PHOTOCATALYTIC OXIDATION OF PHARMACEUTICAL MICROPOLLUTANTS IN A FLOW-THROUGH REACTOR

BY

LAURA DALE ASMUTH

THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering in Civil Engineering in the Graduate College of the University of Illinois at Urbana-Champaign, 2011

Urbana, Illinois

Adviser:

Associate Professor Timothy J. Strathmann
Abstract

The presence of pharmaceutical micropollutants in drinking and natural waters has recently become increasingly publicized. The increased presence of pharmaceutical micropollutants in drinking water requires additional water treatment strategies. Diatrizoate, carbamazepine, sulfamethoxazole, and ibuprofen represent several classes of common drug compounds that are present in natural and drinking water and are not effectively treated by conventional methods. Past experiments with TiO$_2$ suspensions as a photocatalyst show the potential for the degradation of these drugs using this method. The photocatalyst works by the excitation of electrons in the TiO$_2$ semiconductor by photons with energy exceeding the materials’ band gap energy. The resulting valence band holes are strong oxidants that can directly react with contaminants or oxidize adsorbed water molecules to form hydroxyl radicals, which can then react with the micropollutants. However a continuous, rather than batch, method would be more desirable to the water treatment industry. Deposition of TiO$_2$ in thin films on glass slides was used to develop a model flow-through reactor to study dynamic photocatalytic treatment processes. Light is supplied by black light bulbs, which emit light in the ultraviolet-A range. Experiments have shown this to be an effective method for degradation of these four drug compounds as they flow through the reactor. The drug compound entering the reactor experiences a rate of decay that leads to reasonable degradation of the drug at the effluent.
Acknowledgements

Funding for this project was provided by NSF and GAANN. I would like to thank Tias Paul and Lanhua Hu for their advice on HPLC. I would like to thank my advisor Timothy Strathmann for guidance and help on this project.
Table of Contents

Chapter 1: Introduction ........................................................................................................1

Chapter 2: Experimental ..................................................................................................4

Chapter 3: Results and Discussion ................................................................................7

Chapter 4: Conclusions and Environmental Implications ............................................11

Chapter 5: References ....................................................................................................12

Appendix A: Data ..........................................................................................................17
Chapter 1
Introduction

There is increasing concern about pharmaceuticals in drinking water. It is increasingly likely that there are cumulative unnoticed effects on aquatic organisms. (Daughton and Ternes, 1999) According to literature studies, many pharmaceutical compounds have been found in rivers, ground water, sediments, oceans, and soil. Ibuprofen has been found in concentrations of 17-139 ng/L in river water samples. (Halling-Sorensen et al., 1998) Other studies have looked at organic wastewater contaminant presence in natural waters (Kolpin 2002 and Miao 2004). A mixture of several drugs at ng/L concentrations was shown to inhibit the growth of human embryonic cells. (Pomati 2006) Also, wild rodents have been found to have antibiotic resistance. (Gilliver 1999) The current methods of treatment are not sufficient. (Ingerslev 2000; Perez 2005)

Figure 1 Structures of model micropollutants used in this study

![Carbamazepine (CBZ)](image1)

![Ibuprofen (INN)](image2)

Therefore the development of more effective treatment technologies is necessary. Advanced oxidation processes have shown better results than traditional methods for especially recalcitrant compounds. Some of the most effective methods use hydroxyl radicals including application of ozone/peroxide, UV/peroxide and TiO$_2$ photocatalysis. (Benotti 2009, Esplugas 2007, Huber 2003, Huber 2004, Huber 2005)

This research examines the application of fixed film TiO$_2$ to catalyze the oxidation of pharmaceutical micropollutants in a flow-through aqueous reactor. The TiO$_2$ semiconductor has been shown to be effective in photocatalytic degradation of organic molecules. (Hoffmann 1995, Bahnemann 2002, Calza 2004, Kaniou 2005) TiO$_2$ has already been shown to be effective at oxidizing a wide variety of organic compounds when the TiO$_2$ is used in slurry form. (Agrios 2004, Paul 2007, Paul 2010, Hu 2007, Sugihara 2010) TiO$_2$ batch thin film photocatalysis has been shown to be effective. (Noorjahan 2003)

Previously done research is limited because the slurry form of TiO$_2$ requires filtration and has been done as a batch process rather than as a continuous process, which is a poor representation of engineered water treatment processes. (Paul 2007, Paul 2010, Hu 2007) This research addresses the treatment of organic contaminants in flow-through reactors with fixed thin films of photocatalyst. This method is promising because it is
continuous and does not require filtration after treatment. The development of a model flow-through reactor will also be useful for studying the longevity and sustainability of photocatalysts during continuous operation.

The goals of this research project are to evaluate continuous treatment of PPCPs in a flow-through fixed film ultraviolet titanium dioxide photocatalytic treatment of pharmaceutical micropollutants, to demonstrate that steady-state concentration of each drug can be achieved in the effluent of the reactor, and to assess how well observed PPCP removal efficiencies compare with a plug flow reactor model.

Ibuprofen and carbamazepine were chosen as model micropollutants based on relevance, occurrence, and general resistance to oxidation by conventional methods. Pomati et al. (2006) found environmental concentrations of 33 ng/L for carbamazepine and 92 ng/L for ibuprofen. Ibuprofen and carbamazepine have been shown to be resistant to treatment using a variety of methods. (Westerhoff 2005, Onesios 2009)
Chapter 2

Experimental

All materials and reagents were of high purity and used as received. NaClO₄, sodium diatrizoate, sulfamethoxazole, ibuprofen, carbamazepine, TEA, TTIP, diethanolamine, isopropanol, Na₂HPO₄, and NaH₂PO₄ were obtained from Sigma-Aldrich. HClO₄, Methanol, and Acetonitrile (Acros) were obtained from Fisher. P25 titanium dioxide was obtained from Degussa. All water used in reactions was deionized Barnstead Nanopure with a resistivity of 17.3 MΩ cm. All glassware was washed with 1 M HCl prior to use.

TiO₂ thin films were prepared using the method described by Balasubramanian et al. (2004) TTIP (7.33 mL) was mixed with 42.67 mL i-prOH. Then 9.6 mL of DEA was added. Following stirring at room temperature for two hours, 0.903 mL of water and then 1.8 g of P25 TiO₂ were added dropwise.

![Diagram of flow-through reactor](image)

**Figure 2** Diagram of flow-through reactor
All experiments were conducted in a plug flow-through reactor. Water is pumped into the end of one channel, then flows through four more before going over a weir to exit. During batch experiments where measurement of reaction progress in individual lanes was desired, glass microscope covered slides were used to prevent mixing between channels. Weir height was changed by inserting the weir of the desired height at the outlet of the reactor. The flow rate through the reactor can be predicted as a function of weir height (H) using the equation retention time is equal to flow rate (Q) over volume (Area x H). The light source is a set of five fluorescent light bulbs.

Tracer experiments were conducted. The tracer used was rhodamine wt. The test was performed with weir heights of 0.7 cm and 1.3 cm and flow rates of 3.9 mL/min and 6.7 mL/min. Uncoated glass slides lined the bottom of the reactor in place of the TiO₂ slides. Samples were taken just before the weir at the outlet of the reactor. Batch photocatalysis and flow-through photocatalysis reactions were done in the reactor using the same set of weirs and a set of uncoated glass slides. Flow-through photocatalysis experiments were performed using the following procedure. TiO₂-coated slides were placed in the reactor to line the bottom. The volume is determined by the weir height. 20 μM ibuprofen and 20 μM carbamazepine solutions were prepared in a 1 mM HClO₄/9 mM NaClO₄ buffer (pH ~3). Tracer concentration at the outlet was monitored using a UV-Vis spectrophotometer (Shimadzu) at λ = 555 nm. Blank cuvettes contained nanopure water. HPLC was used to determine the concentration of ibuprofen and carbamazepine. The detector is a photodiode array (PDA) detector (Shimadzu AVP System). The stationary phase is a Novapak column (C18, 3.9 x 150 mm, 4 mm particle size) with a guard column of the same material (20 mm). The mobile phase for carbamazepine analysis was 40% ACN
and 60% 10 mM H₃PO₄. Measurements were used from 284 nm. The mobile phase for carbamazepine analysis was 50% ACN and 50% 10 mM H₃PO₄. Absorbance was measured at a wavelength of 194 nm.
Chapter 3
Results and Discussion

The calculated and the measured residence times are listed in the table below. The agreement between the calculated and measured residence times is good.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Calculated</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5 mL/min, 0.7 cm</td>
<td>2.4 hours</td>
<td>2.7 hours</td>
</tr>
<tr>
<td>3.9 mL/min, 1.3 cm</td>
<td>4.0 hours</td>
<td>3.3 hours</td>
</tr>
<tr>
<td>6.7 mL/min, 0.7 cm</td>
<td>1.2 hours</td>
<td>1.6 hours</td>
</tr>
</tbody>
</table>

*Table 1 Calculated and measured retention times (in hours)*

Reaction rates in flow through reactor when operated under batch conditions were modeled with first-order reaction kinetics using the equation $\frac{dC}{dt} = -r \times C$ where $C$ is concentration, $t$ is time, and $r$ is the rate constant for the reaction. Over 3.5 hours, 34.3% of ibuprofen and 56.8% of 34.3% of carbamazepine were removed. The first-order rate constant was found to be $0.24 \pm 0.04 \text{ h}^{-1}$ for ibuprofen and $0.12 \pm 0.01 \text{ h}^{-1}$ for carbamazepine.
During flow-through experiments, there is not complete mixing along the width of each lane. The tracer dye does not move evenly through the reactor.
<table>
<thead>
<tr>
<th>Flow Rate (mL/min)</th>
<th>Weir Height</th>
<th>Drug</th>
<th>Steady-State Concentration (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.61 ± 0.03</td>
<td>0.7</td>
<td>Ibuprofen</td>
<td>12.4 ± 0.5</td>
</tr>
<tr>
<td>3.94 ± 0.05</td>
<td>1.3</td>
<td>Ibuprofen</td>
<td>13.0 ± 0.8</td>
</tr>
<tr>
<td>6.3 ± 0.5</td>
<td>0.7</td>
<td>Ibuprofen</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>3.86 ± 0.05</td>
<td>1.3</td>
<td>Carbamazepine</td>
<td>12.4 ± 0.9</td>
</tr>
</tbody>
</table>

Table 2 Steady-state concentrations

Using retention time, reaction rate, and flow rate, an equation relating final concentration to flow rate, initial concentration, and reaction rate was determined. From the differential form of the first-order rate equation,

\[
dC/dt = -r \times C
\]

Integrating over the concentration change and time elapsed over the length of the reactor gives:

\[
\ln C_f - \ln C_i = -r \times t_f - r \times t_i
\]

Rearranging and substituting 0 for \( t_i \) gives

\[
C_f = C_i \exp(-r \times t_f)
\]

The time elapsed, represented by \( t_f \), is equal to the average retention time in the reactor.

The retention time \( t_f \) can be related to \( Q \), the flow rate, and \( H \), the depth of fluid in the reactor, by comparing calculated and measured retention times. Fitting an equation to related measured and calculated retention times,

\[
t_f = t_r = 1.47 \times (t_{r, \text{calc}})^{0.61}
\]

\[
t_{r, \text{calc}} = Q / (L \times W \times H)
\]

\[
t_r = 1.47 \times ( Q / (L \times W \times H) )^{0.61}
\]

Substituting \( t_r \) into the equation for \( C_f \),

\[
C_f = C_i \exp(-1.47 \times r \times ( Q / (L \times W \times H) )^{0.61})
\]
<table>
<thead>
<tr>
<th>Drug</th>
<th>Rate constant r (h(^{-1}))</th>
<th>Flow rate Q (mL/min)</th>
<th>Weir height H (cm)</th>
<th>Predicted final concn. (μM)</th>
<th>Actual final concn. (μM)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ibuprofen</td>
<td>0.24 ± 0.04</td>
<td>3.61 ± 0.03</td>
<td>0.7</td>
<td>16.2</td>
<td>12.4 ± 0.5</td>
<td>23%</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>0.24 ± 0.04</td>
<td>3.94 ± 0.05</td>
<td>1.3</td>
<td>17.2</td>
<td>13.0 ± 0.8</td>
<td>24%</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>0.24 ± 0.04</td>
<td>6.3 ± 0.5</td>
<td>0.7</td>
<td>14.8</td>
<td>15 ± 1</td>
<td>1%</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>0.12 ± 0.01</td>
<td>3.86 ± 0.05</td>
<td>1.3</td>
<td>18.5</td>
<td>12.4 ± 0.9</td>
<td>33%</td>
</tr>
</tbody>
</table>

Table 3 Predicted and actual effluent concentrations

Two reasons for discrepancies between expectation and observations are that the channel has turns that affect the rate of different parts of the reactor, and mixing across the channel width may not be complete.
Chapter 4
Conclusions and Environmental Implications

The goal of this project was to determine the effectiveness of the TiO$_2$ photocatalysis flow-through reactor in the removal of pharmaceuticals from water. After testing with two pharmaceutical compounds and various reactor conditions, the effectiveness of the reactor was determined and modeled. This reactor setup is effective in removing pharmaceutical compounds at $\mu$M concentrations. The resulting products of this treatment method are better for the environment, and this method would be easier to use at a wastewater treatment plant. Areas for further research include testing of a wider variety of compounds in water containing more components. The system would also be useful for assessing the long-term activity of catalysts during water treatment and the accumulative effects of exposure to non-target constituents over extended operating times.


Halling-Sorensen, B.; Nors Nielsen, S. N.; Lanzky, P. F.; Ingerslev, F.; Holten Lutzhof, H. C.; Jorgensen, S. E. Occurrence, fate and effects of pharmaceutical substances in the


Appendix A

Data

Figure 5  Batch photocatalysis of ibuprofen

Figure 6  Batch photocatalysis of carbamazepine
Figure 7  Data for a flow rate of 3.5 mL/min and a weir height of 0.7 cm
Figure 8  Data for a flow rate of 3.9 mL/min and a weir height of 1.3 cm
Figure 9  Tracer data for a flow-rate of 3.9 mL/min and a weir height of 0.7 cm
Figure 10  Flow-through photocatalysis of Ibuprofen with a flow rate of 3.64 mL/min and a weir height of 0.7 cm
Figure 11  Flow-through photocatalysis of Ibuprofen with a flow rate of 3.94 mL/min and a weir height of 1.3 cm

Figure 12  Flow-through photocatalysis of Ibuprofen with a flow rate of 6.3 mL/min and a weir height of 0.7 cm
Figure 13  Flow-through photocatalysis of Carbamazepine with a flow rate of 3.86 mL/min and a weir height of 1.3 cm