

# Treatment of Alaska Water Using Titanium Dioxide Photocatalyst

By  
Athea M. Alabanzas  
B.S. Engineering/Specialization in Mechanical Engineering

Project Adviser  
Dr. Nyrée McDonald

Expected Graduation Date  
May 2008

Date of Report Submittal  
May 30, 2008

University of Alaska Anchorage  
School of Engineering  
3201 Providence Drive  
Anchorage, AK 99508

## **ACKNOWLEDGMENTS**

I would like to thank the UAA Undergraduate Research Program for giving me this wonderful opportunity to apply my knowledge and skills in engineering as well as learn new ones through research. I am also greatly indebted to the sponsors of the Parasca Science Research Award, Dorin and Argentina Parasca, for without them this research would not have been possible. My heartfelt gratitude also goes out to my adviser, Dr. Nyrée McDonald who with her engineering expertise, guided and supported me throughout the project. Lastly, I extend my sincerest thanks to those who assisted me in all my laboratory needs: Maury Riner and Theresa Alabanzas of the UAA Chemistry Department; Dr. Birgit Hagedorn and Benjamin Applegate of ASET Laboratory; my fellow engineering students, Shawn Takak and Jenny Jemison.

## **ABSTRACT**

The potential harmful environmental implications of pharmaceuticals and personal care products (PPCP's) continue to worry scientists. Although the specific effects of these compounds are not entirely identified, water treatment processes have to be employed to ensure water quality. Removal of PPCP from wastewater or drinking water requires advanced oxidation processes, such as ozonation and activated titanium dioxide (TiO<sub>2</sub>). This proposal investigates the impact ultraviolet (UV) light activated TiO<sub>2</sub> may have on the degradation of common PPCP's like caffeine and aspirin. In addition, the treatise examines the degradation of natural organic matter by UV activated TiO<sub>2</sub>. The TiO<sub>2</sub> catalyst will be added to the water and exposed to UV activation with samples of the water taken periodically and tested to determine a variety of water quality parameters including total organic carbon and color. All tests are performed in accordance with the Standard Methods for the Examination of Water and Wastewater manual. This project seeks to determine the effectiveness of titanium dioxide photocatalysis in the treatment of Alaska waters.

# TABLE OF CONTENTS

|  |    |
|--|----|
| <b>ACKNOWLEDGMENTS</b> .....                     | 1  |
| <b>ABSTRACT</b> .....                            | 2  |
| <b>INTRODUCTION</b> .....                        | 4  |
| <b>METHODS AND PROCEDURES</b> .....              | 6  |
| Description of Water Source .....                | 6  |
| Collection, Transportation & Storage .....       | 6  |
| Description of Water Quality Parameters .....    | 7  |
| Project Design .....                             | 9  |
| Water Quality Parameters Testing Procedures..... | 11 |
| <b>RESULTS</b> .....                             | 14 |
| <b>DISCUSSION OF RESULTS</b> .....               | 18 |
| Creek Water True Color vs. Time.....             | 18 |
| Creek Water TOC vs. Time.....                    | 19 |
| Caffeinated Water TOC vs. Time .....             | 19 |
| Aspirinated Water TOC vs. Time .....             | 20 |
| <b>CONCLUSIONS &amp; RECOMMENDATIONS</b> .....   | 20 |
| <b>PROJECT REFERENCES</b> .....                  | 22 |
| <b>APPENDIX</b> .....                            | 23 |
| Figures .....                                    | 23 |
| Tables.....                                      | 34 |

## INTRODUCTION

USGS studies have shown the pervasive nature of pharmaceuticals, hormones and other organic wastes in waterways throughout the nation (Kolpin *et al.*, 2002). Common commodities such as medicinal tablets, cosmetics and fragrances are examples of pharmaceuticals and personal care products (PPCP's) that have been found in various streams at low concentrations (Kolpin *et al.*, 2002). The presence of stable organic compounds has been recently detected, and scientists and engineers are struggling to discern the implications of the compounds in our environment (Buxton *et al.*, 2002). Nonetheless, while the levels of these compounds may not seem significant, scientists worry that prolonged exposure might lead to adverse health and environmental implications; of particular concern is the threat that the compounds pose to the fresh water drinking supply (Huber *et al.*, 2003).

The growing demand for personal care products may never be stopped especially with the continuous growth of the world population; hence, any accumulation in the aquatic environment must be prevented. To be able to do this advanced wastewater treatment methods have to be developed. Other methods do exist but they include processes that only have a marginal effect on PPCP levels. These include chlorine and UV rays which are common disinfectants used to eliminate microorganisms in the water. Another water treatment alternative that was found to be effective is ozone; however, this proves to be a costly, power and man-hour intensive process. The limitations of the aforementioned processes have driven the environmental community to seek alternatives; one option is  $\text{TiO}_2$ .

Recent studies have shown that titanium dioxide could be used to treat water contaminated with some of the most challenging organic compounds such as phenol, (Manalo *et al.*, 2004), dyes (Zou *et al.*, 2005) and natural organic matter (Eggins *et al.*, 1997). As a photocatalyst, titanium dioxide generates free radicals when exposed to ultraviolet light (Fujishima *et al.*, 1999), thereby oxidizing organic matter to CO<sub>2</sub> and H<sub>2</sub>O (Parsons, 2004).

The research seeks to extend the findings of these studies to Alaska where unusually high levels of natural organic matter (NOM) and extremely low temperatures may impact the water treatment process. NOM are responsible for the brown, “tea-like” color often seen in rural Alaska waters. Its removal has presented many challenges for public water systems; hence, many have avoided surface raw water sources. Like NOM, low temperatures also pose a challenge to treatment because they reduce the rate of degradation in the environment. This is because the kinetics or rate of reaction is usually directly correlated with temperature, i.e., higher temperature equals higher rates.

Titanium dioxide is expected to reduce the concentration of organic matter in the water samples by as much as 80%. Complete disinfection of water will not be possible due to several factors such as coagulation of the titanium dioxide particles during the process.

Coagulation reduces the amount of catalyst surface area that is illuminated per volume of the water sample; as a result, the ability of the TiO<sub>2</sub> to degrade organic compounds is diminished.

## **METHODS AND PROCEDURES**

### **Description of Water Source**

Originally, the source for raw water was intended to be the Barrow Utilities & Electric Cooperative, Inc. (BUECI), but a delayed response from BUECI prompted the search for an alternative. The part of Chester Creek flowing under the spine connecting the UAA School of Engineering to the Student Union building proved to be a convenient and appropriate choice. In the said site, the creek separates into two segments: one that meanders through the east side of the Student Union building and the other, through the back of the School of Engineering building. The raw water for this study was collected from the latter site with the basis for selection being the high turbidity value determined through a preliminary test. The ambient temperature during the time of collection was about 30°F.

The spiked water samples, on the other hand, were prepared in the environmental lab. Aspirin and caffeine pills were bought from a local grocery store, pulverized and then mixed with tap water from the lab.

### **Collection, Transportation and Storage**

Two buckets of different volumes were used separately for collection and transportation purposes. A one-gallon bucket was used to draw water from the creek and subsequently transfer it to a five-gallon container. When the five-gallon container was filled, it was covered with a lid and then manually transported to the environmental laboratory where

the raw water sample was divided for storage into three amber glass bottles, each with a volume of 2,360 milliliters (mL).

The storage bottles had to be sterilized before use in order to prevent contamination of the samples. Each of the 2, 360 mL bottles was first soaked for at least 24 hours in a 0.2 fl oz. per gallon chlorine solution. The bottles were then rinsed multiple times with distilled water and subsequently air dried for another 24 hour. The same sterilization process was applied for storage bottles used for the spiked water samples.

### **Description of Water Quality Parameters**

At the beginning of the research, ten parameters were selected to evaluate the water quality of both the raw and treated water samples. These were namely, pH, conductivity, TOC, Color, UV<sub>254</sub> Absorbance, Total Nitrogen, Nitrate, Phosphorus, Sulfate and Chloride. Equipment malfunction prevented the testing for most of the anions while the Chloride test using Hach Method 8113 was not pursued even though it may have been performed using the Hach DR 2800 Spectrophotometer. This was mainly because the test involves handling of highly hazardous chemicals, namely, mercury and ferrous ion solutions for which the researcher was not properly trained. Although testing for these parameters could have produced significant data, these are only secondary to the main focus of the research, which was to determine the effectiveness of titanium dioxide photocatalysis in breaking down organic matter in Alaska waters.



Table 1 summarizes the tests to be used in analyzing the data of the experiment and their corresponding functions and significance. These are standard tests that scientists use to measure water quality. They are all conducted using the Standard Methods for the Examination of Water and Wastewater manual.

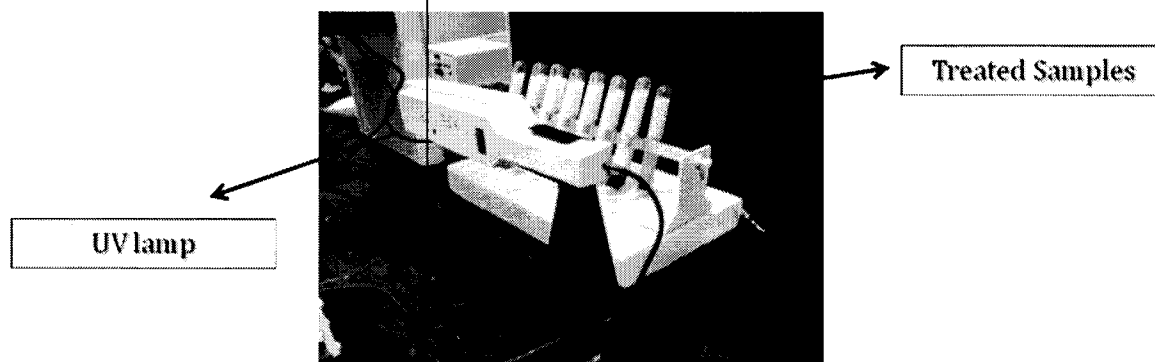
**Table 1. Summary of Water Quality Parameters and Their Functions**

| <b>Parameter</b>            | <b>Function</b>  | <b>Significance</b>   |
|-----------------------------|--|---|
| pH                          | To test whether the water is acidic or basic                               | Plays a key role in the rate of reaction  |
| Conductivity                | To measure the ability of water to pass an electric current                | Indicative of level of dissolved solids in the solution                         |
| Total Organic Carbon (TOC)  | To measure the amount of organic carbon present in the water               | Representative of NOM content   |
| Turbidity                   | To measure the cloudiness of water   | Indicative of the amount of suspended matter like clay, silt and organic matter |
| *Nitrate, Sulfate, Chloride | To test for the nitrate, sulfate and chloride contaminant content of water | Indicative of water quality   |
| True Color                  | To test for the color of filtered water                                    | Indicative of the amount of dissolved organic material in water                 |
| Apparent Color              | To test for the color of water containing suspended matter                 | Indicative of the amount of suspended organic matter                            |
| Nitrogen, *Phosphorus       | To test for the nitrogen and phosphorus content of water                   | Reduced quantities of N and P would be desirable                                |
| UV 254 absorbance           | To test for the levels of natural organic matter present in the water      | Indicative of amount of NOM in the water  |

\*Not performed for reasons stated in the paragraph above

## Project Design

Testing of the water samples followed the schedule outlined in Table 1. Note that Chester Creek water was treated first for various concentrations (0.01%, 0.1% and 1%  $\text{TiO}_2$ ) of titanium dioxide. As shown in Figure 1 below, the said samples were then placed in a Labquake® Shaker to be agitated and simultaneously exposed to UV light for three hours with testing done hourly. Comparing the results obtained the tests determined that the optimum photocatalyst concentration was 0.01%  $\text{TiO}_2$ .



**Figure 1. Experimental set-up showing the treated samples being thoroughly mixed by the Labquake® Shaker while being exposed to UV light.**

Selecting the optimum  $\text{TiO}_2$  concentration was important because it allowed the researcher to focus on the sample with that particular concentration and extend its treatment to 12 hours with testing performed after every three hours. In addition, the same concentration was used for treating the aspirinated and caffeinated waters.

Testing location, equipment and methods used are outlined in Table 3. Note that all testing were performed according to the *Standard Methods for the Examination of Water and Wastewater* manual.

**Table 2. Frequency of test and TiO<sub>2</sub> concentration for each water sample**

| Water Source           | Concentration<br>(mass % TiO <sub>2</sub> ) | Time (Hours) |   |   |   |   |    |
|------------------------|---|--------------|---|---|---|---|----|
|                        |   | 1            | 2 | 3 | 6 | 9 | 12 |
| Chester Creek<br>Water | 0.01%                                       |              |   |   |   |   |    |
|                        | 0.1%  |              |   |   |   |   |    |
|                        | 1%  |              |   |   |   |   |    |
| Aspirinated Water      | 0.01%                                       |              |   |   |   |   |    |
| Caffeinated<br>Water   | 0.01%                                       |              |   |   |   |   |    |

**Table 3. A summary of the equipment and methods used in testing for the selected water quality parameters**

| Parameters Tested | Facility | Equipment                                  | Method                   |
|-------------------|----------|--|--------------------------|
| TOC               | ASET lab | HS9000 Tekmar-Dohrmann Apollo TOC Analyzer | SM 5310 B                |
| UV254             | ASET lab | HP 8452A Diode Array Spectrophotometer     | SM 5910 B                |
| Turbidity         | SOE lab  | Hach Model 2100P Portable Turbidimeter     | SM2130 B                 |
| Total Nitrogen    | SOE lab  | DR2800 Spectrophotometer                   | SM 4500-N                |
| pH                | SOE lab  | Ultrameter II™ by Myron L Company          | SM 4500-H <sup>+</sup> B |
| Conductivity      | SOE lab  | Ultrameter II™ by Myron L Company          | SM 2510 B                |
| Color             | SOE lab  | DR2800 Spectrophotometer                   | SM 2120 C                |

## **Water Quality Parameters Testing Procedures**

### **pH**

The pH of each of the water samples was determined using UltrameterII™ by Myron L Company. Following manufacturer procedures, the pH sample cell was first rinsed three times then filled to the line with the sample to be tested. Five different pH measurements were then taken using the same sample.

### **Conductivity**

The conductivity of each of the water samples was determined using UltrameterII™ by Myron L Company. Following manufacturer procedures, the conductivity sample cell was first rinsed three times then filled to the line with the sample to be tested. Five different conductivity measurements were then taken using the same sample.

### **TOC**

A 12 cc syringe with a 0.45µm membrane filter was used to filter both the deionized water blank and the sample. Before a sample was tested, three filtrations had to be done using the same syringe and filter. The first involved rinsing the membrane filter by running 5 mL of deionized water through the apparatus. This was followed by a second filtration using the water sample. After the first 10 drops were discarded, a vial was filled with the filtered sample and then shaken before the sample was discarded. The third and final filtration was then performed using a fresh sample.

## **Turbidity**

The Hach Model 2100P Portable Turbidimeter was used for turbidity measurements. Procedures followed were based on Standard Method 2130 B. Furthermore, the samples were warmed up to room temperature before any measurement was made.

Before the turbidimeter was used for the first time in the experiment, it was calibrated according to procedures outlined in the manufacturer's manual. Turbidity analysis made later on no longer required recalibration, as the Formazin standards that were checked before each use were well within 0.1 nephelometric turbidity units (NTU), which meant that the instrument was still accurate. Prior to making any measurements, the vial containing the sample was wiped first with soft, lint-free cloth and applied with a thin film of silicone oil to get rid of proteins that might have adhered to the vial from handling it. It was then placed in the turbidimeter to measure the turbidity of the sample.

## **Color, True and Apparent**

The true and apparent color of the samples were analyzed using the Hach DR2800 Spectrophotometer using Hach Method 8025 (SM 2120 C). The samples were warmed up to room temperature before any measurement was made.

To measure true color, a 12 cc syringe with a 0.45 $\mu$ m membrane filter was used to filter both the deionized water blank and the sample. Before a sample was tested, three filtrations had to be done using the same syringe and filter. The first involved rinsing the membrane filter by running 5 mL of deionized water through the apparatus. This was

followed by a second filtration using the water sample. After the first 10 drops were discarded, a vial was filled with the filtered sample and then shaken before the sample was discarded. The third and final filtration was then performed using a fresh sample.

No filtration was necessary in the determination of apparent color. Hence, sample was directly poured into a clean vial and compared to an unfiltered water blank.

### **Total Nitrogen**

Testing for total nitrogen in water samples was performed using the Hach DR2800 spectrophotometer according to Hach Method 10071 (SM 4500-N).

Total Nitrogen Persulfate Reagent Power Pillows were added to each of two Total Nitrogen Hydroxide Digestion Reagent vials. Two milliliters of sample were then added to one vial while the other was filled with 2 mL of deionized water to serve as blank.

Both vials were capped, shaken and mixed for 30 seconds. They were then heated in the reactor for 30 minutes and subsequently cooled down to room temperature. Thereafter, a Total Nitrogen (TN) Reagent A Powder was added and the vials were both shaken again.

Each solution was allowed to react for 3 minutes before adding the TN Reagent B Powder Pillow to each vial. After a 15 second agitation, and letting the vials stand for 2 minutes, 2 mL of TN Reagent C was added. To allow the solution to mix, the vials were inverted 10 times and then left to stand for a 5 minute reaction. The total nitrogen content of the samples was then determined by inserting each vial to the spectrophotometer, the blank being first.

### **UV<sub>254</sub> Absorbance**

A 12 cc syringe with a 0.45 $\mu$ m membrane filter was used to filter both the deionized water blank and the sample. Before a sample was tested, three filtrations had to be done using the same syringe and filter. The first involved rinsing the membrane filter by running 5 mL of deionized water through the apparatus. This was followed by a second filtration using the water sample. After the first 10 drops were discarded, a vial was filled with the filtered sample and then shaken before the sample was discarded. The third and final filtration was then performed using a fresh sample.

### **RESULTS**

The effectivity of titanium dioxide photocatalyst in degrading organic carbon may be evaluated using the results obtained from true color and total organic carbon (TOC) tests. True color, which is a good indicator of NOM, was used in the experiment as the basis for comparison in determining the optimum titanium dioxide concentration. This was mainly because the TOC test takes relatively longer than that of true color, which may be performed in only a few minutes. True color results for 0.01% TiO<sub>2</sub>, 0.1% TiO<sub>2</sub> and 1% TiO<sub>2</sub> in creek water are presented in Figures 2, 3 and 4, respectively. Values for true color are expressed in Pt. Co. units (PCU).

A more accurate representation of the amount of organic carbon in the treated water samples is given by the TOC test. Figures 5, 6 and 7 show TOC in ppm C using the previously determined optimum TiO<sub>2</sub> concentration for treated creek, caffeinated and aspirinated waters respectively.

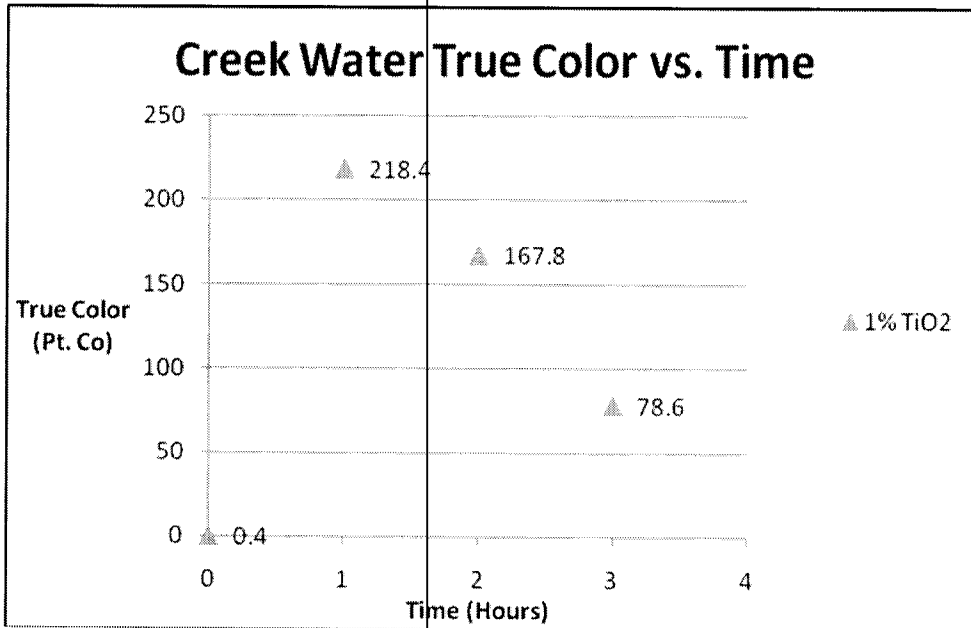


Figure 2. True Color vs. Time for creek water treated with 1% TiO<sub>2</sub> photocatalyst

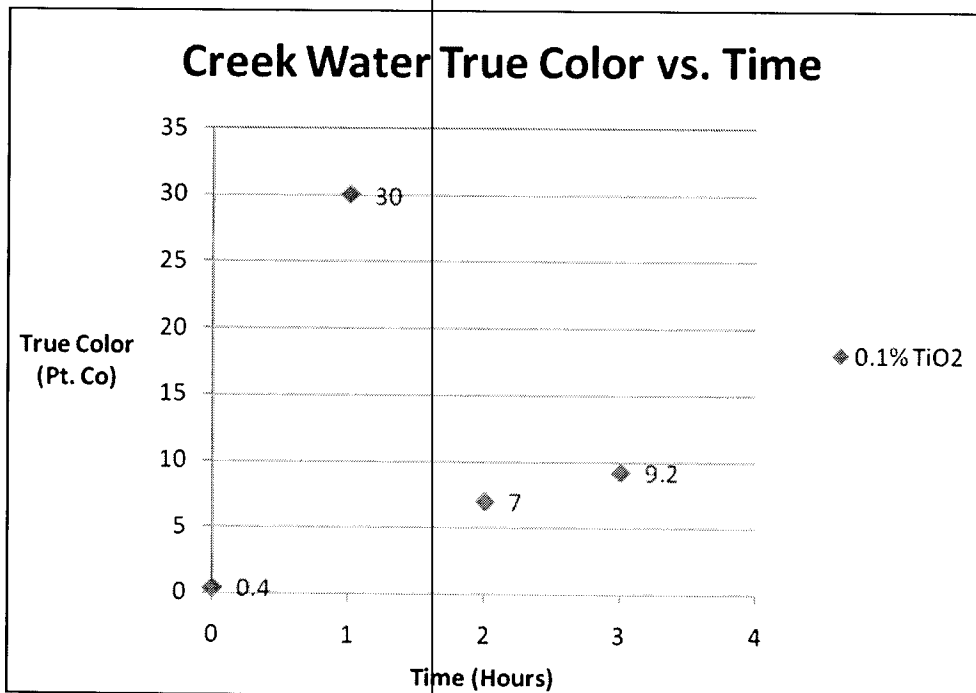


Figure 3. True Color vs. Time for creek water treated with 0.1% TiO<sub>2</sub> photocatalyst



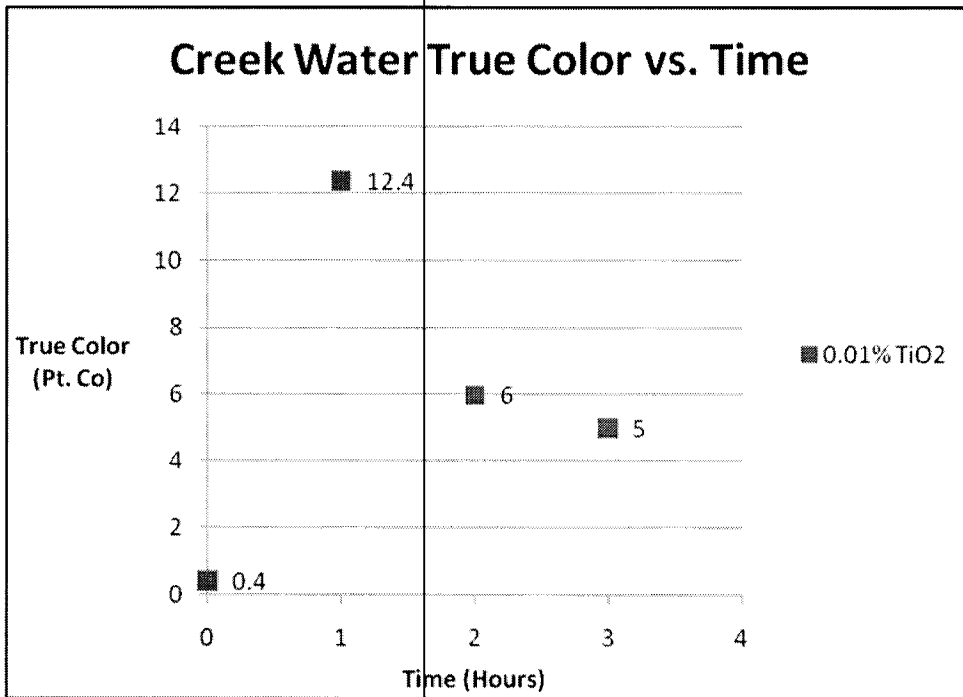


Figure 4. True Color vs. Time for creek water treated with 0.01% TiO<sub>2</sub>

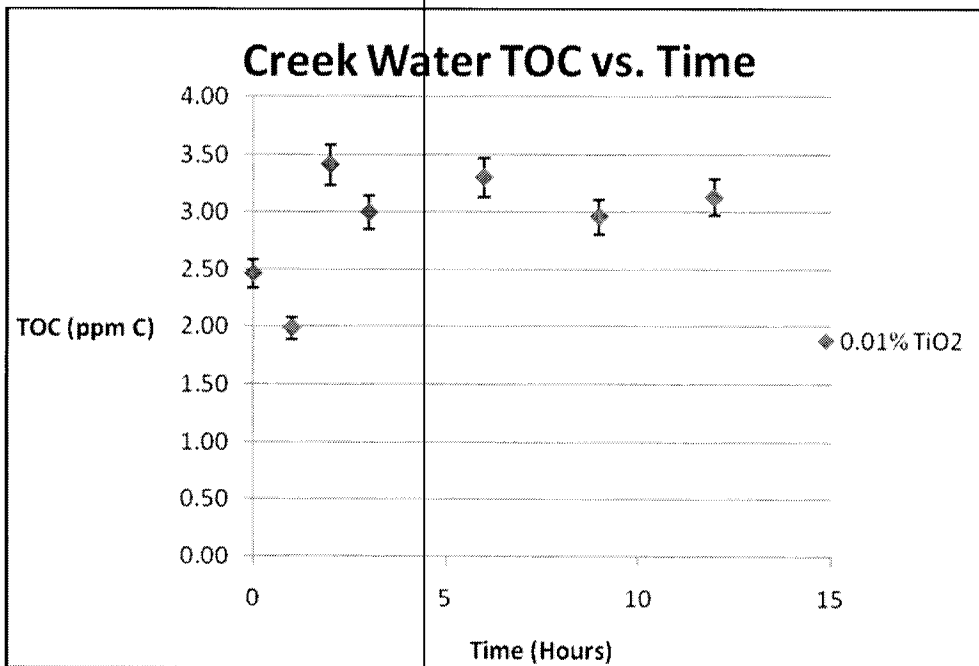


Figure 5. TOC vs. Time for creek water treated with 0.01% TiO<sub>2</sub>

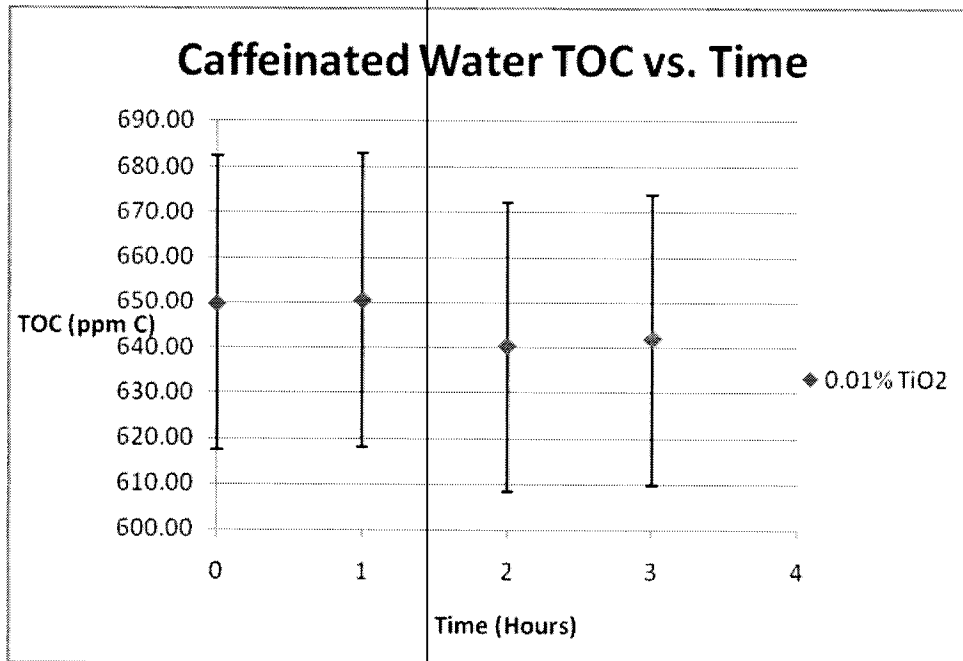


Figure 6. TOC vs. Time for caffeinated water treated with 0.01% TiO<sub>2</sub>

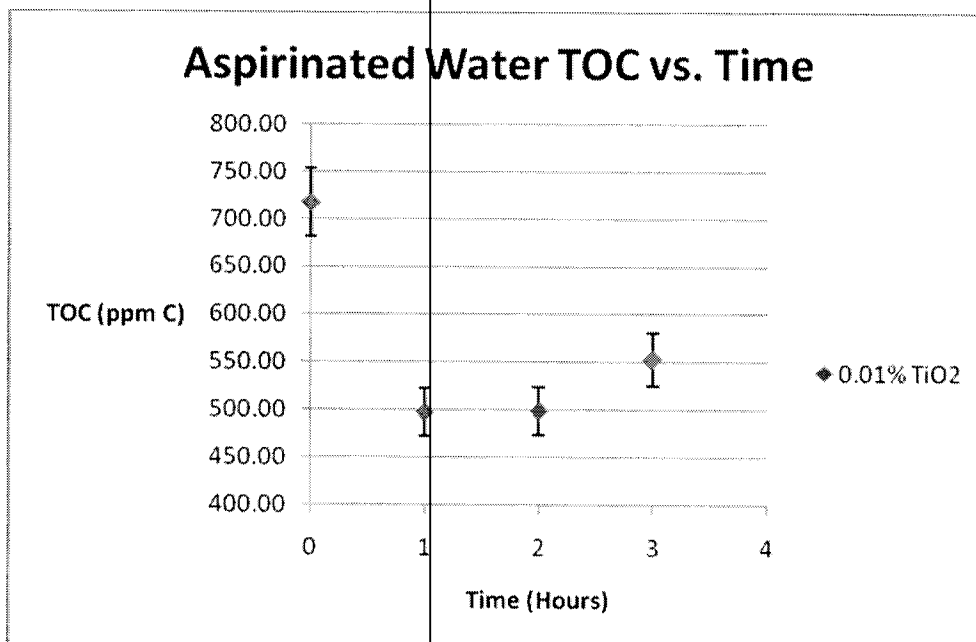


Figure 7. TOC vs. Time for aspirinated water treated with 0.01% TiO<sub>2</sub>

## **DISCUSSION OF RESULTS**

### **Creek Water True Color vs. Time**

To be able to determine the optimum concentration of  $\text{TiO}_2$ , the true color results presented in Figures 2-4 were studied. It is noteworthy that for all three concentrations, the true color of the creek water showed a significant increase after an hour of treatment. Looking at Figure 2 for treatment with 1%  $\text{TiO}_2$ , the spike in the true color value from zero (when creek water was yet untreated) to first hour was about 500% from the original whereas for 0.1% and 0.01%  $\text{TiO}_2$  this change was about 74% and 30%, respectively. However, after one hour of agitation and exposure to UV light, the creek water showed a generally decreasing trend in true color for all three concentrations. While the trends were very similar for all three data sets, the optimum concentration of 0.01%  $\text{TiO}_2$  was chosen because it showed the least percent increase in true color after one hour of treatment. Given the limited range of the spectrophotometer used to measure true color, it was decided that it was ideal to investigate the least saturated treated sample so that trends may be better observed over an extended period of time. Otherwise, excessive increase in true color value would have forced the instrument to go out of range, in which case, it would no longer be accurate. Thus, 0.01%  $\text{TiO}_2$  was chosen as the optimum concentration not necessarily because it was the most effective, but mainly due to the fact that it was most likely to produce a useful data set from which conclusions can be made regarding the performance of  $\text{TiO}_2$  photocatalyst as treatment for Alaska waters.

### **Creek Water TOC vs. Time**

From Figure 5, it can be seen that the TOC level of creek water decreased from 2.47 ppm to 1.99 ppm after being treated for one hour. This decrease, however, does not necessarily warrant the effectivity of  $\text{TiO}_2$  since after another hour of treatment, there was actually a spike in the TOC level. This is interesting because for TOC to increase, a source containing carbon must have been introduced into the system. Since  $\text{TiO}_2$  does not contain carbon, this spike may be due to errors in the handling of samples or the use of unthoroughly cleaned glassware.

In addition, it can be noted that the total organic carbon content of the creek water sample basically fluctuated around the 3.0-3.5 ppm range, which indicates either of two things: the titanium dioxide was not effective in treating the creek water or the rate of reaction was simply too slow that the photocatalyst may have been in need of more time to degrade organic matter.

### **Caffeinated Water TOC vs. Time**

The caffeinated water sample did not show much change in the TOC level over time as seen in Figure 6. The TOC content stayed between 640 ppm to 651 ppm throughout the three hours indicating that again, either titanium dioxide was not effective or more time is necessary for the photocatalyst to break up into free radicals and subsequently degrade organic carbon.

### **Aspirinated Water TOC vs. Time**

The treated aspirinated water sample showed a 30% decrease in ppm C after one hour of treatment as seen in Figure 7. Compared to the creek water data set, this decrease may be more representative of titanium dioxide breaking down organic matter because more hours of treatment did not cause a spike in the TOC level. While the TOC in the third hour may be seen as an increase, it actually is not because as the standard error bars show, the value is just well within the range of the previous two values. A possible coagulation of  $\text{TiO}_2$  particles may have prevented further decrease in TOC values after hour of treatment.

## **CONCLUSIONS & RECOMMENDATIONS**

The main objectives of this research were to determine whether or not  $\text{TiO}_2$  can remove NOM from water as well as break minute traces of aspirin and caffeine in water. Contrary to expectations, this research showed that  $\text{TiO}_2$  photocatalysis may have a slow rate of reaction in treating organic compounds present in Alaska waters as well as those in pharmaceuticals. The TOC results from creek and caffeinated water samples indicate that more time may be necessary to allow free radicals generated by the UV activated  $\text{TiO}_2$  to degrade organic carbon. On other hand, treated aspirinated water, while it showed promising results with a significant reduction in TOC, would also benefit from extending the time of agitation so that the trend in TOC level would be clearly seen.

Therefore, for future studies, it is recommended that more reaction time be allowed for each sample. In addition, one could also investigate the reasons for the spike in TOC for creek and caffeinated water samples when treated with  $\text{TiO}_2$ . One could also increase the concentration of  $\text{TiO}_2$  to see its effect in the rate of reaction, as well as investigate new reactor designs that allow better mixing and UV light distribution than the one used in this research.

## PROJECT REFERENCES

- Buxton, H.T., and D.W. Kolpin, "Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in US Streams", U.S. Geological Survey Fact Sheet FS-027-02, 2 p. (2002).
- Eggins, B.R., Palmer, F.L. and J.A. Byrne, "Photocatalytic treatment of humic substances in drinking water", *Water Research*, 31(5), 1223-1226 (1997).
- Fujishima, A., Hashimoto, K., and T. Watanabe, *TiO<sub>2</sub> Photocatalysis: Fundamentals and Applications*, BKC, Tokyo (1999).
- Huber, M.M., Canonica, S., Park, G-Y. and U. von Gunten, "Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes", *Environmental Science Technology*, 37(5), 1016-1024 (2003).
- Kolpin, D. W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. and H.T. Buxton "Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in US Streams, 1999-2000: A National Reconnaissance", *Environmental Science Technology*, 36(6), 1202-1211 (2002).
- Manalo, F., Vaisman, E., Langford, C. and A. Kantzas, "Remediation of Hydrocarbon Contaminated Soil and Water", 2004 Soil and Groundwater Forum and Poster Session, March 23-24, 2004 <http://www.ptac.org/env/dl/envf0401p33.pdf> (2004).
- Parsons, S.A., *Advanced Oxidation Processes for Water and Wastewater Treatment*, IWA Publishing, London, UK (2004).
- Zou, L., Li, Y., and E. Hu, "Photocatalytic Decolorization of Lanazol Blue CE Dye Solution using a Flat-Plate Reactor", *Journal of Environmental Engineering*, 131(1), 102-107 (2005).

# APPENDIX

## Figures

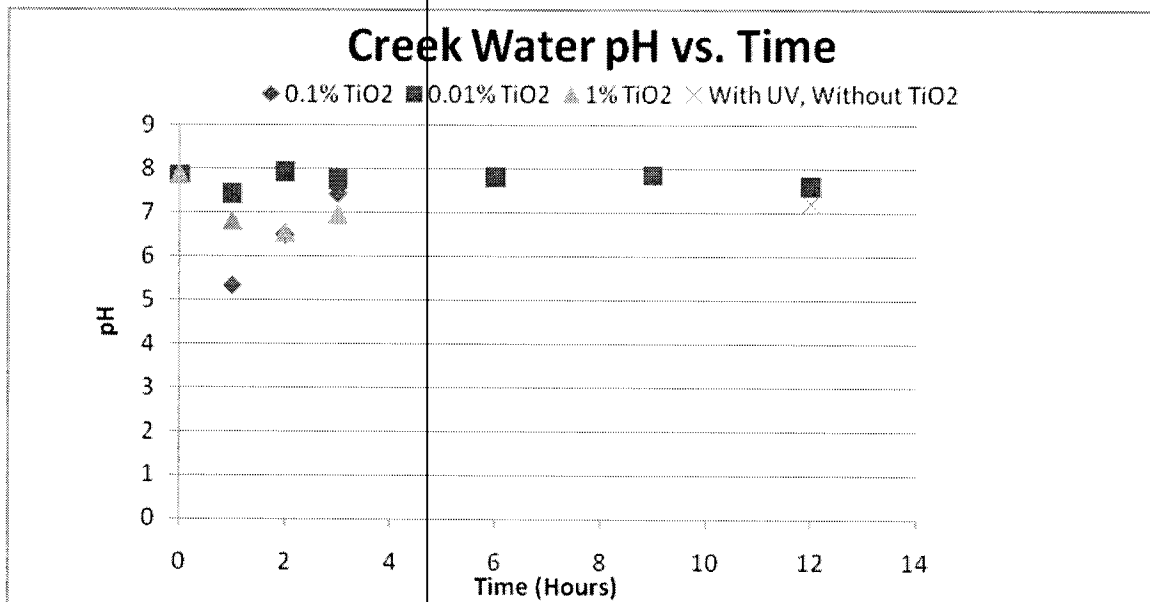


Figure A 1. Creek Water pH vs. Time for various TiO<sub>2</sub> concentrations including blank

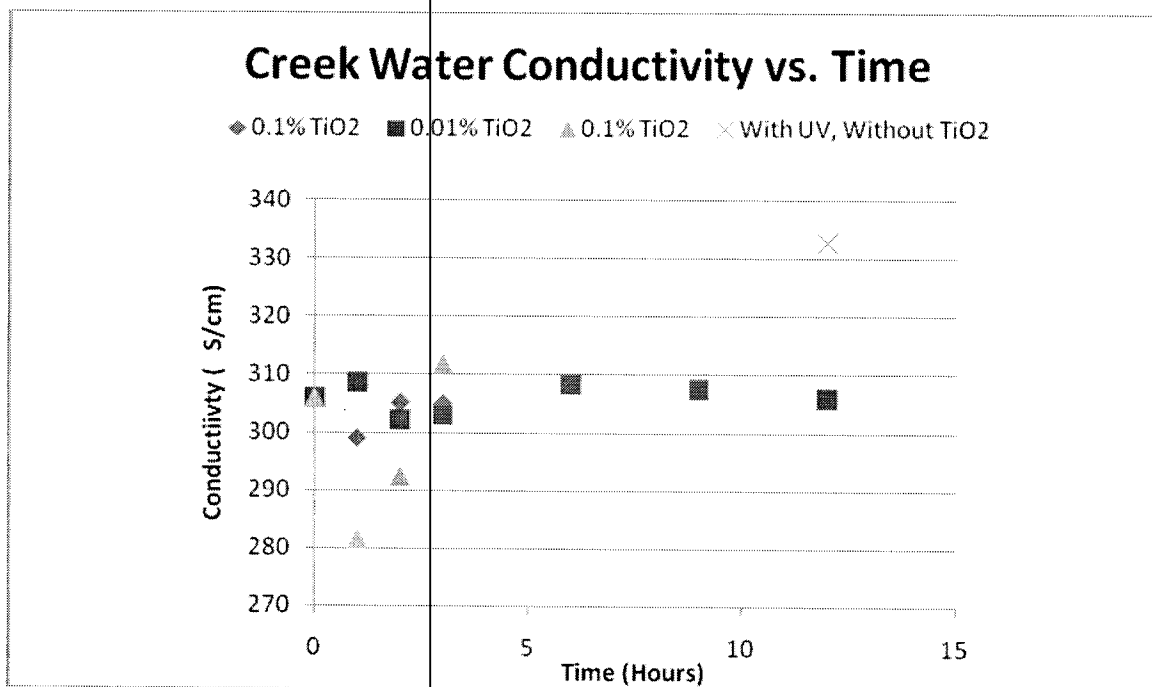


Figure A 2. Creek Water Conductivity vs. Time for various TiO<sub>2</sub> concentrations including blank



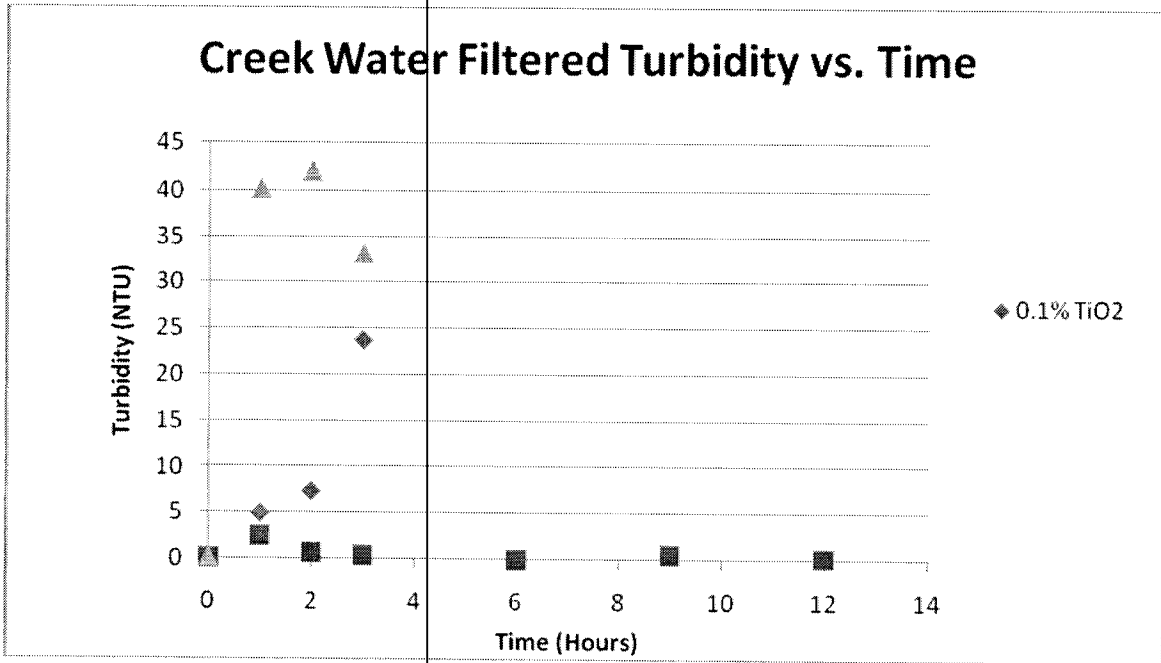


Figure A 3. Creek Water Filtered Turbidity vs. Time for various TiO<sub>2</sub> concentrations

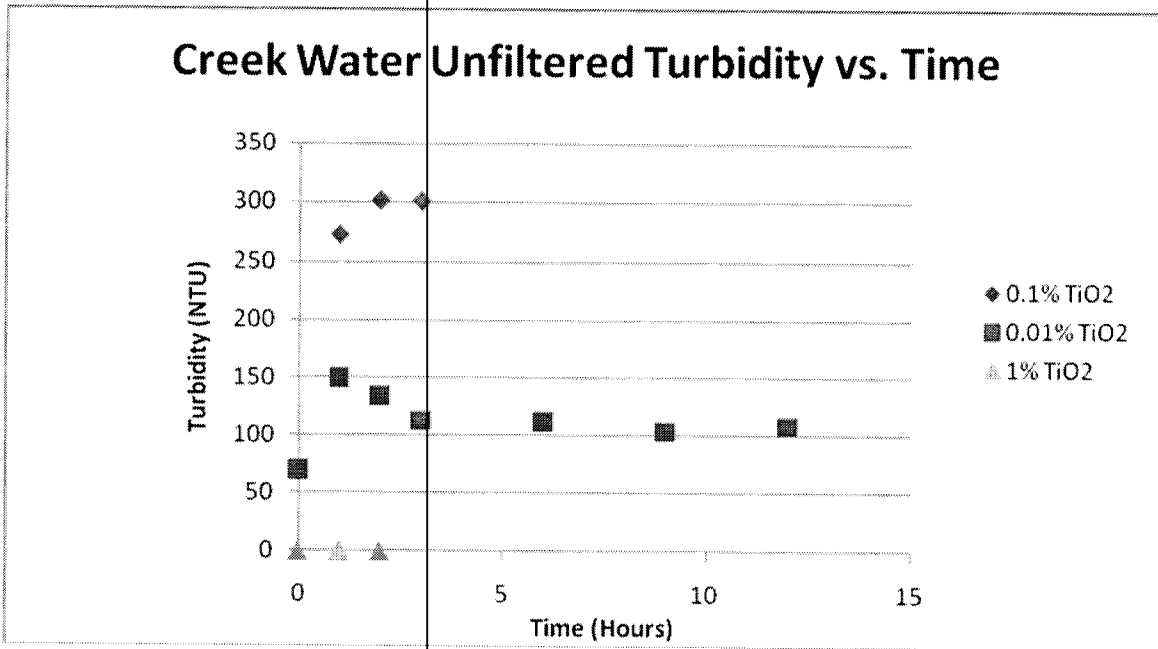


Figure A 4. Creek Water Unfiltered Turbidity vs. Time for various TiO<sub>2</sub> concentrations

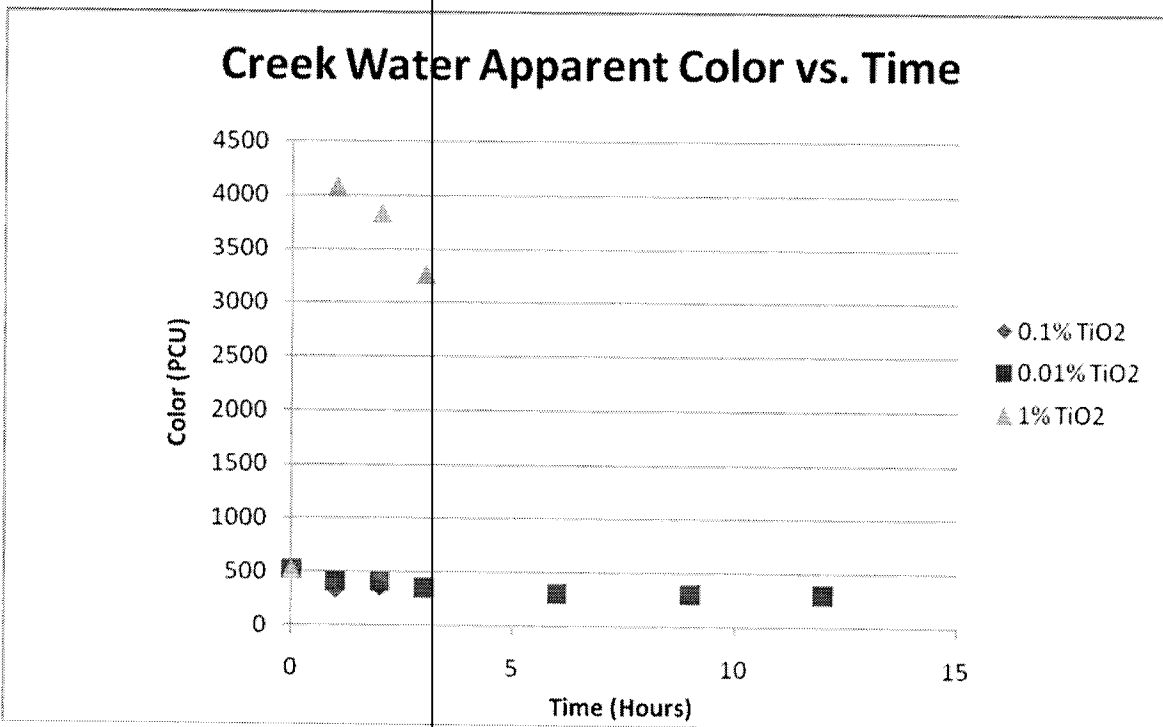


Figure A 5. Creek Water Apparent Color vs. Time for various TiO<sub>2</sub> concentrations

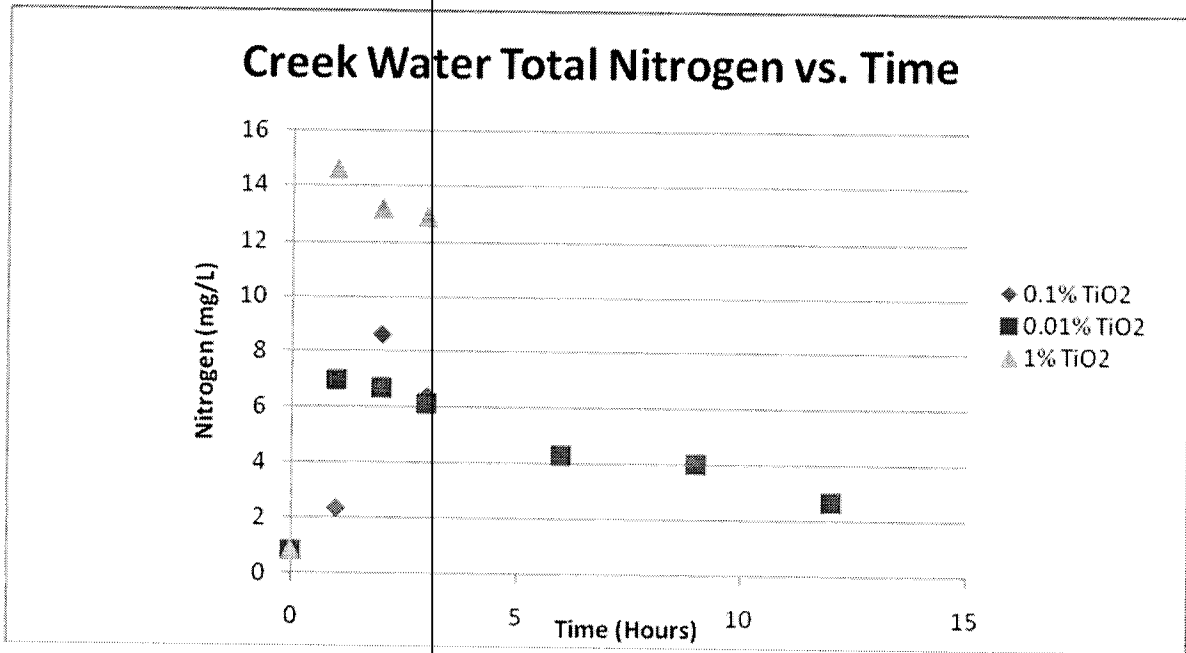


Figure A 6. Creek Water Total Nitrogen vs. Time for various TiO<sub>2</sub> concentrations

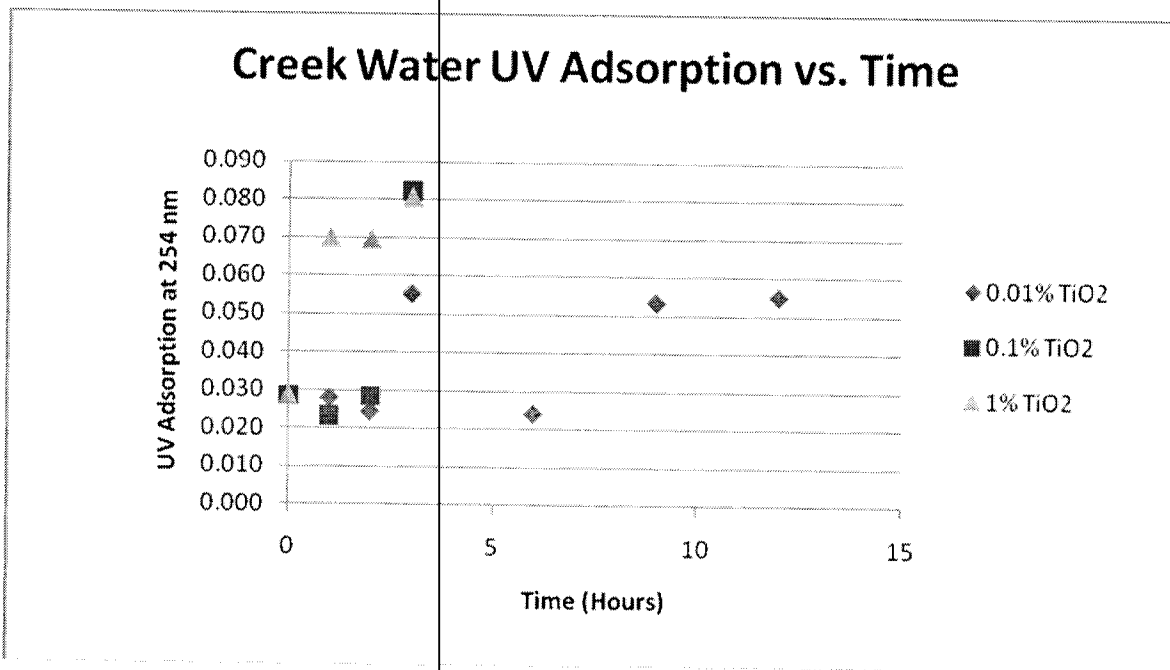


Figure A 7. Creek Water UV Adsorption vs. Time for various TiO<sub>2</sub> concentrations

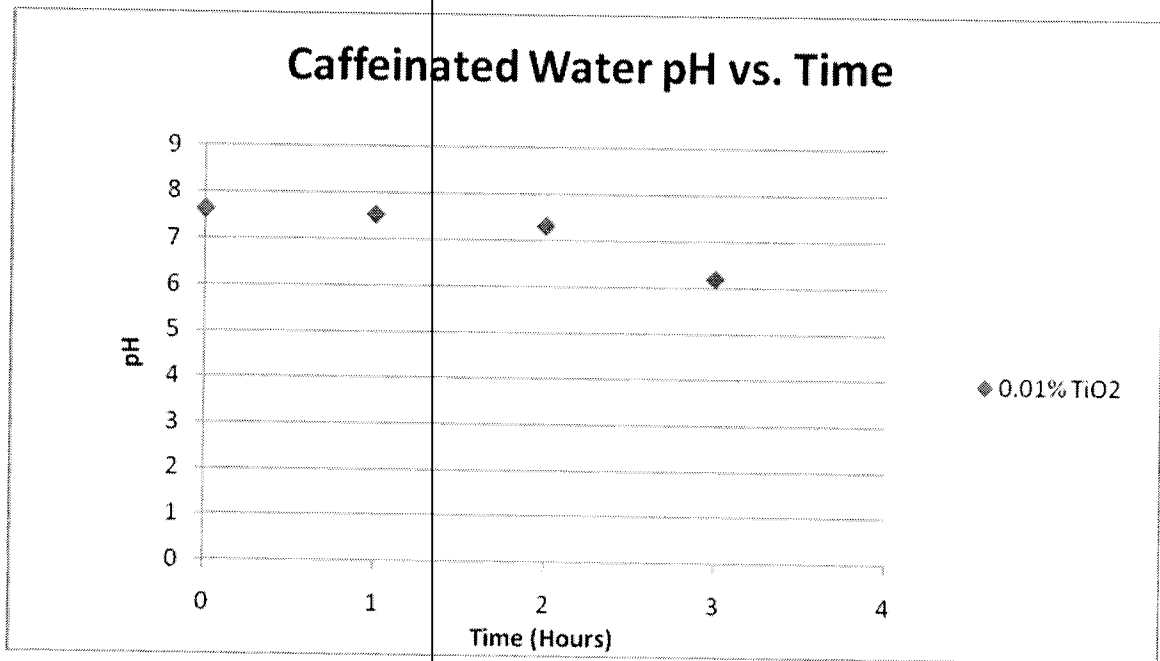


Figure A 8. Caffeinated Water pH vs. Time for optimum TiO<sub>2</sub> concentration (0.01% TiO<sub>2</sub>)

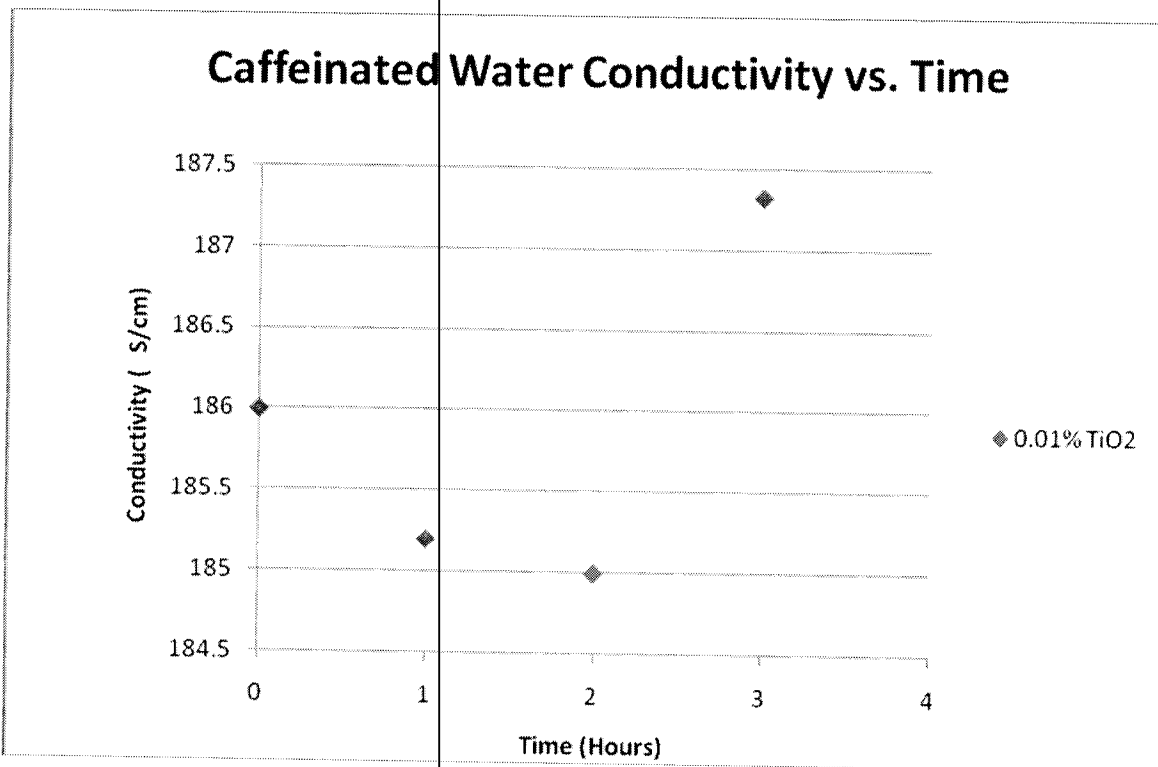


Figure A 9. Caffeinated Water Conductivity vs. Time for optimum TiO<sub>2</sub> concentration (0.01% TiO<sub>2</sub>)

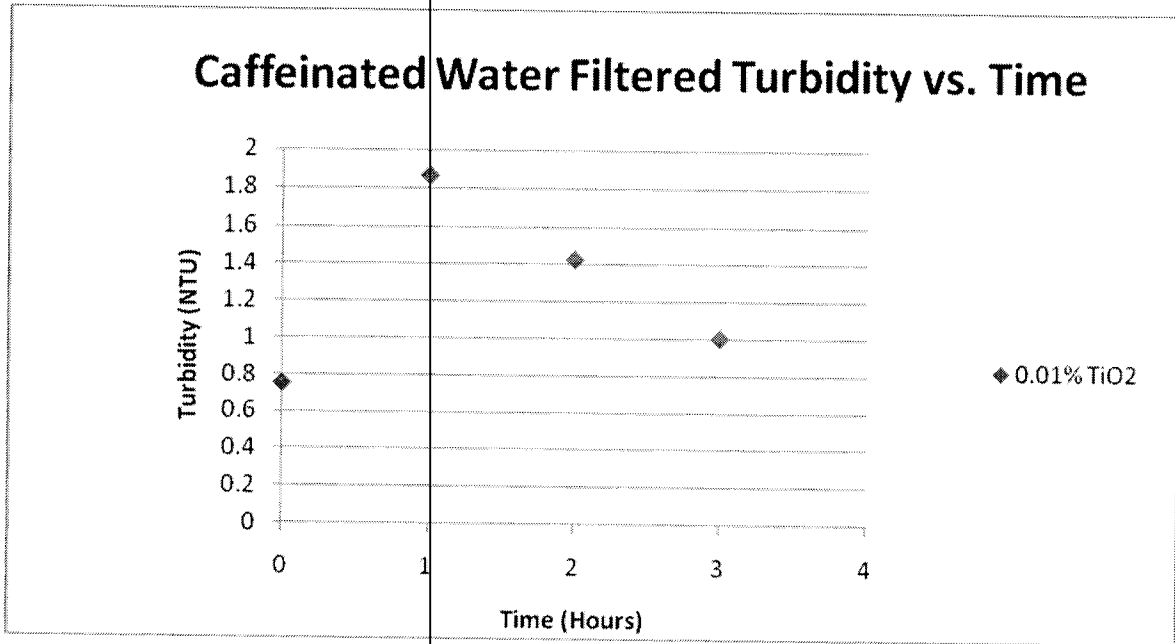


Figure A 10. Caffeinated Water Filtered Turbidity vs. Time for optimum TiO<sub>2</sub> concentration (0.01% TiO<sub>2</sub>)

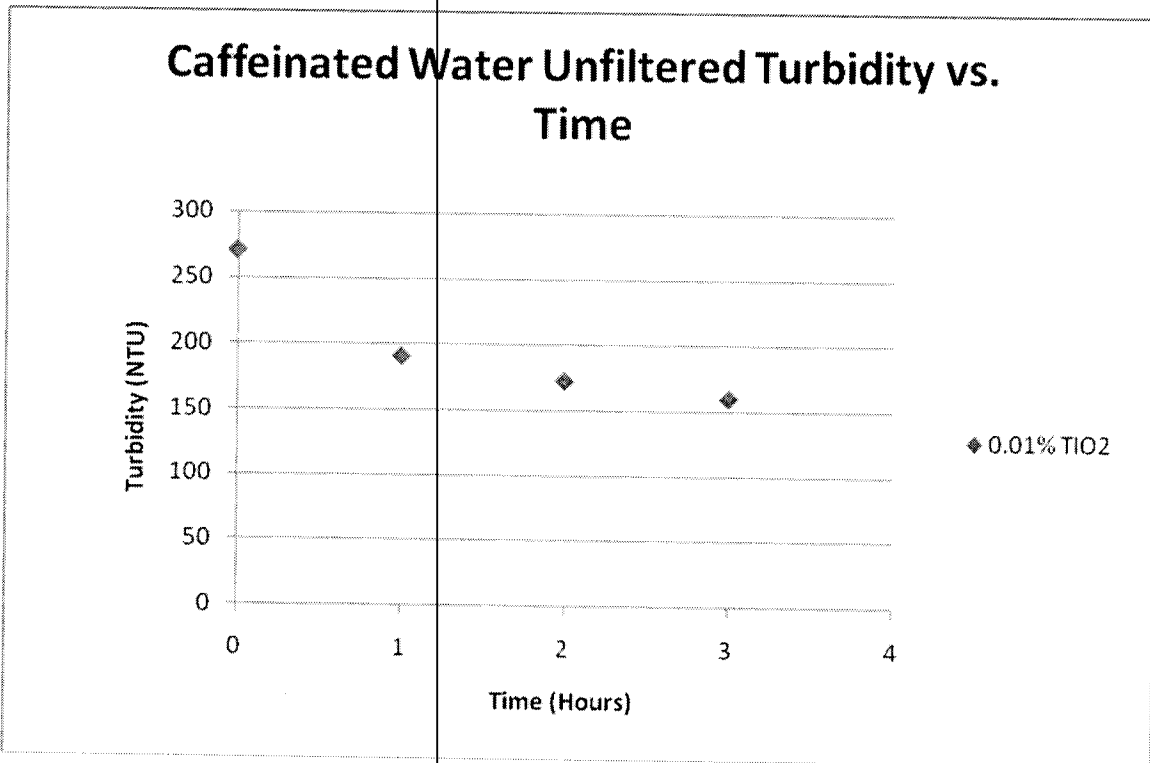


Figure A 11. Caffeinated Water Unfiltered Turbidity vs. Time for optimum TiO<sub>2</sub> concentration (0.01% TiO<sub>2</sub>)

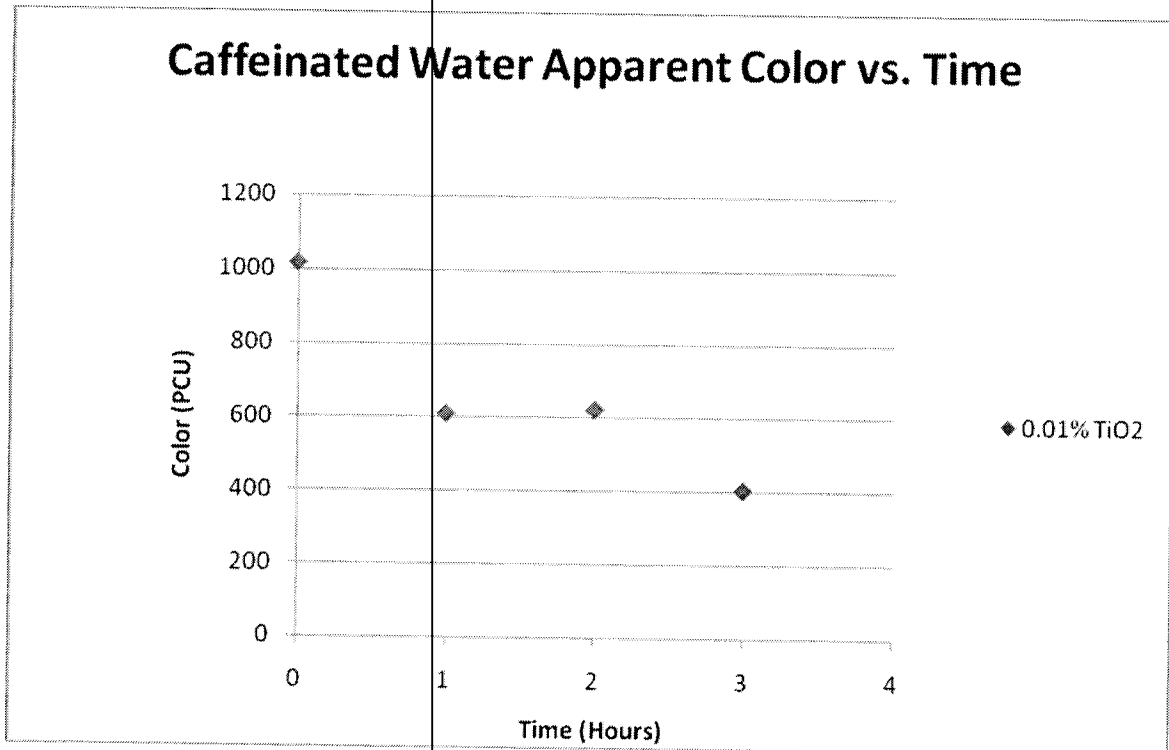


Figure A 12. Caffeinated Water Apparent Color vs. Time for optimum TiO<sub>2</sub> concentration (0.01% TiO<sub>2</sub>)

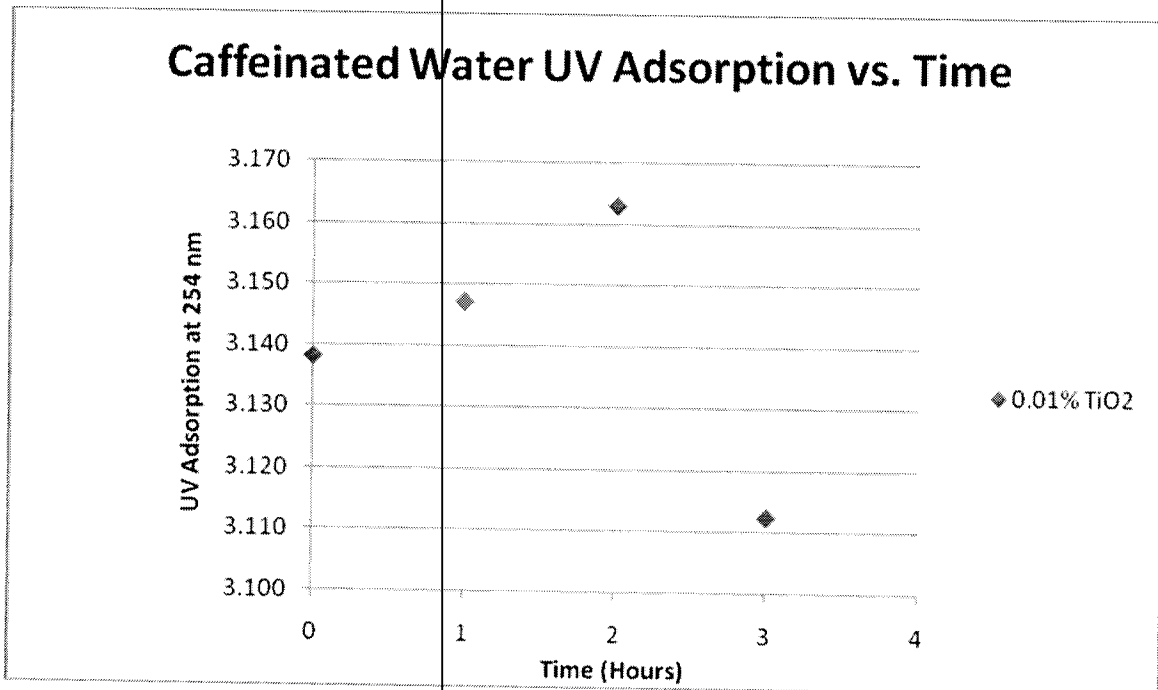


Figure A 13. Caffeinated Water UV Adsorption vs. Time for optimum TiO<sub>2</sub> concentration (0.01% TiO<sub>2</sub>)