

A method for coating glass beads with TiO_2 and comparison of photocatalytic effectiveness for contaminant degradation

A Major Qualifying Project Report

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Abstract

Photocatalytic reactors are being investigated for their effectiveness in degrading contaminants in water and wastewater streams. Titanium dioxide (TiO_2) is a promising photocatalyst and is used for its low toxicity and environmental impact, its effectiveness, and its ability to degrade a diverse range of contaminants. The types of reactors used in photocatalysis are either fixed media reactors or slurry reactors. This MQP investigated a method for fixing TiO_2 onto glass beads for use in a TiO_2 /UV fixed-media photocatalytic reactor. It was found that the apparent rate constant for the degradation of methylene blue using a single layer of the glass beads coated in TiO_2 was 0.003 min^{-1} and that the apparent rate constant for three to four layers of the beads was 0.0065 min^{-1} . This indicates the possibility of UV transmissibility through the glass beads and suggests that the glass beads may be a better substrate for the photocatalyst than other available non-transmissible substrates such as activated carbon pieces. The rate constants determined in this MQP were comparable to those found by others who used both activated carbon pieces for a photocatalyst substrate in a bubbling fluidized bed reactor and a slurry reactor. These results indicate that glass beads are a very effective substrate for fixing a photocatalyst. However, comparison to results obtained by another group showed that the rate constants obtained in this report were not comparable. This indicates that further research must be done to eliminate the differentiating factors such as the contaminant itself, the concentration of the photocatalyst, and the pH of the solution in order to more definitively determine if glass beads are the most effective photocatalyst support.

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Table of Contents

Abstract	2
Acknowledgements	3
Table of figures.....	5
Introduction	6
Background	9
Catalyst Properties.....	9
Radiation Properties	10
Mechanisms of radical formation	10
Charge-carrier generation.....	11
Charge transport	11
Charge trapping.....	11
Charge recombination	11
TiO ₂ surface mechanisms	12
Active species generation.....	12
Hydroxyl radical formation	12
Superoxide radical formation	12
Adsorption.....	12
Radical reaction mechanisms	13
Factors affecting degradation efficiency	13
The effect of pH.....	13
The effect of temperature	13
TiO ₂ morphology.....	13
Types of reactors	14
Slurry reactors	14
Fixed-media reactors	16
Hypothesis	20
Materials.....	21
Methodology.....	21
TiO₂ Application	21
Experiments.....	22
Determination of dye concentration.....	23
Determination of reaction order.....	23
Elementary rate law method	23
Graphical method	24
Determination of reaction rate constant.....	27
Determination of UV permissibility.....	27
Results and Discussion	28
Application of the photocatalyst to the glass beads	28
Reaction order	29
Reaction analyzation.....	29
Batch reaction method	29

Overall determination of reaction order	32
Apparent reaction rate constant.....	32
Comments	32
Conclusion.....	36
Recommendations for future research	37
Application of the photocatalyst	37
Comparison to other types of photocatalyst support	37
Considerations.....	37
Reference List	39

Table of figures

FIGURE 1: ILLUSTRATION OF THE ENERGY GAP IN SEMICONDUCTIVE MATERIALS. ADAPTED FROM ALVAREZ-CORENA 2015	9
FIGURE 2: MECHANISMS OF HYDROXYL REACTIONS.....	13
FIGURE 2: MECHANISMS OF HYDROXYL RADICAL REACTIONS.....	13
FIGURE 4: DIAGRAM OF THE BENCH-SCALE PHOTOCATALYTIC REACTOR USED BY JOSE ALVAREZ-CORENA	15
FIGURE 5: DIAGRAM OF A TYPICAL NON-REMOVABLE FIXED MEDIA PHOTOCATALYTIC REACTOR.....	17
FIGURE 6: A DIAGRAM OF THE FIBER OPTIC NON-REMOVABLE FIXED MEDIA PHOTOCATALYTIC REACTOR USED BY NICOLA PEILL AND MICHAEL HOFFMANN	18
FIGURE 7: GRAPHS REPRESENTING METHODOLOGY FOR DETERMINING REACTION ORDER ADAPTED FROM HTTP://WWW.CHEM.PURDUE.EDU/GCHELP/HOWTOSOLVEIT/KINETICS/INTEGRATEDRATELAWS.HTML	26
FIGURE 8: SAMPLES TAKEN FROM PRELIMINARY TESTING	28
FIGURE 9: GRAPH TO DETERMINE IF THE REACTION IS ZERO ORDER	30
FIGURE 10: GRAPH TO DETERMINE IF REACTION IS FIRST ORDER	30
FIGURE 11: GRAPH TO DETERMINE IF REACTION IS SECOND ORDER	31
FIGURE 12: A DIAGRAM TAKEN FROM (GENG AND CUI 2010)	34

Introduction

Water is one of the most valuable resources on our planet. Since the Federal Water Pollution Control Act of 1948¹, public concern over the state of the United States' waters has grown. Recently, the presence of emerging contaminants in wastewater streams² has prompted the research of new technologies to effectively and efficiently remove contaminants from the water. Photocatalytic reactors have become a particular area of interest due to their effectiveness at degrading a wide range of contaminants. Photocatalytic reactors utilize a catalyst activated by ultraviolet radiation to break down organic contaminants within the wastewater. The photocatalyst forms a highly reactive hydroxyl radical (OH•) which can degrade almost any organic material due to its extremely high oxidation capacity. Several catalysts can be utilized in photocatalytic reactors including titanium dioxide (TiO₂), zinc sulfide (ZnS), and zinc oxide (ZnO). Titanium dioxide is the most popular choice due to its low toxicity, photocatalytic efficiency, and low cost (Konstantinou 2002).

Titanium dioxide exists in three different forms, anatase, rutile and brookite. The difference between them lies in their crystalline structure. Anatase is more photocatalytically active than rutile due to the structure of rutile. The titanium molecules in rutile lie more closely together in rutile than in anatase allowing for the formation of a unique surface structure Ti-OO-Ti.³ This structure breaks water down to form O₂ rather than forming a reactive species such as a hydroxyl radical. Rutile is the most stable form of titanium dioxide at room temperature. Anatase and rutile are the most commonly studied forms of titanium dioxide due to their performance and abundance while brookite is less often because it is very difficult to synthesize (Chiarello, Di Paola et al. 2011). P25 powder, a commercially available mixture of anatase and rutile titanium

¹ EPA, U. (2016, May 25, 2016). "History of the Clean Water Act." 2016, from <https://www.epa.gov/laws-regulations/history-clean-water-act>.

² USA.gov (2016). "Contaminants of Emerging Concern in the Environment." Retrieved October 2016, 2016, from <http://toxics.usgs.gov/investigations/cec/index.php>.

³ Kakuma, Y., et al. (2015). "Difference in TiO(2) photocatalytic mechanism between rutile and anatase studied by the detection of active oxygen and surface species in water." Phys Chem Chem Phys **17**(28): 18691-18698.

dioxide, has a greater photocatalytic effectiveness than either of its pure constituents. Although pure anatase is more photocatalytically effective than pure rutile, in the P25 powder, rutile gives the mixture greater photocatalytic effectiveness due to its greater stability and its interactions with the anatase.

There are two types of common TiO_2 photocatalytic reactors: slurry reactors and fixed media reactors. Slurry reactors use a slurry made of TiO_2 powder that is added to an aqueous solution of the contaminant. The slurry containing the photocatalyst can be easily mixed within the reactor providing high surface area for reactions involving the photocatalyst to occur. The major drawback to these types of reactors is that once decontamination is complete the TiO_2 must be separated from the effluent stream for reuse. The separation processes involved in doing so are quite costly and time consuming.

Fixed media reactors are reactors in which the photocatalyst is fixed by some means within the reaction chamber. Since the photocatalyst is fixed within the reactor, fixed media reactors do not require the separation of the photocatalyst from the water post-treatment. However, treatment effectiveness is limited due to a smaller total TiO_2 surface area within the reactor.

Traditionally, the photocatalyst within a fixed media reactor would be attached to a long strip or plate of glass or some other material that would remain in the reactor at all times. As was stated before, the main drawback of this type of reactor is the extremely limited amount of photocatalyst within the reactor and therefore the limited surface area available for photocatalytic reactions to take place. A possible solution to this problem is to coat the photocatalyst on many small pieces of a material that can be easily fluidized and also easily separated from the water post-treatment. An example of this is a TiO_2/AC fluidized bed system that uses activated carbon coated with TiO_2 to degrade a brilliant red dye.⁴ Since the TiO_2 is coated on the surface of the small activated carbon pieces, it can be easily fluidized within the reactor and can also be

⁴ Geng, Q. and W. Cui (2010). "Adsorption and Photocatalytic Degradation of Reactive Brilliant Red K-2BP by TiO_2/AC in Bubbling Fluidized Bed Photocatalytic Reactor." Ind. Eng. Chem. Res. **2010**(49): 11321-11330.

physically separated from the exiting water stream both quickly and inexpensively.

The objective of this MQP is to investigate the possibility of fixing titanium dioxide on glass beads for TiO_2 /UV chemical oxidation. The possible advantages of using glass beads as a substrate for fixing the photocatalyst include increased TiO_2 surface area for reactions as compared to that available with a traditional fixed bed reactor, inexpensive and quick removal of the photocatalyst post-treatment, and the possibility of UV transmissibility through the glass substrate. Other research has been done to study the possibility and performance of fixing titanium dioxide on a small substrate such as activated carbon. The ability of glass beads to transmit UV light would be advantageous then since it would offer the benefits available using activated carbon as a substrate, but would also provide increased photocatalytic activity since passing UV light would effectively increase the surface area available for UV light to interact with the photocatalyst.

Background

Photocatalysis falls under the category of Advanced Oxidation Processes (AOPs) which means that it uses hydroxyl radicals ($\text{OH}\cdot$) to oxidize organic contaminants in the water. Hydroxyl radicals are powerful, non-selective oxidants which react at very fast rates. The radicals have a high oxidizing potential which is only surpassed by that of the fluorine molecule (Alvarez-Corena 2015). In order to understand how the hydroxyl radicals are formed within a photocatalytic reactor, it is important to first understand the properties of the catalyst and the radiation, and how they interact.

Catalyst Properties

Titanium dioxide is a semiconductor. A semiconductor has electrical conductive properties that lie between that of a metal (effective electrical conductor) and an insulator (ineffective electrical conductor). The difference between conductive and insulating materials is shown in Figure 1 below.

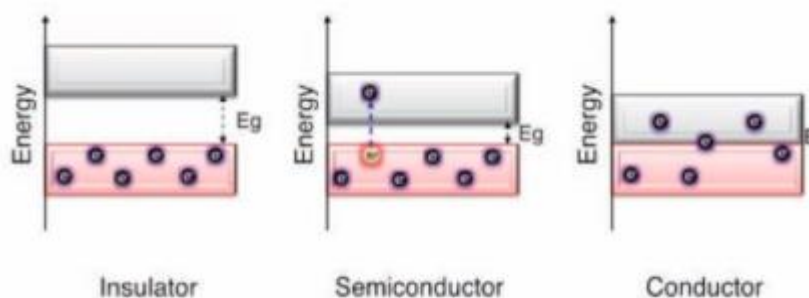


Figure 1: Illustration of the energy gap in semiconductive materials. Adapted from Alvarez-Corena 2015

As Figure 1 above shows, all three types of materials have a lower energy valence band (shown as the red band) and a higher energy conduction band (shown as the white band). Insulating and semiconducting materials both have a gap between the bands (an energy gap). Since the valence band is lower in energy, the electrons of the materials typically lie within it. For a material to be electrically conductive, the electrons must pass from the lower energy valence band to the higher energy conduction band. For insulators, this is nearly impossible since the energy gap is so large. For conductors, this is very easy since there is no energy gap. For semiconductors, the electrons

must be excited by heat or radiation and provided the energy needed to cross the energy gap. Once the electrons cross the energy gap, the semiconductive material begins to exhibit conductive properties.

The electron gaps of different photocatalysts used in the treatment of wastewater contaminants are compared in Table 1 below.

Table 1: Energy gaps for different materials

	TiO ₂ (Anatase)	TiO ₂ (Rutile)	ZnS	CdS
Energy Gap (eV)	3.2	3.0	3.6	2.4

ZnS has the highest energy gap followed by anatase TiO₂, rutile TiO₂, and CdS, in that order.

Radiation Properties

UV radiation is used to excite the electrons of the semiconductive photocatalyst within a photocatalytic reactor in order to cause them to jump from the valence band to the conductive band. UV radiation is an electromagnetic wave with wavelengths in the range of 100 nm to 400 nm. Radiation with lower wavelengths enters the x-ray region of the electromagnetic spectrum. Radiation with higher wavelengths enters the region of visible light.

Mechanisms of radical formation

There are 5 primary mechanism steps that take place in TiO₂ photocatalysis that are responsible for the degradation of contaminants in the water, although other side reactions do occur.

- 1) Charge-carrier generation
- 2) Charge transport
- 3) Charge trapping
- 4) Charge recombination
- 5) Overall TiO₂ surface mechanisms that occur among the other steps

Charge-carrier generation

UV light is used to provide energy to the electrons in the TiO_2 needed to cross the energy gap from the valence band to the conductive band. Generally, UV light with a wavelength of less than 387.5 nm provides enough energy for electrons to cross the energy gap for pure anatase (U.S. EPA, 1999). When an electron of TiO_2 travels from the valence band to the conduction band it leaves an electron hole in the valence band and creates an electron presence in the conduction band.

Charge transport

In this step, the charge that was previously generated in the lattice of the TiO_2 structure is now transported to the bulk face where the interactions with other compounds will take place. Charge separation and thermalization mechanisms are critical components in charge transport (Alvarez-Corena 2015).

Charge trapping

In this step, electrons are trapped on the TiO_2 surface by hydroxyl groups or other electron seeking molecules such as O_2 . A trap site is defined as a location where there is greater charge carrier stability. These sites typically are on the TiO_2 surface but can also be found on particle interfaces, grain boundaries, or in the bulk lattice. There are several factors limiting the rate of the charge trapping step including the structure of the lattice. The detrapping step consists of the localized electrons in the charge trapping step becoming free electrons.

Charge recombination

This step is the end of the charge generation mechanism and is considered an adverse outcome in a photocatalytic process because it decreases the probability of keeping a favorable condition for the oxidation of contaminants (Tang 2015). It involves the recombination of charges formed in previous steps and can decrease the production of radicals. Crystallinity plays a large role in this step. Factors such as surface deformities and defects play an important role in this mechanism (Alvarez-Corena 2015).

TiO₂ surface mechanisms

There are two surface mechanisms that occur on the surface of the TiO₂ molecule that allow for the degradation of organic contaminants in the water. Adsorbed oxygen and water molecules can interact with the charge carriers and produce active species such as hydroxyl radicals that have a high oxidation potential in the first mechanism. In the second mechanism, trapped electrons and electron holes can attack pollutants that are adsorbed to the photocatalyst surface.

Active species generation

There are two active species that are primarily responsible for the degradation of contaminants in the water. The first is the hydroxyl radical ($\bullet\text{OH}$). The second is the superoxide radical ($\text{O}_2^{\bullet-}$). Hydrogen peroxide, trapped electrons and O_2 are also produced but on a minor scale and do not contribute to the overall effectiveness of the photocatalytic process.

Hydroxyl radical formation

Hydroxyl radicals are considered to be one of the main species responsible for the degradation of organic material in the water. They are highly reactive and are able to degrade a wide range of pollutants within the water. Hydroxyl radicals are formed when adsorbed water molecules are oxidized by positive electron holes in the photocatalyst. Hydroxide molecules (OH^-) can also be oxidized by the electron holes to form hydroxyl radicals.

Superoxide radical formation

The superoxide radical ($\text{O}_2^{\bullet-}$) is formed through the reduction of adsorbed oxygen molecules by the electron that is present in the conduction band of the photocatalyst.

Adsorption

When the electrons of the photocatalyst jump from the valence band to the conductive band, the recombination of the hole and electron formed in each band can occur very quickly. Therefore, it is necessary for the species that will be interacting with the hole or electron, such as oxygen or water molecules, to be present at the site before the process begins. Adsorption is therefore extremely important.

Radical reaction mechanisms

The radicals formed on the surface of the TiO₂ will react with different organic contaminants and each other through a variety of mechanisms shown in the table below.

Mechanism	Example Reaction
Hydrogen abstraction	$\text{OH}^\cdot + \text{CHCl}_3 \rightarrow \text{CCl}_3^\cdot + \text{H}_2\text{O}$
Addition	$\text{OH}^\cdot + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_6 - \text{OH}$
Electron transfer	$\text{OH}^\cdot + [\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + \text{OH}^-$
Radical interaction	$\text{OH}^\cdot + \text{OH}^\cdot \rightarrow \text{H}_2\text{O}_2$

Figure 2: Mechanisms of hydroxyl reactions

Factors affecting degradation efficiency

There are many factors that can have a negative impact on the efficiency of the photocatalytic reactor such as pH, temperature, type of reactor, photocatalyst morphology, and UV intensity.

The effect of pH

The surface charge of the photocatalyst is influenced by the pH of the solution that it is in. Under low pH conditions, the surface of the photocatalyst has an increasingly positive charge. This leads to the adsorption of negatively charged molecules to the surface of the photocatalyst which can lead to a higher rate of radical formation since it is so dependent on adsorption of molecules to the photocatalyst surface.

The effect of temperature

Temperature has little effect on the efficiency of a photocatalytic reactor for temperatures between 20 and 80 °C. Temperatures above 80 °C have been shown to inhibit photocatalytic activity (Gaya and Abdullah 2008).

TiO₂ morphology

The morphology of TiO₂ refers to the form of the molecules such as the crystallinity, the phase, the particle size, and the surface area. These characteristics are factors that affect the efficiency

of the photocatalytic process (Porkodi and Arokiamary 2007). Titanium dioxide materials consist of crystalline and amorphous phases (Bertoni, Beyers et al. 2006).

Types of reactors

There are two main types of photocatalytic reactors used in the destruction of contaminants in wastewater streams, slurry and fixed-media reactors. There are advantages and disadvantages to each as described below.

Slurry reactors

Slurry reactors are the traditional type of reactor in which the photocatalyst (TiO_2) is mixed with an aqueous solution of the contaminant that is added to the reactor prior to treatment. There are advantages to this type of reactor including high surface area for UV contact with photocatalyst as well as photocatalyst and contaminant contact. Slurry reactors also provide a very uniform catalyst concentration within the reactor. The disadvantages to this type of reactor lie in the separation process. Since the photocatalyst is directly added to the reactor, it must be separated from the effluent stream. This process is very time consuming and expensive.

In his PhD thesis, Jose Alvarez-Corena utilized a slurry reactor to study the treatment of organic contaminants in the water. He mixed together aqueous solutions of contaminants and added titanium dioxide powder to them. The resulting solution was a slurry which was added directly into the reactor prior to any irradiation. His reactor was a bench-scale reactor and was set up as displayed by Figure 3 below.

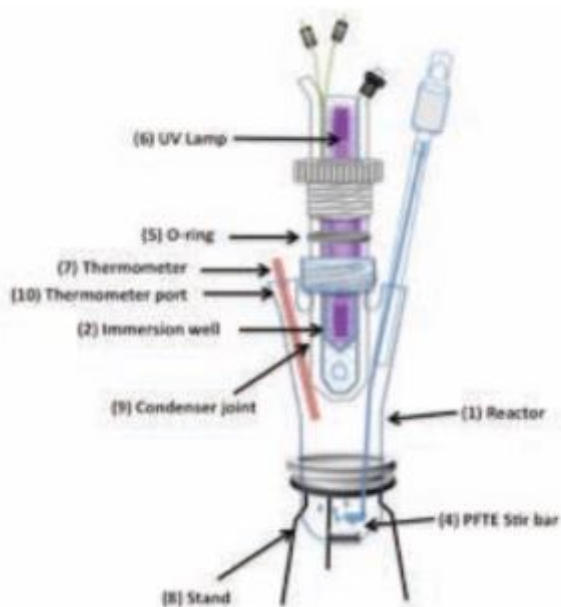


Figure 3: Diagram of the bench-scale photocatalytic reactor used by Jose Alvarez-Corena

As you can see from Figure 3 above, in the bottom of the reactor there is a space in the glass where the slurry is placed and where the reactions occur. A stirring bar is placed at the bottom of the reactor space, ensuring the complete mixing of the slurry during the reaction. The reactor was a one liter water-jacketed batch photoreactor supplied from Ace Glass in New Jersey and was equipped with a double-walled quartz immersion well and a removable inner cooling tube. The UV lamp was a medium-pressure, 100-watt mercury vapor lamp which emitted approximately 40-48% of its radiated energy in the UV spectrum. His reactor was also equipped with a refrigerated bath circulator which kept the reactor temperature at 20 °C.⁵

A slurry reactor was also utilized by Ioannis Konstantinou and his team when they studied the photocatalytic degradation of propachlor. Titanium dioxide powder was added to aqueous solutions of the contaminant and the resulting slurry was irradiated in the reactor under conditions that mimicked solar irradiation. They used a Suntest CPS+apparatus from Heraeus equipped with a 1500 W xenon arc lamp (a bench-scale reactor). Special glass filters were used

⁵ Alvarez-Corena, J. R. (2015). Heterogeneous photocatalysis for the treatment of contaminants of emerging concern in water. Department of Civil and Environmental Engineering, Worcester Polytechnic Institute. **PhD**: 125.

to restrict any irradiation with a wavelength less than 290 nm and an average irradiation intensity of 750 W/m² was maintained throughout the experiments.⁶

Yusuke Kakuma also performed experiments using a slurry reactor while studying the difference in photocatalytic mechanisms of rutile and anatase titanium dioxide⁷. These are just a few of the examples available of the use of slurry reactors in TiO₂/UV photocatalytic research. Many researchers use slurry reactors when studying photocatalytic reactions because of the large amount of photocatalyst that can be contained within the reactor and the corresponding increased photocatalytic activity due to increased photocatalyst surface area.

Fixed-media reactors

Fixed-media reactors, as the name implies, consist of photocatalyst fixed on media that is placed within the reactor. There are two types of fixed-media reactors, non-removable media reactors and removable media reactors.

Non-removable media reactors

Non-removable media reactors comprise of a media that is fixed within the reactor itself that is coated in the photocatalyst. This can be a sheet of metal or glass as well as bars of metal or glass. A diagram of a non-removable media reactor is shown in Figure 4 below.

⁶ Konstantinou, I. K. (2002). "Photocatalytic degradation of propachlor in aqueous TiO₂ suspensions. Determination of the reaction pathway and identification of intermediate products by various analytical methods." , *ibid.*

⁷ Kakuma, Y., et al. (2015). "Difference in TiO₂ photocatalytic mechanism between rutile and anatase studied by the detection of active oxygen and surface species in water." Phys Chem Chem Phys **17**(28): 18691-18698.

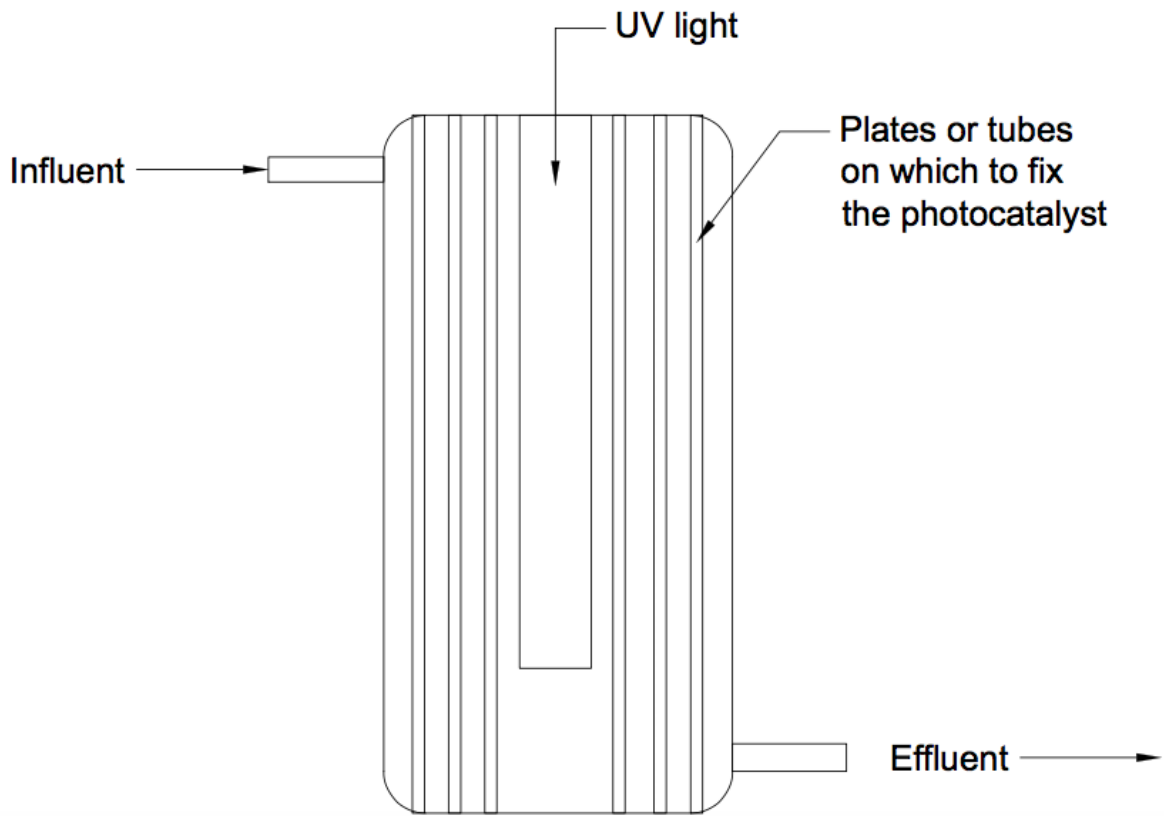


Figure 4: Diagram of a typical non-removable fixed media photocatalytic reactor

The advantages to using this type of reactor are mainly in the separation process. When the photocatalyst is fixed on a media such as a sheet of glass within the reactor, no separation process is needed to remove the photocatalyst from the reactor effluent. The disadvantages to using this type of reactor lie in the limited photocatalyst surface area. This type of reactor possesses a smaller surface area for UV-TiO₂ and TiO₂-contaminant interactions, as compared to that offered by a slurry reactor, which decreases the photocatalytic activity and effectiveness of the reactor.

Nicola Peill and Michael Hoffmann of the California Institute of Technology used a non-removable fixed media reactor in their study of the degradation of 4-chlorophenol using a fiber optic cable reactor. Their reactor used 3mm quartz rods and 1mm fiber optic cables coated in TiO₂. They used fiber optic cables to transmit the UV light from a UV lamp into the reactor

rather than placing the UV bulb directly into the reactor as is traditionally done with non-removable fixed-media reactors. A diagram of their reactor is shown below.⁸

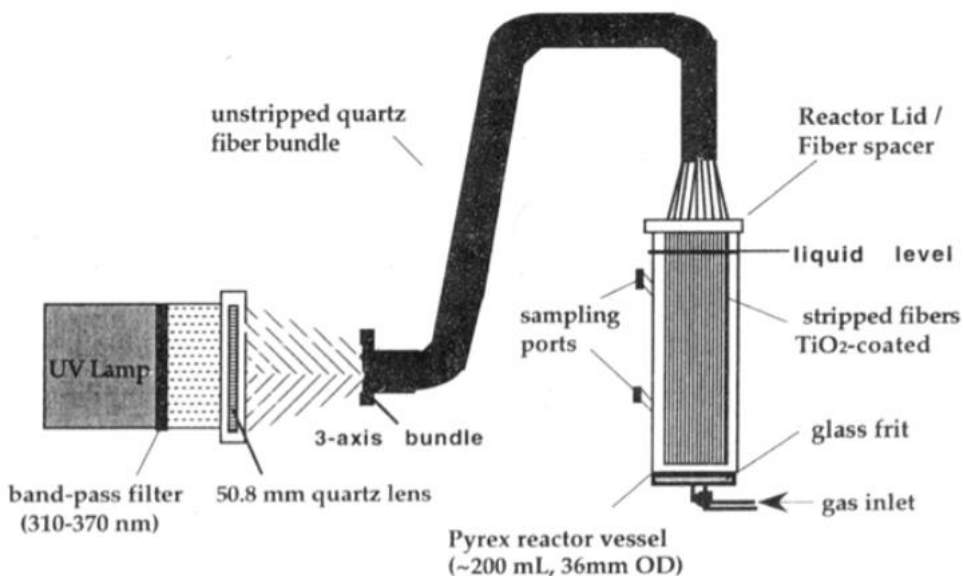


Figure 5: A diagram of the fiber optic non-removable fixed media photocatalytic reactor used by Nicola Peill and Michael Hoffmann

Removable media reactors

Removable media reactors are an emerging type of reactor. They consist of small diameter pieces of media that are coated in photocatalyst and can be easily fluidized or removed from the reactor taking the photocatalyst with them. Examples of the media that can be used in this type of reactor are activated carbon, glass beads, quartz sand, etc. The advantages to using this type of reactor include those of non-removable media reactors but also have the added benefit of an increased amount of surface area available for UV-TiO₂ and TiO₂-contaminant interactions. This in turn increases the photocatalytic activity as compared to that of non-removable media reactors.

⁸ PEILL, N. J. and M. R. HOFFMANN (1995). "Development and Optimization of a TiO₂-Coated Fiber-Optic Cable Reactor: Photocatalytic Degradation of 4-Chlorophenol." *Environ. Sci. Technol.* **29**: 2974-2981.

, *ibid.*

Qijin Geng and Wenwen Cui of Weifang University in China fixed titanium dioxide on activated carbon pieces using the spin coating method. They then built a reactor which could fluidize the photocatalyst and tested the degradation of a red dye.⁹

While fixing the photocatalyst on small carbon pieces is useful, no UV radiation can pass through the carbon pieces and the degrading capacity of the reactor per unit Titanium and UV is lessened. Fixing the photocatalyst on small glass beads would allow the material to be fluidized in a similar manner as the carbon pieces but could also pass some UV light through the beads which could enhance the degrading capacity of the reactor.

The only application of TiO₂ adhesion to glass found in literature is that of self-cleaning glass applications. Self-cleaning glass is a relatively new product that has entered the market which makes use of TiO₂'s photocatalytic activity. A film of TiO₂ is applied to glass sheets which make up the external face of a window. When UV radiation hits the TiO₂ and activates it, any dirt or dust particles that may be on the face of the window are degraded and washed off with the next rain.

⁹ Geng, Q. and W. Cui (2010). "Adsorption and Photocatalytic Degradation of Reactive Brilliant Red K-2BP by TiO₂/AC in Bubbling Fluidized Bed Photocatalytic Reactor." Ind. Eng. Chem. Res. **2010**(49): 11321-11330.

Hypothesis

This MQP seeks to determine the feasibility and usefulness of fixing TiO_2 on small diameter glass beads that can be used in a removable media reactor. The ability of UV light to pass through the beads will be estimated by observing the apparent rate of dye degradation for various vertical layers of beads. If UV light is able to pass through the glass beads, the degradation rate (due to uniform photocatalytic activity) will be greater with larger numbers of beads as compared to a single layer of beads.

Materials

- Reagent alcohol from Fisher scientific, HPLC grade
- Thermo Scientific Nanopure, RO system
 - Water from this machine is what is referred to as “DI water” in this report
- Titanium (IV) oxide, Aeroxide P25 from Fisher Scientific (Acros Organics)
- Polyethylene oxide (MW 100,000) from Fisher Scientific (Alfa Aesar)
- Polyethylene glycol (MW 10,000) from Fisher Scientific (Alfa Aesar)
- 3mm solid glass beads from Fisher Scientific
- 2,4 pentanedione from Fisher Scientific (Acros Organics)
- UVP UVS-28 UV lamp, 8 watts, 2 tubes, 254 nm
- Methylene blue from Fisher Scientific
- 2-propanol from Fisher Scientific

Methodology

The methodology for getting the titanium dioxide to adhere to the glass beads was gathered and adapted from a variety of existing methodologies used by other researchers in the area of self-cleaning glass applications.

TiO₂ Application

First the glass beads were cleaned by rinsing with DI water followed by acetone. They were again rinsed with DI water followed by ethanol. They were a third time rinsed with DI water followed by isopropyl alcohol. They were rinsed a final time with DI water and stored in DI water overnight. Next, 420 μ L of 2,4-pentanedione was added to 1.2 g of P25 TiO₂ in a mortar and ground for 3 minutes. 1 mL of DI water was added and the mixture was ground again. 0.24 g of polyethylene oxide (avg MW = 100,000) was ground into the mixture followed by a further 1 mL of DI water. 0.24 g of polyethylene glycol (avg MW = 10,000) was ground into the mixture followed by 1 mL of DI water. The steps to prepare the TiO₂ solution up to this point were repeated and a final 10 mL of DI water was ground into the mixture at the end. At this point, a non-uniform white solution was obtained.

The glass beads were then submerged in the solution and mixed to ensure that the viscous portion of the solution came in contact with each bead. The beads were allowed to sit in the solution for at least 10 minutes. The entire solution along with the beads was then placed in a drying oven overnight to evaporate the excess water. The beads were then calcined at 400 °C for at least 3 hours. The beads were then visually inspected for color change and stored in plastic bottles.

Experiments

Before any experiments were completed with differing layers of beads, a preliminary experiment was executed to determine whether or not the TiO₂ was adhering to the glass beads properly. First, the beads were placed in a beaker with an aqueous methylene blue dye solution. A sample of the solution was removed using a pipette and measured in a spectrophotometer. The UV light was then placed over the beaker and turned on. In intervals of 15 minutes, samples were taken and measured using the spec for a total of 30 minutes. The beads were then rinsed with DI water and the experiment was repeated. The beads were then rinsed and stored in the dryer until the next experiments.

In order to determine the apparent rate constant of the degradation of methylene blue with both a single layer and three to four layers of beads, the following experiment was performed. First, a single layer of beads previously treated with TiO₂ were placed in the bottom of a 500 mL beaker and the beaker was filled to the 400 mL line with an aqueous solution of methylene blue dye. Next, the spec was zeroed using DI water. A sample of the solution was taken from the beaker with a syringe filter and placed in the spectrophotometer and the reading was recorded. Next, the UV light was placed on top of the beaker and turned on. Samples of the solution were periodically taken and measured in the spectrophotometer. The experiment was run for 30 min. The experiment was then repeated with three to four layers of beads.

Determination of dye concentration

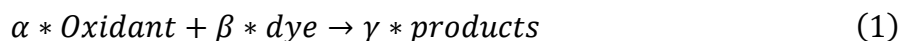
A spectrophotometer was used to determine the concentration of the methylene blue dye in the reactor at various points throughout the experiment. The spec was set to 611 nm and zeroed with DI water. The results from the spec were recorded and converted to a concentration of methylene blue dye using an experimentally determined calibration curve¹⁰.

Determination of reaction order

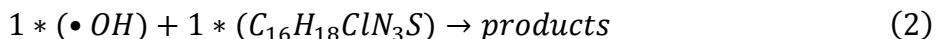
In order to determine the apparent rate constants for the two experiments, it is first necessary to determine the order of the reaction for the photocatalytic degradation of methylene blue dye. Two methods were used to analyze the possible reaction order and the most logical conclusion was selected.

Elementary rate law method

In determining the order of the reaction between the oxidants and the contaminants, it will be assumed that the reaction is elementary. The equation below shows the general reaction of an oxidant (mainly hydroxide radicals) reacting with the methylene blue particles to form products.



The reaction can be more specifically written as is shown by the equation below.



As the reaction shows, one hydroxide radical reacts with one molecule of the methylene blue. The elementary rate law can then be shown as it is in the equation below.

$$r_a = -k[\bullet OH]^\alpha [C_{16}H_{18}ClN_3S]^\beta \quad (3)$$

¹⁰ Calibration curve developed by Jose Alvarez

Assuming that the radical concentration does not change since the radicals are constantly being formed as UV light and water molecules interact with the photocatalyst, the reaction can be simplified to:

$$r_a = -k_1[C_{16}H_{18}ClN_3S]^\beta \quad (4)$$

This demonstrates that the rate is only dependent on the concentration of the dye and is independent from the concentration of the radicals. Looking at the reaction shown in Equation (2), $\beta = 1$. Therefore, it is reasonable to assume that the reaction is first order.

Graphical method

Another method was used to determine the order of the reaction. The rate equation shown above (equation (4)) was used in the equation describing the performance of a batch reactor shown below.

$$\frac{dC}{dt} = -kC \quad (5)$$

- where C is the concentration of the methylene blue

Integrating this equation yields

$$\frac{dC}{C} = -kt \, dt \quad (6)$$

Solving

$$\ln(C) = -kt + c \quad (7)$$

- where c is a constant of integration

Applying a boundary condition at $t = 0$ of $C = C_0$ yields

$$\ln(C) = -kt + \ln(C_0) \quad (8)$$

Plotting $\ln(C)$ vs t will yield a straight line with a slope of $-k$ and a y-intercept of $\ln(C_0)$ for a first order reaction. Similarly, the equation for a batch reactor can be manipulated for a zero and second order irreversible reaction and plotted as a straight line. A plot of C vs t will yield a straight line with a slope of $-k$ and a y-intercept of C_0 for a zero order reaction. A plot of $1/C$ vs time will yield a straight line with a slope of k and a y-intercept of $\frac{1}{C_0}$ for a second order reaction.

A graphical representation of this is shown below where $[A]$ is the concentration of the methylene blue dye and is equal to what is referred to as “C” above.

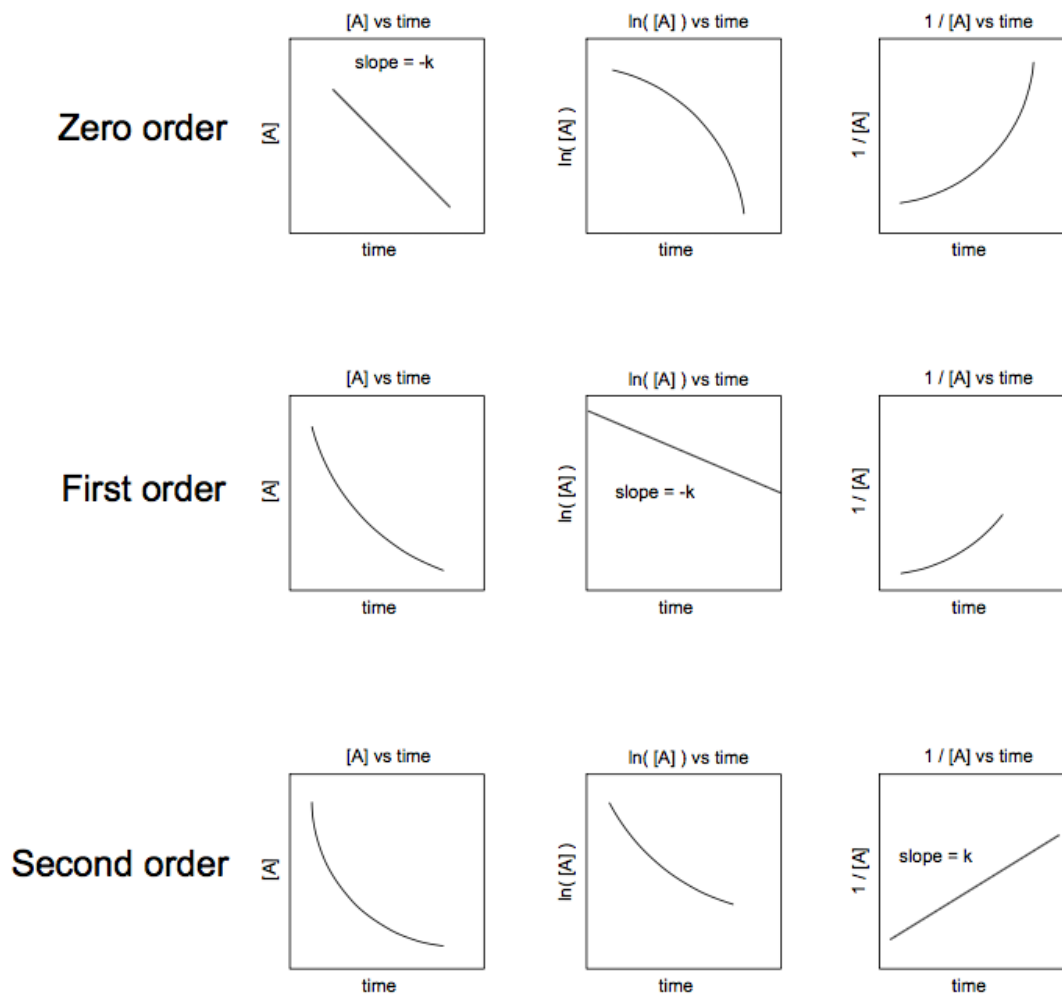


Figure 6: Graphs representing methodology for determining reaction order adapted from <http://www.chem.purdue.edu/gchelp/howtosolveit/Kinetics/IntegratedRateLaws.html>

As Figure 6 above shows, a zero order reaction will yield a straight line when the concentration of the dye is plotted against time. A plot of the natural log of the concentration of the dye vs. time and a plot of the inverse of the concentration of the dye vs. time will yield lines that are non-linear. A first order reaction will be linear for the natural log of the concentration of the dye vs. time and non-linear for the other two plots. Finally, a second order reaction will be linear for the inverse of the concentration of the dye vs. time and non-linear for the other two plots. All three plots were made from data collected in the lab and each was fitted with a linear trendline. The R^2 values were analyzed to determine which plot had the most linear fit.

Determination of reaction rate constant

Once the order of the reaction is known, finding the reaction rate constant is straightforward. Reaction rate constants can be determined from data of concentration as a function of time as is shown in Figure 6 above. For a zero order reaction, the reaction rate constant is the negative of the slope of the line when the data is plotted as the concentration of the dye vs. time. The same is true for a first order reaction when the data is plotted as the natural log of the concentration of the dye vs. time. For a second order reaction, the reaction rate constant is the slope of the line when the data is plotted as the inverse of the concentration of the dye vs. time.

Determination of UV permissibility

In order to determine if UV light was able to pass through the glass beads, the reaction rate constants were analyzed for the single layer of beads experiment and for the three to four layer of beads experiment. A higher reaction rate constant with a higher number of layers of beads as compared to the single layer of beads could indicate that the beads were able to pass UV light.

Results and Discussion

Application of the photocatalyst to the glass beads

After completing the preliminary testing, it seemed that the methods used were successful in adhering the TiO_2 to the glass beads. Before the beads were treated with the titanium solution, they appeared to be clear. After being treated, there was an obvious white layer on the surface of the beads. Since the titanium solution and the titanium dioxide powder are both white it was clear that the solution had adhered to the surface of the beads. Since the beads were placed in a muffle furnace, it was assumed that all of the organic components of the titanium solution were evaporated and what remained adhered to the surface of the beads was almost completely composed of titanium dioxide. It was also observed that during preliminary trials, the TiO_2 would easily come off of the glass beads with little or no agitation. However, once the beads were rinsed thoroughly, it became clear that what was coming loose in the preliminary trials was simply excess photocatalyst and that a layer of the photocatalyst still remained after the beads were rinsed. Figure 7 below shows samples taken from the preliminary testing.

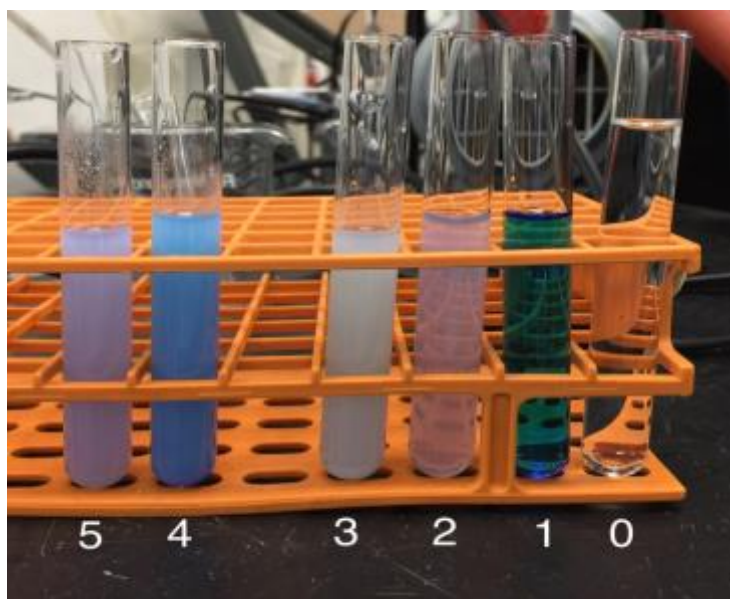


Figure 7: Samples taken from preliminary testing

The samples shown in Figure 7 above are numbered zero through five. Zero represents the DI water used to calibrate the spectrophotometer. Numbers one through three represent samples

taken throughout the first preliminary experiment with one being the first sample taken before the UV light was turned on and three being the last sample taken. Samples four and five represent samples taken from the second preliminary experiment. As can be seen qualitatively, the samples decrease in blueness as the first preliminary experiment continues but also increase in whiteness. The samples of the second preliminary experiment seem to decrease in blueness but to remain at relatively the same whiteness. This would indicate that the concentration of the methylene blue dye within the reactor decreased with each experiment as would be expected given the presence of the TiO_2 on the glass beads. The qualitative increase in whiteness is explained by a combination of excess TiO_2 powder within the reactor and TiO_2 that was removed from the glass beads by agitation. Since the beads were dried and calcined in the TiO_2 preparation solution, an excess amount of TiO_2 powder was present with the beads. Since the beads were not rinsed thoroughly before the preliminary experiments, much of that excess TiO_2 was placed into the reactor along with the beads. In addition, it is probable that multiple layers of TiO_2 were adhering to each bead. The outermost layers could then have a weaker grip to the layers beneath them while the innermost layers would most likely have a stronger grip on the bead itself. This would make it easy for the outermost layers to be dislodged by agitation.

Reaction order

The following is the reaction order as determined by each of the two methods used.

Reaction analyzation

The reaction is determined to be first order according to this method as was described in the methodology.

Batch reaction method

The plots of the concentration of the dye vs. time, the natural log of concentration of the dye vs. time, and the inverse of the concentration of the dye vs. time are shown in Figure 8, Figure 9, and Figure 10 below.

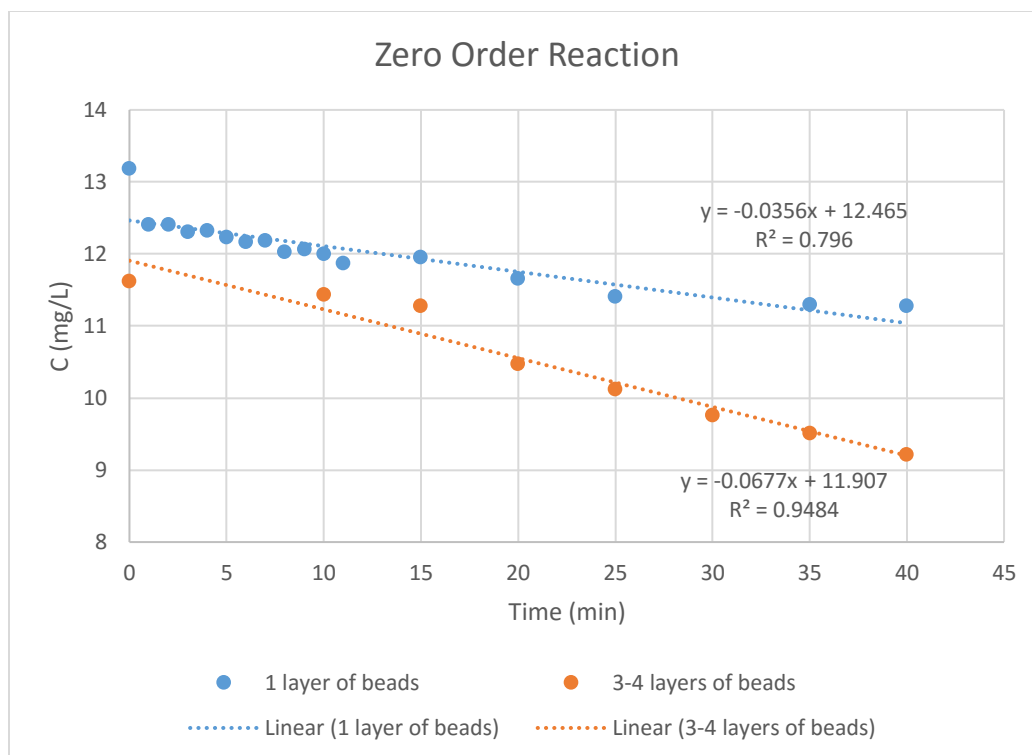


Figure 8: Graph to determine if the reaction is zero order

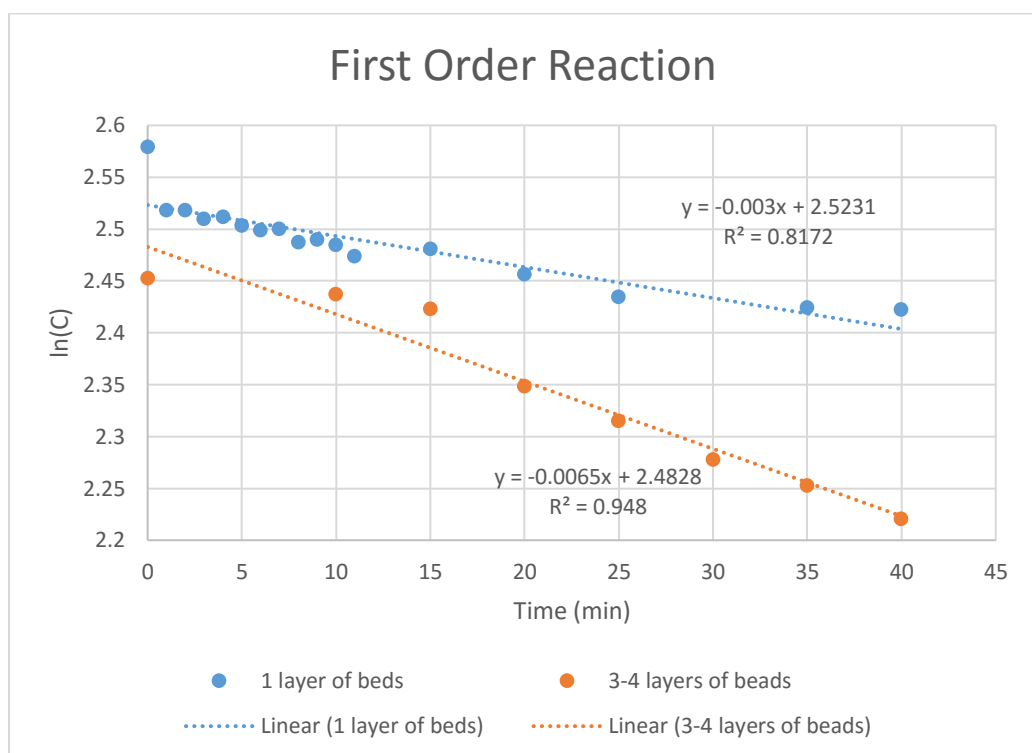


Figure 9: Graph to determine if reaction is first order

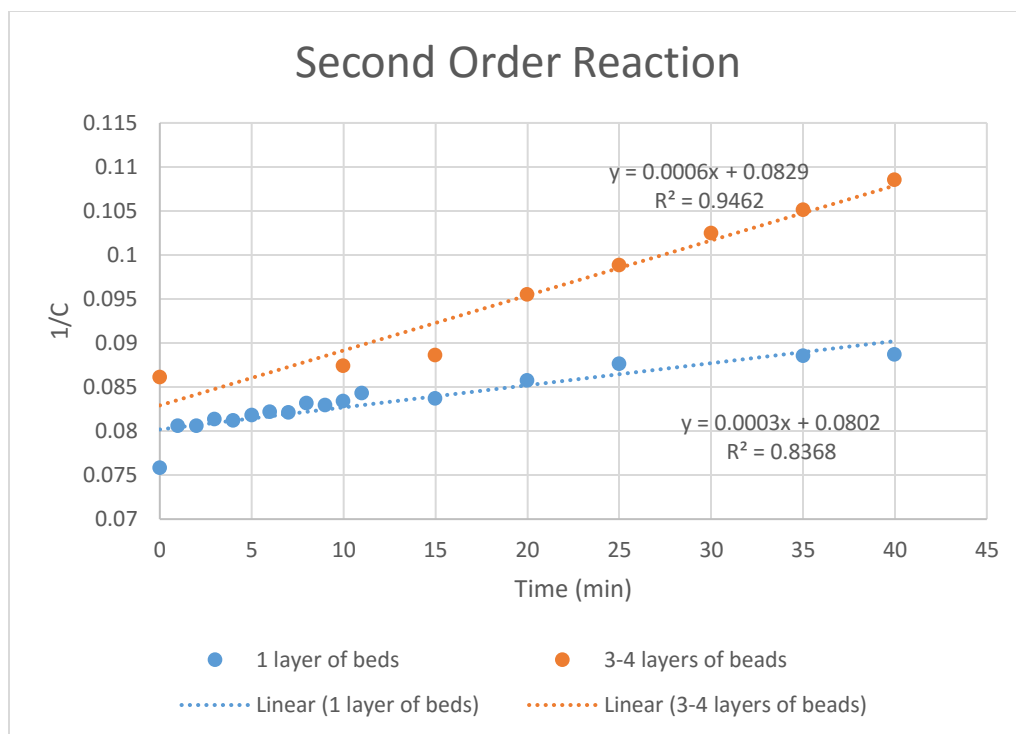


Figure 10: Graph to determine if reaction is second order

As Figure 8 shows, the concentration of the dye within the reactor decreases with time for one layer of beads as well as for three to four layers of beads. This is to be expected since the dye should be degraded by the photocatalytic reaction over time. In order to better understand the order of the reaction (as is determined by this method), the plot with the most linear data points must be found. A table of the R^2 values from each trendline will give more insight into this matter as Table 2 below.

Table 2: R squared values for the three graphs used to determine the reaction order

	Zero Order	First Order	Second Order
1 layer of beads	0.79603	0.81717	0.83685
3-4 layers of beads	0.94845	0.94798	0.94621

As Table 2 displays, the highest R^2 value for the experiment with one layer of beads is the second order reaction. However, the highest R^2 value for the experiment with three to four layers of beads is the zero order reaction. Since the difference between the R^2 value for the 3-4 layers of beads experiment at zero and second order is only 0.0224 and all values are greater than 0.9,

using this method it would be justifiable to say that the reaction could be either first, second, or third order. Since the R^2 value for the zero order 1 layer of beads experiment is less than 0.8, it would not be justifiable by this method to say that the reaction is zero order. Since the difference between the first and second order R^2 values for the 1 layer of beads experiment is only 0.01968, it is justifiable to say that the reaction could be either first or second order by this method.

Overall determination of reaction order

Given the fundamental understanding of the steps involved in the degradation of the dye, it is acceptable to assume that one hydroxyl radical molecule reacts with one molecule of the dye. This would indicate that the reaction is first order when the oxidant is in excess. Given that the reaction could be first or second order by the graphical analysis and that many reactions in the environmental engineering field are modeled as first order reactions, it will be assumed that this reaction is first order.

Apparent reaction rate constant

Since the reaction is first order, the reaction rate constant of each experiment is simply the negative of the slopes given in Figure 9. They are listed in Table 3 below.

Table 3: Reaction rate constants for each experiment

	Rate constant (min^{-1})
1 layer of beads	0.003
3-4 layers of beads	0.0065

As Table 3 shows, the reaction rate constant for the experiment with three to four layers of beads is more than two times greater than the reaction rate constant for the experiment with just a single layer of beads. This indicates that the degradation of the methylene blue dye is more effective with multiple layers of beads than it is with only one layer of beads.

Comments

Although the rate constant of the 3-4 layer of beads experiment is nearly twice as great as the rate constant of the 1 layer of beads experiment, this does not entirely indicate that UV light is

passing through the beads. Other factors influence the rate constants. For instance, the amount of photocatalyst per unit volume of methylene blue dye was not constant between the experiments. When there was just one layer of beads in the reactor the reactor was filled to the 400 mL mark. When there were multiple layers of beads in the reactor, the reactor was also filled to the 400 mL mark. Because of this, the amount of photocatalyst per unit volume of solution was not constant between the experiments. This could influence the reaction rate constant to be greater for the experiment with three to four layers of beads than it would be if the photocatalyst per unit volume of solution ratio were kept constant.

In their study of the decomposition of aqueous hydroquinone, Qijin Geng, Qingjie Guo, Changqing Cao, and Lintong Wang studied the kinetics of their reaction of interest. They found that for a slurry reactor, their apparent rate constants varied from 0.002632 to 0.01003 min⁻¹ with the ratios of TiO₂ to hydroquinone ranging from 0.18 to 0.98 wt. %.¹¹ This demonstrates that the rate constants found in this MQP are comparable to those found by these researchers. Furthermore, it demonstrates effective degradation of a contaminant comparable to that demonstrated by a slurry reactor.

It was also found that the rate constants determined in this report exceeded those determined by Qijin Geng and Wenwen Cui who used activated carbon as a substrate on which to fix TiO₂ for use in their designed bubbling fluidized bed photocatalytic reactor. A figure from their findings is shown below.

¹¹ Geng, Q., et al. (2008). "Investigation into NanoTiO₂ ACSPCR for Decomposition of Aqueous Hydroquinone." Ind. Eng. Chem. Res. **47**: 2561-2568.

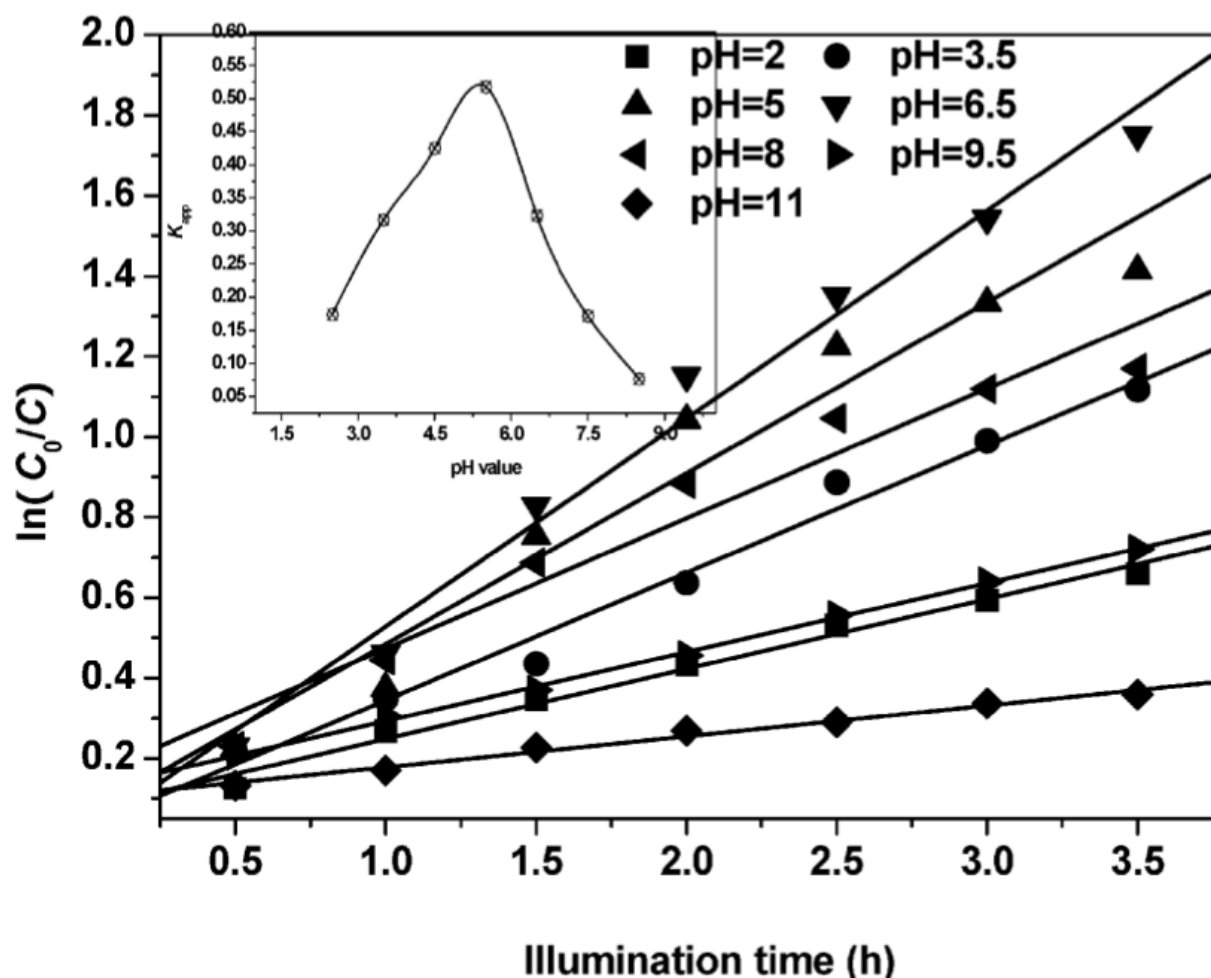


Figure 11: A diagram taken from (Geng and Cui 2010)

As you can see from Figure 11 above, the researchers determined that their reaction was first order since the units on the larger graph's y-axis are the natural log of the concentration. In the smaller graph, a plot of the apparent rate constant K vs the solution pH is shown. In order to compare the results found by Geng and Cui, the correct rate constant from their results must be chosen at a similar pH to that used in the experiments for this report. Since the solutions used in this report were mainly comprised of pure water, it will be assumed that a comparable pH value would be about 7. Reading from Figure 11 above, at a pH of 7, the apparent rate constant for the degradation of brilliant red dye is about 0.25 hr^{-1} . Converting to inverse minutes yields a value of about 0.0042 min^{-1} .¹² This is greater than the value of 0.003 min^{-1} that was found in this report

¹² Geng, Q. and W. Cui (2010). "Adsorption and Photocatalytic Degradation of Reactive Brilliant Red K-2BP by TiO_2/AC in Bubbling Fluidized Bed Photocatalytic Reactor." *Ind. Eng. Chem. Res.* **2010**(49): 11321-11330.

for one layer of beads but less than the value of 0.0065 min^{-1} that was found for three to four layers of beads. This further indicates that UV light may be passing through the glass beads, enhancing the photocatalytic activity as compared to that of activated carbon or other substrates that are non-transmissible to UV light.

Although the results from these comparisons are promising, the apparent reaction rate constant found by Jose Alvarez-Corena was 0.49 min^{-1} for the degradation of 17β Estradiol. This would indicate that the rate constant found in this MQP is 100 times less than that found by Jose and the degradation is not as effective. However, several factors do affect the apparent rate constant of the reaction such as the contaminant, the UV source, the photocatalyst to contaminant ratio and the pH. As can be seen from Figure 11, the apparent rate constants found by Geng and Cui varied from a low of 0.07 hr^{-1} to a high of 0.53 hr^{-1} with pH ranging from 0.5 to 3.5. It is evident that the rate constant is very dependent on the pH of the solution. Factors like pH were not necessarily kept constant between the studies done by these researchers and the experiments performed in this MQP. Further research must be done to compare the effectiveness of the treatment with glass beads to that of a slurry or other type of reactor by holding constant some of these variables.

Conclusion

It was demonstrated that the apparent reaction rate constant for multiple layers of beads was greater than that for a single layer of beads. This indicates that UV light was likely able to pass through the beads and interact with contaminants on lower levels of the beads. It was also demonstrated that the apparent reaction rate constants discovered in this MQP were comparable to those found by other researchers, particularly those found using a slurry reactor or activated carbon in a bubbling fluidized bed reactor. This is a positive result since slurry reactors typically achieve relatively high degradation rate constants. Since this MQP found that comparable degradation can be performed using glass beads as a substrate for fixing a photocatalyst as compared to using a slurry, and that equivalent or better degradation rate constants can be achieved using glass beads rather than activated carbon, it can be concluded that glass beads are a promising substrate for photocatalysis. However, since it was also found that the rate constant found in this report was 100 times smaller than that found by Jose Alvarez-Corena who used a slurry reactor to degrade 17 β Estradiol, it is recommended that further research be done to perform a more in-depth analysis of the effectiveness of using glass beads as a substrate to eliminate variables such as contaminant type, solution pH, and photocatalyst concentration in order to obtain more comparable and reliable results.

Recommendations for future research

There is substantial research that could be done to further study the feasibility of using glass beads in a TiO₂/UV photocatalytic reactor.

Application of the photocatalyst

Further research should be done to find a way to adhere a greater amount of the photocatalyst to the surface of the beads. One possible solution would be to use porous glass beads. Robuglass makes porous beads in 1.5, 4, and 8 mm diameter. They are made with borosilicate glass and have pore sizes of 60 microns. Using porous glass beads could increase the amount of photocatalyst per bead since the surface area of porous glass beads would likely be greater than that of non-porous glass beads. In addition, it is possible that the photocatalyst could sit within the pores and would not be dislodged from the surface of the beads by physical contact with other surfaces. This would be beneficial since it would increase the amount of time that the beads could be used before they would need to be re-treated and it would also keep the amount of photocatalyst in the reactor effluent lower.

Comparison to other types of photocatalyst support

Further research should also be done to test other types of support for the photocatalyst such as activated carbon or activated alumina and compare the results to those obtained using glass beads. This would give a clearer picture into the benefits of using glass beads over other photocatalyst supports, particularly whether or not they exhibit enhanced photocatalytic activity possibly due to UV transmissibility. This would require the researcher to find a way to standardize the amount of photocatalyst within each batch of photocatalyst. Experiments could be run with differing layers of each photocatalyst support and the reaction rate constants of each photocatalyst support from each experiment could be compared.

Considerations

Certain considerations should be taken into account before any further work is done. Factors such as initial dye concentration, pH, photocatalyst concentration, strength of the UV light, and

others affect the degradation of the dye. As many of these factors as possible should be kept constant.

Reference List

Alvarez-Corena, J. R. (2015). Heterogeneous photocatalysis for the treatment of contaminants of emerging concern in water. Department of Civil and Environmental Engineering, Worcester Polytechnic Institute. **PhD**: 125.

Bertoni, G., et al. (2006). "Quantification of crystalline and amorphous content in porous samples from electron energy loss spectroscopy." Ultramicroscopy **106**(7): 630-635.

Chiarello, G. L., et al. (2011). "Effect of titanium dioxide crystalline structure on the photocatalytic production of hydrogen." Photochem Photobiol Sci **10**(3): 355-360.

EPA, U. (2016, May 25, 2016). "History of the Clean Water Act." 2016, from <https://www.epa.gov/laws-regulations/history-clean-water-act>.

Gaya, U. I. and A. H. Abdullah (2008). "Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems." Journal of Photochemistry and Photobiology C: Photochemistry Reviews **9**(1): 1-12.

Geng, Q. and W. Cui (2010). "Adsorption and Photocatalytic Degradation of Reactive Brilliant Red K-2BP by TiO₂/AC in Bubbling Fluidized Bed Photocatalytic Reactor." Ind. Eng. Chem. Res. **2010**(49): 11321-11330.

Geng, Q., et al. (2008). "Investigation into NanoTiO₂ ACSPCR for Decomposition of Aqueous Hydroquinone." Ind. Eng. Chem. Res. **47**: 2561-2568.

Kakuma, Y., et al. (2015). "Difference in TiO₂ photocatalytic mechanism between rutile and anatase studied by the detection of active oxygen and surface species in water." Phys Chem Chem Phys **17**(28): 18691-18698.

Konstantinou, I. K. (2002). "Photocatalytic degradation of propachlor in aqueous TiO₂ suspensions. Determination of the reaction pathway and identification of intermediate products by various analytical methods."

PEILL, N. J. and M. R. HOFFMANN (1995). "Development and Optimization of a TiO₂-Coated Fiber-Optic Cable Reactor: Photocatalytic Degradation of 4-Chlorophenol." Environ. Sci. Techno/ **29**: 2974-2981.

Porkodi, K. and S. D. Arokiamary (2007). "Synthesis and spectroscopic characterization of nanostructured anatase titania: A photocatalyst." Materials Characterization **58**(6): 495-503.

USA.gov (2016). "Contaminants of Emerging Concern in the Environment." Retrieved October 2016, 2016, from <http://toxics.usgs.gov/investigations/cec/index.php>.

Tang, H., et al., *Photoluminescence in TiO₂ anatase single crystals*. Solid State Communications, 1993. **87**(9): p. 847"850.

Center for Environmental Research, I., *Handbook: advanced photochemical oxidation processes*. EPA 625/R. 1999: Center for Environmental Research Information, National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency.