higher at high values of dye, irrespective of [DCF], and these changes are considerable</td>
<td></td>
</tr>
<tr>
<td>A+, D-</td>
<td>Same as A-, D-</td>
<td></td>
</tr>
<tr>
<td>A+, D+</td>
<td>Same as A*, D*</td>
<td></td>
</tr>
<tr>
<td>BD</td>
<td>A-, C-</td>
<td>% Degradation is higher for higher TiO$_2$ loading at all [DCF] – the changes are marginal for both loadings of TiO$_2$</td>
</tr>
<tr>
<td>A-, C+</td>
<td>Same as A-, C-</td>
<td></td>
</tr>
<tr>
<td>A*, C*</td>
<td>Same as A-, C-, but the % degradation is more in this case</td>
<td></td>
</tr>
<tr>
<td>A+, C-</td>
<td>At low DCF concentration the % degradation is higher for low TiO$_2$ loading, but after 27 mg/L of DCF, the responses is reversed. That</td>
<td></td>
</tr>
</tbody>
</table>
is the percent degradation is higher for higher TiO2 loading - This is good because the dye concentrations is minimum.

<table>
<thead>
<tr>
<th>A+, C+</th>
<th>% Degradation is higher for higher TiO2 loading at all [DCF] –the changes are considerable for both loadings of TiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD</td>
<td>A-, B-</td>
</tr>
<tr>
<td></td>
<td>% degradation is higher for high TiO2 loading at all [dye] –the changes are marginal in terms different loading of TiO2</td>
</tr>
<tr>
<td></td>
<td>A-, B+</td>
</tr>
<tr>
<td></td>
<td>Same as A-, B-</td>
</tr>
<tr>
<td></td>
<td>A*, B*</td>
</tr>
<tr>
<td></td>
<td>Same as A-, B-, but the changes are considerable in terms of different loadings of TiO2</td>
</tr>
<tr>
<td></td>
<td>A+, B-</td>
</tr>
<tr>
<td></td>
<td>At low [dye] the % degradation is high for low TiO2 loading up to [dye] of 2.62mg/L. After this concentration of dye the effect is reversed.</td>
</tr>
<tr>
<td></td>
<td>A+, B+</td>
</tr>
<tr>
<td></td>
<td>Same as A-, B-, but the changes are considerable in terms of different loadings of TiO2</td>
</tr>
</tbody>
</table>

### 6.4.4 Numerical Optimization

The goals for numerical optimization of the parameters for photocatalytic degradation of DCF were performed to minimize dye concentration while maximizing DCF degradation (the response). The target for intensity ranges between 250 and 750 mW/cm² despite the fact that an intensity level of up to 1000 mW/cm² can be reached in the set-up used in this study. This lower target range was selected to simulate real-life weather condition, i.e. the full intensity of solar light is not realistic due to fluctuating weather. The target for DCF concentration ranges between 25 to 35 mg/L, and the TiO2 loading mass ranges between 37.5 to 112.5 mg/cm². In addition, extreme conditions for the parameters were avoided because when the process is scaled up, the high extreme values would be economically unfeasible. In this case the optimized results produced a response of 39.8%.
Figure 6.7 Goals for numerical optimization of parameters for photocatalytic degradation of DCF

Subsequently, optimization study was done to maintain the dye concentration in a range of 2 to 4 mg/L based on the fact that the response does not have a significant effect beyond this range. Figure 6.8 shows a graphical representation of the optimization. In this case the optimized results produced a response of 49%.

Figure 6.8 A schematic representation of the second goal of optimization
6.4.5 Cost Estimation

In order to understand the financial benefit of the process a cost estimation of the current process was performed. The cost of the process at the optimum conditions (I=750W, TiO$_2$=84.62mg/cm$^2$ of fiberglass, Eosin Y=2mg/L, fiberglass sheet=25cm$^2$) were determined in this study. The prices of the items are listed in Table 6-6. Figure 6.10 shows the significant contribution of each parameter. As it can be seen, TiO$_2$ is the major expense covering 72 percent of the total cost. The second major contributor to the cost is energy provided by the solar simulator, which sums up to 18 percent. The remaining 10 percent is divided equally between dye and fiberglass sheet.

![Pie chart showing the cost contribution of each parameter]

Figure 6.9 Cost of significant parameters at the optimum condition ([DCF] = 29.88mg/L, Intensity = 750W, TiO$_2$= 84.62mg/L, [Dye] = 2mg/L)

Table 6-6 lists the cost of each individual item involved in the process. It costs $0.36 (CAD) to treat one liter of contaminated water in 10 minutes utilizing this system. However, if we consider the renewable and reusable items on the list, Eosin Y dye is the only cost. The photocatalyst TiO$_2$ is reusable as it is immobilized in the system. It can be reused multiple times, and furthermore it can be reactivated if it no longer is efficient. In the same regard, fiberglass sheets are reusable. As
for the energy, it can be replaced with solar light provided by the sun. Therefore, it only costs $0.06 to treat one liter of the contaminated water.

The purpose of using the Eosin Y was to activate TiO$_2$ under visible light. Utilizing the larger portion of the light, which is the visible or the full spectrum of the light source. Therefore, it we can instead utilize the abandon source of energy provided by the sun. Taking that into consideration, the only contributor to the cost is the Eosin Y. Therefore, making this process economical, efficient, and green. According to the principles of green chemistry, it is desirable to utilize processes that minimize energy consumption and minimize the use and generation of hazardous substances.

A cost analysis for optimum dye (2mg/L) concentration determined showed to be the most cost effective while effectively removing DCF from the water. Increasing dye concentration to 4 mg/L (as shown in Figure 6.8) only contributed an extra 10% in terms of DCF concentration that was degraded, with the risk of halogenated compound formation. In short, the cost of 4mg/L of dye would double the cost of the initial process without significantly contributing to DCF degradation and would require additional treatment to remove subsequently formed halogenated, which contributes an extra cost not determined by this study.

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost (CAD)</th>
<th>Reference</th>
<th>Calculated cost (CAD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>10.5 cent/kWh</td>
<td>Ontario Hydro</td>
<td>0.01</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>$151/100g$</td>
<td>Evonik Degussa Corporation</td>
<td>0.13</td>
</tr>
<tr>
<td>Eosin Y</td>
<td>$47/5g$</td>
<td>Sigma-Aldrich Canada Ltd</td>
<td>0.01</td>
</tr>
<tr>
<td>Fiberglass</td>
<td>$20/16,200m$</td>
<td>McMaster-Carr</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### 6.4.6 Model confirmation and sensitivity analysis
The mathematical model presented in Equation 3 shows the relationship between the model terms and their interactions. It further describes the effect of model parameters and their interactions on the response (% degradation of DCF). In order to validate the accuracy of the model, a sensitivity analysis was performed. Within the range of the experimental study, different values of the process
conditions were randomly selected. Figure 6.10 shows a graphical representation of the predicted and actual responses. The actual response obtained from the experiments was in agreement with the responses predicted by the model. In addition, the normal probability plot of Figure 6.10 justifies the assumption of the residual being normally distributed.

![Graphical representation of predicted and actual responses](image)

**Figure 6.10** Actual response obtained versus predicted by the model (solid dots indicates the randomly performed experiments)

### 6.5 Conclusions

This study showed that Eosin-Y dye is an effective electron donor and was able to activate the photocatalyst making the catalyst suitable for operating under solar light, the most abundant and renewable source of energy. In addition, the concentration of Eosin-Y was optimized by incorporating a central composite design. The CCD aided in finding the minimum concentration of dye required without compromising the percentage degradation of DCF. This model presented two important pieces of information. First, the minimum dye concentration (2 ppm) was found, which presented a combination of process parameters that provides an appreciable percentage DCF degradation. This value is approximately 40% degradation in a 5 m reaction time. Secondly, a range of workable dye concentrations (2-4ppm) was determined, above which DCF degradation does not significantly improve. This upper range provides a degradation of 49%.
In addition, because the interaction of all the significant factors on the response has been previously studied, a sound systematic report of the effects of different experimental conditions on the response could be produced in this study. Understanding the interaction effects between the variables reported in this study helps in understanding the complex interplay of various process parameters. For design and development of large-scale and high-rate reactor, this information is crucial.

Significant background research revealed that no previous work in the design and optimization of a photocatalytic experiment using Eosin-Y dye sensitized TiO₂ for solar visible degradation of DCF has been carried out and that this is the first of its kind. This study opens the door to further research in pharmaceutical and PCP degradation processes using Advanced Oxidation Processes.
6.6 Nomenclature

A  Light intensity (I)
A⁺, A⁻  +, -, *, represent high, low, and mid values of light intensity of the respectively
AdjR²  It is modified version of R², adjusted for the number of predictors in the model
B  [DCF]
B⁺, B⁻  +, -, *, represent high, low, and mid values of [DCF] of the respectively
C  [Dye]
C⁺, C⁻  +, -, *, represent high, low, and mid values of [Dye] of the respectively
D  [TiO₂]
D⁺, D⁻  +, -, *, represent high, low, and mid values of [TiO₂] of the respectively
Df  Degree of freedom
DCF  Diclofenac
EDCs  Endocrine disruptive compounds
F  F value is obtained when an ANOVA test is performed. Used to determine significant of a parameter
HPLC  High pressure liquid chromatography
LOF  Lack of fit
PCPs  Pharmaceutical and personal care products
PreR²  Predicted R². Shows how well a regression model predicts responses for new observations

Greek Letters
λ  Wavelength of incident light (nm)
6.7 Reference


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Chapter 7

7 Solar Degradation of Diclofenac using Eosin Y Activated TiO$_2$: Identification of Intermediate and toxicity analysis

7.1 Introduction

Diclofenac (DCF) \([2\text{-}(2,6\text{-dichloranilino})\text{ phenylacetic acid}]\) is ingested by patients to reduce inflammation and is one of the most heavily used, non-steroidal anti-inflammatory drugs (NSAIDs) in the world. Concentrations as high as \(4.11\ \mu\text{g l}^{-1}\) and \(5.45\ \mu\text{g l}^{-1}\) have been detected in surface water and effluent streams of wastewater treatment plants (WWTPs).\(^{30} 31\)

DCF was believed to be the cause of the catastrophic decline of vulture populations in Western Asia. Concentrations as low as ng/l levels were reported to inhibit cell proliferation by affecting their physiology and morphology (citation). Recent research reported that sub-chronic exposure to diclofenac at ng/l levels could interfere with the biochemical functions of fish and cause tissue damage as well. DCF also presents the highest acute aquatic toxicity.\(^{32}\) Therefore, it increases the potential to harm organisms at a cellular level. The presence of \(1\ \mu\text{g l}^{-1}\) of DCF has been reported to damage liver and kidney cell functions in aquatic animals.\(^{33}\) Furthermore, ingestion of DCF by birds results in death shortly after exposure to the contaminated source.\(^{34}\) As a result, intensive research for the development of novel technologies to treat DCF and other pharmaceutical contaminates in wastewater are in high demand.

The potency or half the maximal effective concentration (EC50) for DCF reported in the literature is considered to be very toxic to bacteria (EC50<1mg/L) and algae (EC50 =1-10mg/L).\(^{131}\) As a result, it poses a significant risk to aquatic. Therefore, DCF is placed in the EU priority list of water contaminates.\(^{36}\) During the photodegradation of DCF, new compounds form, known as the intermediates or transformed compounds (TPs). It is important to study this transformation pathways because the TPs might be more toxic to the environment compared to the model compound. Understanding and analyzing the intermediates is an essential step for their environmental fate.

The purpose of this study is to investigate the photo transformation of DCF in a solar photocatalytic treatment, utilizing a dye sensitized photocatalyst. The dye utilized in this study is Eosin-Y (EY), and sensitization of EY with TiO$_2$ is explained elsewhere.\(^{3}\) The photo transformation of DCF will
be monitored at the optimized parameters ([EY] =2mg/L, TiO$_2$=85mg/L, solar light intensity=750W, and [DCF] =30mg/L) obtained statistically in the previous study for our process (citation?).

The current study investigated the application of liquid chromatography mass spectrometry for the elucidation of the intermediates resulting from the photocatalytic degradation of DCF. In this study intermediates (transformed products) formed are identified. In addition, toxicity of untreated DCF solution to treated DCF solution at five different stages of the photodegradation process were assessed and reported. According to the authors’ knowledge, currently there are no study available in the literature revealing data regarding EY-sensitized TiO$_2$ with solar irradiation.

7.2 Results and discussion

7.2.1 Degradation kinetics

7.2.1.1 Dark Reaction
Prior to photocatalytic experiments, the adsorption of DCF on the surface of TiO$_2$ was observed. Without irradiating the solar visible light, an experiment was performed for two hours, known as the dark reactions. In addition to the dark reaction, a photolysis reaction was also performed. These two experiments ensure that disappearance and degradation of DCF was not due to adsorption of the TiO$_2$ surface, or without the absence of TiO$_2$ (photolysis). An adsorption of 4% of DCF was measured on the surface of the photocatalyst in the dark reaction. No photolysis of DCF was observed under the visible light source. These results are in agreement with studies in the literature.

7.2.1.2 Photo-stability of TiO$_2$ on fiberglass
When a photocatalyst is immobilized it is important to assess its stability on the support medium (fiberglass sheet). Immobilizing a photocatalyst helps eliminate the catalyst reuse, therefore reducing the operational costs.
Five photodegradation of DCF (at the same experimental conditions) were performed and the apparent rate of degradation of each experiment was recorded (Table 7-1). After a photocatalytic experiment, the recovered immobilized catalysts were dried at 100°C in a furnace. The recovered immobilized catalysts were used to repeat four new sets of experiments at the same conditions (flow rate, initial concentration of DCF, pH etc.). The rate of disappearance of DCF was observed using HPLC as mentioned above. The natural log of \((C/Co)\) vs. degradation time was plotted and the rate of degradation \((k_{\text{apparent}})\) was calculated from the slope of the line when linear regression was performed. Table 7-1 summarizes the values of the \(k_{\text{apparent}}\), and the linear regression coefficients \((R^2)\). The values of the apparent rate constants demonstrate, the stability of the photocatalyst and its reusability.

Table 7-1 Apparent rate constants of DCF during the photocatalytic treatment. Experimental conditions: \(Q = 1.15 \times 10^{-5} \text{ m}^3/\text{s}, V_L = 4 \times 10^{-4} \text{ m}^3, \text{pH} = \text{neutral}; T = 298K, O_2 \text{ saturated}, [\text{EY}] = 2\text{mg/L}, \text{TiO}_2 = 85\text{mg/L}, \text{ solar light intensity} = 750W, \text{ and } [\text{DCF}] = 30\text{mg/L}.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(k_{\text{apparent}} \times 10^{-3}), min(^{-1})</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (original)</td>
<td>90.85</td>
<td>0.9871</td>
</tr>
<tr>
<td>2</td>
<td>91.23</td>
<td>0.9921</td>
</tr>
<tr>
<td>3</td>
<td>89.85</td>
<td>0.9745</td>
</tr>
<tr>
<td>4</td>
<td>92.12</td>
<td>0.9525</td>
</tr>
<tr>
<td>5</td>
<td>90.01</td>
<td>0.9896</td>
</tr>
</tbody>
</table>

7.2.2 Identification of DCF Intermediate products
The photo degradation of DCF utilizing EY-sensitized TiO\(_2\) led to the formation of intermediates, which were identified using an HPLC/MS-orbitrap (ESI(+)) mode. Both treated and untreated sample of DCF were analyzed.

The treated samples of DCF in ESI (+) scan mode showed twenty three (Figure 7.1) different mass spectrums (including the protonated DCF), indicating the formation of intermediates during the photo mineralization of DCF. In order to identify the transformed products, the detected mass
fragments were compared with several studies from the literature\textsuperscript{36, 22, 16} who also studied the photo mineralization of DCF under different AOPs.

Figure 7.2 shows screening of untreated sample of DCF ((1) and (2)), indicates the mass spectrum of DCF and its protonated molecules (4) and (6).

The chemical structures corresponding to the mass spectrum are identified by comparing the results obtained to the literature. Diclofenac sodium salt ((1), m/z=301.90) loses the sodium atom, resulting in the formation of (2), m/z=296.01. According to Michael et al.\textsuperscript{36}, this spectrum shows the profile of the protonated DCF molecules. It shows the process of DCF molecule losing H\textsubscript{2}O, CO\textsubscript{2}, and Cl atoms to form (4) (m/z = 278.01) and (6) (m/z = 215.09) respectfully. A similar sequential loss of atoms are also reported by Michael et al.\textsuperscript{36} with an addition of another protonated DCF compound with a molecular weight of 250.018 g/mole. This protonated compound however, was not detected in this process.
Figure 7.1 Identified structure of DCF and some its transformed by products. Experimental conditions: \( Q = 1.15 \times 10^{-5} \) m\(^3\)/s, \( V_L = 4 \times 10^{-4} \) m\(^3\), pH = neutral; \( T = 298 \)K, O\(_2\) saturated, [EY] =2mg/L, TiO\(_2\)=85mg/L, solar light intensity=750W, and [DCF]

Figure 7.2 Mass spectra of DCF and protonated DCFs. Experimental conditions: \( Q = 1.15 \times 10^{-5} \) m\(^3\)/s, \( V_L = 4 \times 10^{-4} \) m\(^3\), pH = neutral; \( T = 298 \)K, O\(_2\) saturated, [EY] =2mg/L, TiO\(_2\)=85mg/L, solar light intensity=750W, and [DCF] =30mg/L
Figure 7.3 Mass spectra of five selected DCF intermediate products. Experimental conditions: \( Q = 1.15 \times 10^{-5} \text{ m}^3/\text{s}, V_L = 4 \times 10^{-4} \text{ m}^3, \text{pH} = \text{neutral}; T = 298K, O_2 \text{ saturated}, [\text{EY}] = 2\text{mg/L}, \text{TiO}_2 = 85\text{mg/L}, \text{solar light intensity}=750W, \text{and} [\text{DCF}] = 30\text{mg/L} \)

Numbers (9) and (10) on Figure 7.3 are known as 4-OH-DCF and 5-OH-DCF respectively. These mono hydroxylated product of DCF are metabolites of the oxidative DCF metabolism in humans and are known to catalyze in the human liver. They are the products formed due to addition of electrophilic hydroxyl radical (HO') to aromatic rings, forming a stabilized resonance carbon centred radical. This is known to be the first step in the photo degradation of DCF.

In addition, the formation of 2-chloroaniline (16), 2, 6-dichloranline (18) and 2, 6-dichlorophenol (19) (Figure 7.4) were confirmed with the results obtained by Bartles et al. Figure 7.4 shows transferred product (17). It was confirmed to be TP*7 with a study conducted by Michael et al. This final product was also proposed by other authors in the literature.

The structure and molecular weights of intermediates (5), (8), and (11)-(15) (mass spectra not shown) were compared and confirmed with Agura et al. under Phot-Fenton treatment of DCF.
Product (6) was confirmed with the results obtained by Martinez et al.\textsuperscript{36} utilizing a UV-light photocatalytic treatment of DCF with TiO\textsubscript{2} as a catalyst.

In this study, three (20), (21) and (22)) more mass fragments were absorbed that were not found in the literature. These transformed products are shown in Figure 7.5. Currently, data in the literature is unavailable and lack of a library in HPLC-orbitrap prevents for the proper determination of the chemical structure. The separated chromatograph are tentative identified at this time and needs further investigation.

![Figure 7.4 Mass spectra of four selected DCF intermediates. Experimental conditions: Q = 1.15 x 10\textsuperscript{-5} m\textsuperscript{3}/s, V\textsubscript{L} = 4 \times 10\textsuperscript{-4} m\textsuperscript{3}, pH = neutral; T = 298K, O\textsubscript{2} saturated, [EY] =2mg/L, TiO\textsubscript{2}=85mg/L, solar light intensity=750W, and [DCF] =30mg/L.](image-url)
Figure 7.5 Mass spectra of three unidentified DCF intermediates. Experimental conditions: $Q = 1.15 \times 10^{-5}$ m$^3$/s, $V_L = 4 \times 10^{-1}$ m$^3$, pH = neutral; $T = 298$K, O$_2$ saturated, [EY] = 2mg/L, TiO$_2$=85mg/L, solar light intensity=750W, and [DCF] =30mg/L

From the available data in the literature, it can be observed that the intermediates formed under different AOPs (photolysis, ozonation, sonolysis, heterogeneous photocatalysis etc.) and conditions result in similar product formation during the photo mineralization of DCF.  

Micheals et al.$^{36}$ suggest that DCF degradation mainly proceeds by oxidation and hydroxylation reaction between chloroaniline and phenylacetic acid. In addition, the formation of DCF isomers are the result of non-selectivity of hydroxyl radicals (HO$^-$). Thus, confirming a similar reaction mechanism, regardless of the type of AOPs.

### 7.2.3 Toxicity assessment of DCF on Daphnia Magna

Toxicity of untreated and treated DCF solution was analyzed on *Daphnia magna* organisms. Rate of mortality of the species was monitored after 24h and 48h exposure times based on the treatment process explained above. The toxicity of treated solution (with intermediate products) were compared to the untreated DCF solution. Figure 7.6 shows untreated DCF solution was less toxic to the organisms compared to the treated solutions. The untreated DCF solution showed 11% mortality rate of *D. magna* during the first 24 hours of exposure, which increased to nearly 25%
after 48 hours. The mortality rate of the solution of DCF that was irradiated for 15 min showed a much higher mortality rate, nearly 72% in 24h and up to 96% at 48h. Indicating that the treated DCF are much more toxic.

Treated DCF solution can be much more toxic than the original untreated DCF solution, because photodegradation of DCF contributes to the formation of chloro-derivatives.\textsuperscript{137-139} this can be observed in Figure 7.6. As the intermediates formed during the photo mineralization, the higher the toxicity of DCF which was shown to decrease as the degradation process was continued. Another reason why the treated solution of DCF is more toxic, is due to synergistic effects among the intermediates formed. Michaels et al.\textsuperscript{36,140} studied the effects among the transformed by products and they concluded that the high rate of toxicity is a result of individual and synergistic toxic effects of the DCF and its intermediates.

As it can be seen in Figure 7.6, the toxicity (and formed intermediate products) of the DCF reduced significantly during the 120 min of the reaction. A complete photo mineralization of DCF (and intermediate products) using EY-sensitized TiO\textsubscript{2} activated using solar visible was achievable in 300 minutes.
Conclusions

In order to eliminate post process treatment and reduce the cost of the process, the immobilized TiO$_2$ on fiberglass sheets were assessed in terms of stability and reusability.

22 different intermediate products were absorbed during the visible light photocatalytic degradation of DCF using EY-sensitized TiO$_2$. 19 of the transformed products were identified by comparing the mass spectrums found in the literature. In this study, three more mass fragments were absorbed that were not found in the literature, and identification of these mass fragments are motivation for future work.

Toxicity analysis of the treated and untreated samples of DCF were also assessed. The treated samples indicated an increase in toxic effect to *D. magna* compared to the untreated DCF solution. The treated DCF solution can be much more toxic because photodegradation of DCF contributes...
to the formation of chloro-derivatives. In addition, a synergistic effect among the DCF intermediates formed during the process could also contribute to the increase in toxicity.

The effectiveness of the photo mineralization of DCF at optimized conditions statistically obtained from our previous work was investigated. The stability and reusability of the photocatalyst utilized was examined. Identification of DCF intermediates formed during the photodegradation was established. In addition, toxicity of untreated DCF solution to treated DCF solution at five different stages of the photodegradation process were assessed.
### 7.4 Nomenclature

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>DCF</td>
<td>Diclofenac</td>
</tr>
<tr>
<td>EDCs</td>
<td>Endocrine disruptive compounds</td>
</tr>
<tr>
<td>HPLC</td>
<td>High pressure liquid chromatography</td>
</tr>
<tr>
<td>HPLC/MS</td>
<td>High pressure liquid chromatography + mass spectrometry</td>
</tr>
<tr>
<td>PCPs</td>
<td>Pharmaceutical and personal care products</td>
</tr>
</tbody>
</table>
7.5 References


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Chapter 8

8 Conclusions and recommendation

8.1 Introduction

This chapter provides main conclusions and contributions of this dissertation. In addition, recommendations for future works are also outlined.

8.2 Conclusions

The following points outline the important contributions of this dissertation. The contributions are:

(a) An in-depth analysis on the photo-degradation kinetics of diclofenac (DCF) was performed. A modified swirl flow monolithic type reactor was used in this study that provided better mixing and residence time distribution of fluid by reducing dead zone and bypassing of fluid. The reactor is unique for extracting true kinetic parameters in photocatalysis, as it reduces external mass transfer resistance and allowed to extract true kinetic rates as a function of catalyst layer thickness, light intensity, and pH of the solution. Fiberglass sheets were found to be the better catalyst support when compared to pyrex glass plates. Fiberglass sheets provided more surface area with an optimal catalyst loading of $50 \times 10^{-3}$ kg/m$^2$. External mass transfer resistance exists even for the modified reactor configuration used; however, true kinetic rates could be extracted from the observed reaction rates after correcting for mass transfer resistance. Adsorption equilibrium rate constant for DCF was found to be $33.98$ mM$^{-1}$. Optimum pH, catalyst layer thickness, effect internal mass transfer resistance, and dependence of light intensity on reaction rate were determined experimentally. Eosin Y-sensitized TiO$_2$ was proven to be a more efficient by facilitating considerably high DCF degradation rates at visible wavelength compared to doped TiO$_2$ photocatalyst and Degussa P25 TiO$_2$.

(b) Process optimization and parameter interaction study was performed for solar degradation of Diclofenac using Eosin Y activated TiO$_2$. It was found Eosin-Y dye is an effective electron donor and was able to activate the photocatalyst making the catalyst suitable for operating under solar visible light. Eosin-Y concentration for the process was optimized by incorporating a central...
composite design. The CCD aided in finding the minimum concentration of dye required without compromising the percentage degradation of DCF. This model presented two important pieces of information. First, the minimum dye concentration (2 ppm) was found, which presented a combination of process parameters that provides an appreciable percentage DCF degradation. This resulted in approximately 40% degradation in a 5 min reaction time. Secondly, a range of workable dye concentrations (2-4 ppm) was determined, above which DCF degradation does not significantly improve. This upper range provides a degradation of 49%. The interaction of all the significant factors on the response has been studied, a systematic report of the effects of different experimental conditions on the response was performed in this study. Understanding the interaction effects between the variables reported in this study helps in understanding the complex interplay of various process operating parameters. For design and development of large-scale and high-rate reactor, this information is very crucial. Significant background research revealed that no previous work in the design and optimization of a photocatalytic experiment using Eosin-Y dye sensitized TiO$_2$ for solar visible degradation of DCF has been carried out and that this is the first of its kind.

(c) Identification of diclofenac intermediate products during a solar degradation using Eosin Y activated TiO$_2$ was accomplished. In addition, toxicity levels of treated and untreated diclofenac on Daphnia magna was analyzed and reported. 22 different intermediate products were absorbed during the visible light photocatalytic degradation of DCF using EY-sensitized TiO$_2$. 19 of the transformed products were identified by comparing the mass spectrums found in the literature. In this study, three more mass fragments were observed that were not found in the literature, and identification of these mass fragments are motivation for future work. Toxicity analysis of the treated and untreated samples of DCF were assessed. The treated samples indicated an increase in toxic effect to Daphnia magna compared to the untreated DCF solution. The treated DCF solution can be much more toxic because photo-degradation of DCF contributes to the formation of chloro-derivatives. In addition, a synergistic effect among the DCF intermediates formed during the process could also contribute to the increase in toxicity.

A cost estimation of the process at the optimum conditions ($I = 750$W, TiO$_2$ = 84.62 mg/cm$^2$ of fiberglass, Eosin Y = 2 mg/L, fiberglass sheet = 25 cm$^2$) was performed, and it helped determine
the financial benefit of the process. It was determined that it only costs CAD $0.06 to treat one liter of the DCF contaminated water using this process.

8.3 Recommendation for future work

(1) DCF intermediate formation pathway: we were able to identify the main intermediate by products formed by comparing the results obtained with other authors. It is important to confirm these tentative findings with model standards. In addition, proposing a transformation pathway for DCF intermediates formed during this process will shed light on the exact mechanism of photocatalytic degradation of DCF or other pharmaceutical compounds.

(2) Current work was performed on simulated water. It is ideal to test the process in natural system (for example, river water). In addition, it will be beneficial to test the photocatalytic process on a multi-component (more than one pollutants) system, rather than system for single component. This is a requirement for a fundamental study.

(3) Dye sensitization process: the current process tests the effective of dye-sensitization method on TiO$_2$ as a semiconductor. It will be ideal to compare the findings using other semiconductors, or doped photocatalysts. In addition, utilization organic dyes instead of eosin y (such as from vegetables, or fruits), will beneficial. This is because the natural systems already contain certain amount of the natural dyes from the organic pollutants, and utilizing it will be ideal.

(4) Process scale up: lab scale systems are important early stage tools, however, it is ideal to have a vision for scaling up an engineering process. It is a challenge to design a large-scale reactor to be used for industrial wastewater purposes utilizing green technologies. It will be beneficial to scale up the current process to a pilot scale geometrically and
hydrologically. This is a necessary step towards solving one of the biggest challenge of the future of large-scale reactors for industrial wastewater treatment purposes.
10 Curriculum Vitae

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