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Preliminary Experiments on Photo-Electro Catalytic Oxidation of Recalcitrant Organic Compounds Dissolved in Water

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Preliminary Experiments on Photo-Electro Catalytic Oxidation
of Recalcitrant Organic Compounds Dissolved in Water

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ABSTRACT

This thesis presents the design and analysis of photo-electro catalytic oxidation technology for its potential use in water treatment applications. Doping titanium dioxide can effectively improve oxidative reactions. Using minute reactor design adjustments, such as electrolysis, the bases of degrading soluble organic compounds can be improved within the reactor. Applications of doping and secondary catalysis are effective in increasing the process of photoactivity within the catalytic reactor, theoretically increasing the production of sacrificial electron acceptors. Higher degradations were accomplished using doped chromium titanium dioxide photocatalyst, which degraded significantly larger amounts of organics compared with pure titanium dioxide. Techniques used to accomplish the increased photo-reactivity were doping chromium (III) ion into titanium dioxide crystal lattices and silver ions into the photocatalytic coat. Degradation curves were determined by total organic carbon and the chemical oxygen demand. Calculations of the final rate constants show that lighter molar concentrations have higher rates of degradation.

KEYWORDS

Semiconductor Compound Titanium Dioxide - (TiO_2)	Chromium III Ion - **Cr(III)**
Ultraviolet Light – **UV**	Silver Ion - **Ag+**
Photocatalytic Oxidation – **PCO**	Hydroxyl radical - **·OH**
Advanced Oxidation Process – **AOP**	Hydroxyl Ion – **OH⁻**
Total Organic Carbon - **TOC**	Parts per Million of Carbon - **ppmC**
Chemical Oxygen Demand - **COD**	Hydrogen Gas - $\mathbf{H^2}$
Sacrificial Electron Acceptors - **SEA**	
Sacrificial Electron Donor - **SED**	
Oxygen Gas - $\mathbf{O^2}$	

1. INTRODUCTION

1.1   Objective

The main objective of the research project was to design, build and test an innovative and cost-effective advanced oxidation technology for water and wastewater treatment. The research was designed to show the potential of using a photocatalytic oxidation reactor for the task of breaking down organic material. The research evolved from initial assumptions based on theoretical photocatalysis research, which is supported by many researchers in the environmental and chemistry fields. Experiments were designed to simulate a basic water treatment setup, thus relating critical design points to effectively show indirect oxidation reactions using only semiconducting surfaces of titanium dioxide upon graphite plates with electrolysis, with the performance analyzed using values of total organic carbon. The application of the operation and limitations of this technology were evaluated as part of the project.

The specific research objectives of this project were as follows:

- To design a procedure for creating doped chromium-titanium dioxide and combining the solution with secondary silver nitrate catalyst, and together with a method of applying the coat to graphite plates.
- To evaluate the decomposition of the following degradable organic material: 4-nitro phenol (a hydrocarbon), Rhodamine (a dye), and Tween 40, (a surfactant).
- Show the effectiveness of the electrolysis on organic degradation.
- Ensure all degradation is resulted from primary oxidative radicals from photo-electrocatalytic reactions, and no secondary oxidative properties influenced experimental results, such as if sodium chloride is used.

2. LITERATURE REVIEW

2.1 Photocatalysis Technology for Water Treatment.

Due to increased pollutants in lakes and rivers derived from agricultural and industrial waste run-off, it is apparent that there is demand for effective municipal and industrial water filtration systems. There has been no considerable evolution of water treatment facilities in the past century, but future advances face a dilemma due to the need to balance cost effective treatment with public concerns. For municipal city water to comply with EPA Primary Water Regulations, and effectively remove highly stable organic pollutants, it is therefore necessary to find a method using new and advanced electrochemical processes, which can manage the increased presence of recalcitrant organic compounds in surface waters.

There have been limited breakthroughs in developing innovative technologies that can be used practically and economically within water treatment systems. Two essential criteria need to be adhered to in the design and development: the need to be reliable, and the need to operate with cost effective certainty, in order to ensure pure, clean and healthy water for the use of society (Neuman, 2007). There have been some advances in water treatment research, which have illuminated new purification methods. The study of membrane processes resulted in purification technologies such as reverse osmosis and ultrafiltration, which insured the removal of viruses, harmful ions, and other molecular organic and inorganic compounds (Hendricks, 2006). Adsorption process theories were used to develop granular activated carbon (GAC), which removes both natural and synthetic organic compounds using absorbent material (Hendricks, 2006).

This thesis discusses an attempt at using an advanced oxidation process for organic chemical oxidation. Photocatalytic oxidation was developed in the early 1970's as a means of microbial degradation; this was illustrated by the use of ozone, permanganate, and chlorine dioxide, and understanding the cleavage of organic molecules, which have other names such as effective oxidants and disinfectants (Hendricks, 2006).

There has been speculation that titanium dioxide can act as an effective catalyst in producing the hydroxyl radical which oxidizes a broad range of pollutants through the medium of air or water. However, its photo-efficiency within water reactions has always been low, and the design of TiO_2-based water treatment systems have not been repeatedly attempted in the past decade as many researchers have declared them to be

economically unfeasible (Hendricks, 2006). However, there is room for gaining an understanding of its potential uses, and one idea can potentially be transformed into an innovative technology that has potential for realistic applications. This thesis aims to explain how this can be achieved, and aims to illustrate this by observations of a slight increase in photo degradation from one phase of design to the next.

2.1.1   Definitions and Process

A photocatalytic oxidation batch reactor system contains many inner processes which are employed in the photo-degradation of organic material. Definitions used to assist in the technical comprehension of this research are provided below:

- **_Photocatalysis:_** the acceleration of a photoreaction in the presence of a catalyst. In photolysis, light is absorbed by an adsorbed substrate. In a photo-generated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs upon a transition metal oxide, and exposed to water, free radicals to undergo secondary reactions, and generate hydroxyl radicals (chemical formula: ($^\bullet$OH)). An understanding of this process has been made possible ever since the discovery of water electrolysis using titanium dioxide. In homogeneous photocatalysis, the reactants and the photocatalysts exist in the same phase. The most commonly used homogeneous photocatalysts includes ozone, transition metal oxide (titanium dioxide), and photo-Fenton systems ($Fe+$ and $Fe+$ /$H2O2$). The primary reactive species generated is $^\bullet$OH, which is used for many purposes. An example of this reaction can be represented by applying UV light with ozone, where we have a two step reaction to produce a hydroxyl radical. In this case we have a two step reaction and two photons are needed to produce the hydroxyl radicals.

$$O_3 + h\nu \rightarrow O_2 + O^d \qquad\qquad (1)$$

$$O^d + H_2O \rightarrow 2\ ^{\bullet}OH \qquad\qquad (2)$$
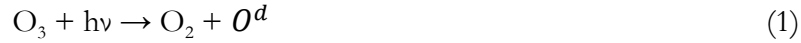
Where, O_3 is ozone, $h\nu$ is the energy of each individual photon of a monochromatic light wave, O^d is the excited oxygen atom (also known as a free radical), and $^{\bullet}OH$ is the hydroxyl radical   (Wang, 2006).

- ***Reduction-Oxidation Reaction***: also known as the REDOX potential. Fundamentally, redox reactions are a family of reactions concerned with the transfer of electrons between species. The term comes from the two concepts of reduction and oxidation. It can be explained in simple terms:

  Oxidation: the loss of electrons or an increase in the oxidation state by a molecule, atom, or ion.

  Reduction: the gain of electrons or a decrease in the oxidation state by a molecule, atom, or ion.

  From an environmental engineering view point, the use of oxidation reactions is commonly associated with the formation of oxides from oxygen molecules; however, this is only one specific example of a more general concept of reactions involving electron transfer. (Clark,2002)

- ***Batch Reactors***: Vessels designed to contain chemical reactions. Reactants are placed inside the reactor and allowed to react over time. Closed systems are typically unsteady state operations Designers ensure that the reaction proceeds with the highest efficiency towards the desired output product, and produces the highest yield of product while requiring the least amount of money to purchase and operate. This is most useful in the application of the understanding of chemical kinetics. (Wang, 2006)

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- **_Photogeneration:_** is excitation of electrons into the conduction band when a photon interacts with an electron.. energy required for photo-generation is equal (or greater than) the band-gap energy of a material. Such as silicon, where its excitation state is at 1.1eV. This results in the creation of an electron-hole pair, which can produce a current, (for example, solar cells) in the form of secondary reactions known as SEA and SED: (Carp, 2004)

  Sacrificial Electron acceptor (SEA): are molecular entities that act as the electron acceptor in a photo-induced electron transfer process and are not restored in a subsequent oxidation process but are destroyed by irreversible chemical conversion (IUPAC, 1997).

  Sacrificial Electron Donor (SED): are molecular entities that enable electrons used for reduction to be generated from the photo-excitation of another molecule and consumed during the process of the degradation of the photosensitizer under long exposure to illumination (IUPAC, 1997).

- **_Electrolysis of Water:_** a technique used by scientists to separate a compound or molecule into its component parts. By adding electricity to water and providing a path for the different particles to follow, the water can be decomposed into oxygen (O_2) and hydrogen gas (H_2). One important use of electrolysis of water or artificial photosynthesis (photoelectrolysis in a photoelectrochemical cell), is to produce hydrogen. This technology provides the conversion of water to hydrogen gas by splitting photocatalytic water using a semiconducting catalyst to create an electron–hole. (Electrolysis, 2013)

- **_Doping Titanium Dioxide:_** to modify the polymorphic structure of the titanium dioxide lattice crystal structure introducing a metallic anion within an atomic percentage of a compound; such as to extend photoactivity into the visible region. (Choi, 2009)

- **_Sol-Gel Process:_** in this chemical procedure, the 'sol' (or solution) is a stable dispersion of colloidal particles or polymers in solvents morphologies, of which range from discrete particles

to continuous polymer networks. The colloidal gel, is the network is built from agglomeration of colloidal particles and is the volume fraction of particles and may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. (Sol-gel, 2006)

- ***Organic Degradation:*** Refers to the disappearance of the initial compound or transformation of that compound into another. The words do not mean that the contaminant has been completely oxidized or entirely removed. But to finally achieve decomposition of the organic substrate into more simple forms of organic compounds, mineral acids, gases, and water. (Holmes, 2003)

2.1.2   Photocatalytic Oxidation Properties

The use of photocatalytic oxidation ("PCO") in the detoxification of water is a fast developing field of research. Photocatalytic detoxification refers to the destruction of possible hazardous waste within a specific controlled environment, where a source of light is used to generate photocatalytic oxidation or reduction reactions. There are a vast number of potential uses for photocatalytic oxidation within air treatment plants, supported by a number of research proposals submitted in the last three decades (Goswami, 2000).

Titanium dioxide (TiO_2) has been commonly used as photocatalyst within solar cell technologies, and its use in water treatment was first demonstrated in 1976 by a chemist, Dr. J.H. Carey. This area of research was chosen for this study, because of its potential of minimizing mechanical processing as well as for its high energy efficiency, in comparison with standard purification methods such as reverse osmosis and ultrafiltration, and its cost effectiveness compared with granular activated carbon and distillation. However, organic compound removal technologies such as reverse osmosis, nano-filtration, and distillation are still superior to single oxidation methods. This is due to the difficulty of stabilizing the oxidation process, and the adding of chemical catalysts in order to produce the same result (Williams, 2003). Organic oxidation

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technologies have many ways of generating an oxidation species. The most common oxidants are chlorine and ozone because of the abundant methods used to successfully synthesize the oxidant and due to their stabilization during treatment. The many forms of oxidant species are listed in Table 1

Oxidation power for various species relative to chlorine

Species	Relative oxidation power
Flourine	2.23
Hydroxyl radical	2.06
Atomic oxygen (singlet)	1.78
Hydrogen peroxide	1.31
Perhydroxyl radical	1.25
Permanganate	1.24
Hypobromous Acid	1.17
Chlorine dioxide	1.15
Hypochlorous Acid	1.10
Chlorine	1.00
Bromine	.80
Iodine	.54

Table 1. List of Oxidation Species, this list is relative to the oxidation power of chlorine (Goswami, 2000)

One of the most potent oxidizing agents is the hydroxyl radical ($^{\bullet}OH$), which can oxidize the most organic compounds, that are considered as pollutants in the environment, into carbon dioxide, water, and mineral acids. The hydroxyl radical is known as the second strongest oxidizing agent achieved using water photogeneration methods (RGF, 2010). Several methods of generating the hydroxyl radical have been developed, and three common methods of generating the hydroxyl radical within water are as follows:

1. The application of photocleavage (UV irradiation to split molecular particles) during ozone dissolution in water.

2. The photolysis of hydrogen peroxide.

3. The photogeneration of an electron hole on a semiconducting particle (such as titanium dioxide) with the sacrificial electron acceptor reacting with a hydroxide ion.

The most sought out photocatalysis oxidation reactor for the organic degradation of contaminated water consists of a heterogeneous semiconducting TiO_2 catalyst suspension exposed to UV light irradiation within a closed environment (that contains the organic substrate to be degraded). The design is similar to that of UV disinfection units within water treatment plants. However, due to the difficulty of recycling TiO_2 from effluent, reactor designs consist of coating or growing nano-sized layers of TiO_2 over the specific surface area of a reactor (Puralytics, 2012).

Nevertheless, a variety of solid-coated reactors with low inflow volumes still have no feasible industrial application. This is because the hydroxyl radical is a highly reactive and powerful oxidant, thus extremely unstable, and must be continuously produced by means of photochemical reactions. And the difficulty is maintaining the generation of hydroxyl radicals in a broad range of water environments for use with a broad range of pollutants. But they are a variety of ways of insuring the increased photogeneration of the hydroxyl radicals, but with limited uses or successes (Wang, 2008).

2.1.2.1 Photocatalytic Theory

When a semiconducting oxide is initiated by the absorption of a photon with energy equal to, or greater than, the band gap of the semiconductor, it produces an electron-hole ($e-/h+$) pairs, as written in (Equation 3):

$$TiO_2 \xrightarrow{\textit{UV light } h\nu} \boldsymbol{e}^- cb(TiO_2) \ + \ \boldsymbol{h}^+ vb\ (TiO_2) \tag{3}$$
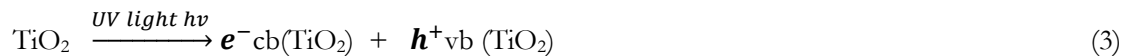
The equation shows when radiation of energy equal to or greater than the bandwidth of the semiconductor; for titanium dioxide anatase TiO_2 is 3.2 eV; a photon excites an electron $\boldsymbol{e}^-$ from the valence band $\boldsymbol{h}^+ vb$ to the conduction band $cb(TiO_2)$ and leaves an electronic vacancy (a hole) in the valence band $\boldsymbol{h}^+ vb\ (TiO_2)$. This reaction is instantaneous.

In the further detail, Figure 1 reveals the irradiation effect (hv) on the TiO_2 particle, which can act either as an electron donor or as an acceptor for molecules in the surrounding medium, which in this case is water, and O_2 and H_2 gases, and other oxides.
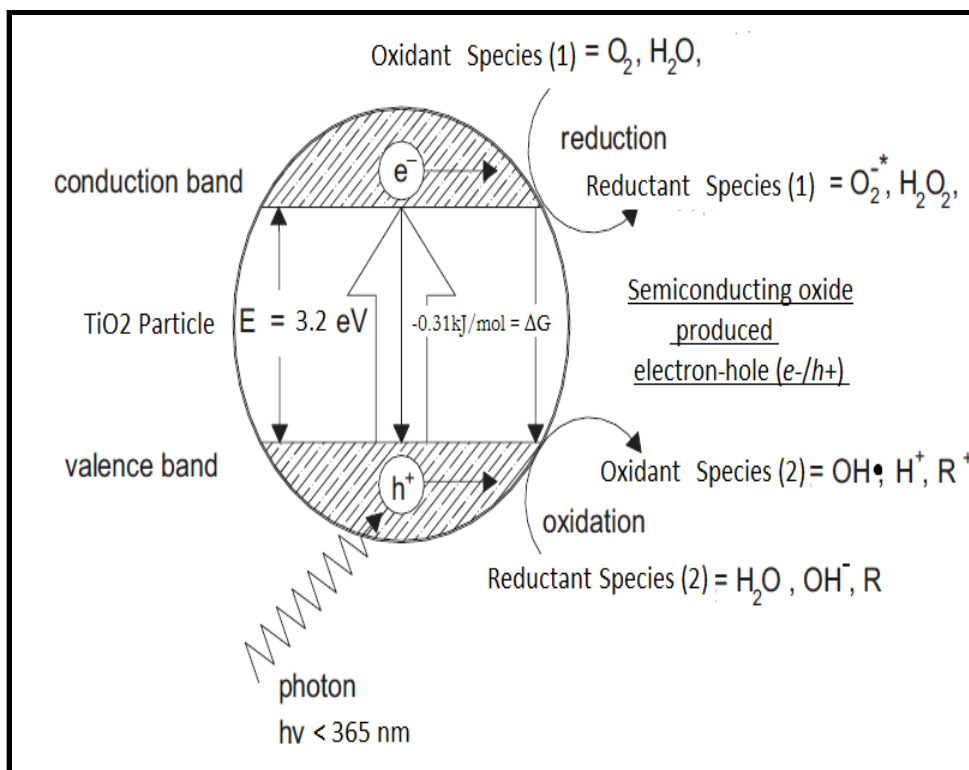
Figure 1. The photo-electro catalytic process of the excitation of the catalyst particle TiO_2, and the effects on the reducing and oxidizing states of other oxides, gases, and water. (Hupka, 2006).

To understand the formation of an electron hole process in the presences of water, there are several steps that are developed between underlying principles governing semiconductor photocatalysis. This is an elaborate simplification to other current literatures in terms of its potential applications in semiconductive chemistry.

1. The photo-electro catalytic process consists of the excitation of the TiO_2 by a UV light with an electromagnetic wavelength (λ) of greater or equal of 365 nanometers ($\lambda \leq 365nm$) and

the charge carried by a photon forms the electron-hole pairs $((e^-_{\text{conduction band}} / h+_{\text{valence band}}))$, as seen in Figure 1.

2. The charge carrier recombination of the conduction and valance band to liberate heat, and can be defined in terms of the Gibbs free energy value, $\Delta G = -0.31 \frac{kj}{mol}$, and since the value is negative, this reaction is to be instantaneous.

3. Initiation of an oxidative pathway by a valence-band hole. The valence band hole is strongly oxidizing, and by using a reductant species "R" such as OH⁻ "diatomic anion", also known as a hydroxide ion, which possess a negative charge, its oxidation can produce an extremely powerful and indiscriminant oxidant, the hydroxyl radical (˙OH) that carries no charge.

4. Initiation of a reductive pathway by the conduction-band electron which is strongly reducing. An important reaction of the conduction band electron is the reduction of adsorbed O_2 to O_2- that is theorized to prevent the electron from recombining with the hole, when O_2 is readily available to take the electron, instead of reacting with the ˙OH radical, which tends to happen as well (Carp, 2004). This can result in an accumulation of oxygen radical species that can also participate in attacking contaminants by oxygenation, and can be increased by the electrolysis of water.

5. Further thermal interactions (e.g., hydrolysis or reaction active oxygen species) will use a degree of association, which cannot be easily measured, within photocatalytic reactions to yield mineralization products from surrounding recalcitrant.

The surface layering of TiO_2 has a large concentration of ˙OH radicals, which rapidly attack pollutants on the nano-surface layer. The objective in this process is, if possible, to rapidly and uniformly allocate and sustain the ˙OH radical within the entire inflow volume of a solution. However, it is extremely difficult to measure the reactivity thickness of the TiO_2 photocatalysis nano-surface layer with an active suspension.

2.2   Titanium Dioxide Photocatalysis

Titanium dioxide (TiO_2) has been extensively studied for its unique physical and chemical properties, excellent optical transmittance in the visible and ultraviolet ranges, high dielectric constant, and photocatalysis for water cleavage. Titanium dioxide (TiO_2), one of the most basic materials in our daily life, has emerged as an excellent photocatalyst material for environmental purification. Vast amounts of research have benefited from using titanium dioxide as a photocatalysis, mainly in air purification, sterilization and cancer therapy. It is prominently used as a material in photoelectrochemical solar energy cell applications and as well in the area of environmental photocatalysis, including the self-cleaning of superhydrophilic surfaces, and most recently in the area of potential water treatment solutions (Fujishima, 2000). One of the most important aspects of environmental photocatalysis is the availability of a material. Titanium dioxide is close to being an ideal photocatalyst in several respects because it is relatively inexpensive, highly stable, can be chemically enhanced, and the photogenerated holes are highly oxidizing. The photogenerated electrons are reducing enough to produce super-oxides from di-oxygen (O_2-), Hydrogen Peroxide (H_2O_2), and even rarer, Ozone (O_3) (Carp, 2004). The energy band diagram for TiO_2 in a water solution of pH 7, is shown below in Figure 2 (the redox potential for photogenerated eH versus the standard hydrogen electrode).
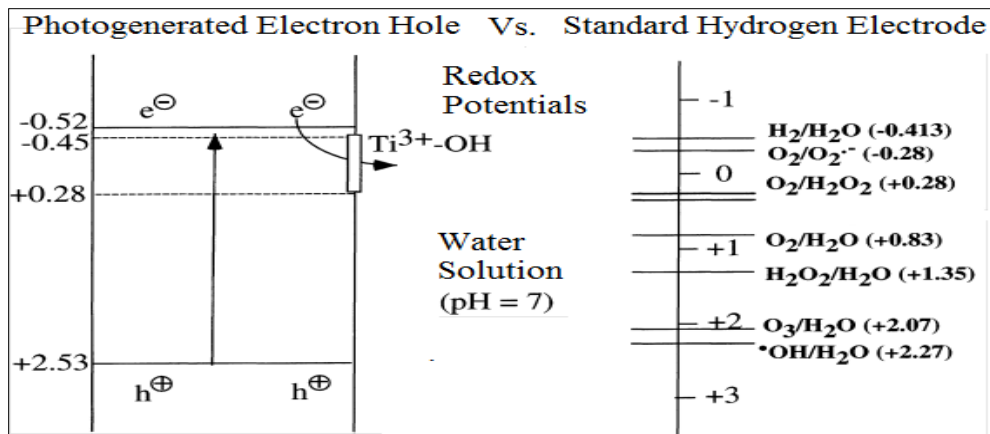
Figure 2. Various redox potential values with described processes on the surface of TiO_2 in a water solution of pH 7 (Hendricks, 2006).

After the reaction with water, the holes on the TiO$_2$ can produce hydroxyl radicals ($^\bullet$OH), with a redox potential which is slightly decreased. The oxidation potential of the hydroxyl radical (($^\bullet$OH is (2.8 V) relative to the normal hydrogen electrode (NHE); and is higher than other substances used for water disinfection such as ozone (O$_3$) (2.07 V), hydrogen peroxide (H$_2$O$_2$) (1.78 V), HOCl (1.49 V) and chlorine (Cl$^-$)(1.36 V) (Carp, 2004).

The redox potential for conduction band electrons is in principle adequately negative to evolve hydrogen from water, enabling hydrolysis. The electrons can also become trapped and lose some of their reducing power. This is significant, as the process of trapping electrons dictates the number of electrons still able to reduce oxygen gas (O$_2$) to hyperoxides, such as hydroxide ion (OH$^-$) or hydrogen peroxide (H$_2$O$_2$) (Carp, 2004). Depending on the exact conditions, the electron holes have the most important role within the photocatalytic reaction mechanism, as they participate in what is produced from it, whether a hydroxide radical (($^\bullet$OH oxide ion (O$_2^-$), peroxide (H2O$_2$), and/or oxygen gas (O$_2$).

The application of titanium dioxide as a recyclable or coated material for water treatment purposes has been investigated, producing results which have promoted further research into photo-degrading (by means of oxidation) a wide range of both organic and inorganic chemicals, bacteria, viruses, and heavy metals (Carp, 2004). The problem has been in the designing of degrading efficiencies that are equal to other AOP technologies, such as photo-Fenton reactors. A single crystallized TiO$_2$ particle in suspension with a substrate, can only react to a limited amount of organic substrate per volumetric inflow. Therefore, a fixed accumulation of the TiO$_2$ reactant can be characterized as being a percentage of the degradation of the overall degradation of system. However, this applies to a fully mixed suspended catalyst where the oxidative range is based upon the concentration of TiO$_2$ within the flow, and it is much more difficult to measure the oxidative range of the hydroxide radical particle from a fixed TiO$_2$ particle to the surrounding fluid. These limitations are caused by two factors: 1) there is no analytical equipment to analyze the surface interface of the TiO$_2$ nano-particles with the surrounding fluid surface; 2) the analytical procedures used to measure the photogeneration rate of the hydroxyl radical through experimental operations are complex, and consist of variables which describe the type of nano-lattice structure of TiO$_2$ and the thermochemical

transformation of TiO₂ during the operations of electrolysis process. (This was visually apparent during experimentation where the TiO₂ was observed to be transparent on the cation side of the cells). It is also difficult to monitor the photo-activity of TiO₂ within the constant water flow, and this makes it overwhelming difficult to control the electron transfer to the oxygen species, which is rate-limiting, and unknown to be indefinitely constant, and the critical step in semiconductor photocatalysis. But even with these limitations, experimental results from other research have shown that TiO₂, whether suspended or fixed, has the potential to be used in the photo-degrading processes using various designs of photo catalytic reactors (Hendricks, 2006).

2.2.1   Doped Titanium Dioxide

In semiconductor chemistry, "doping" is described as intentionally introducing impurities into an extremely pure (also referred to as "intrinsic") semiconductor, (such as titanium dioxide), for the purpose of modulating its electrical properties. (Lightly and moderately doped semiconductors are referred to as "extrinsic"). The impurities are dependent upon the type of semiconductor. If a semiconductor is doped to very high levels (usually over 10%), it will typically act more like a conductor than a semiconductor (Choi, 2009).

Titanium dioxide is a wide gap oxide semiconductor, and used as an electrode in electrochemistry. TiO₂ has three types of crystalline structure: rutile, anatase, and brookite, composed of titanium ions with octahedral coordination. Anatase has the high mobility of an n-type charge carrier, and this describes its large thermopower (thermoelectric power) in its reaction with other forms of oxides. It is more highly photoactive than both rutile and brookite. However, because anatase is not as thermodynamically stable as rutile, the pure anatase phase has a higher crystalline affinity, which is difficult to maintain. The crystallized integrity tends to break down with other chemical processes, but with the use of thin-films and with an appropriate choice of substrate material, research shows that doped titanium dioxide anatase has enabled the growth of thin films with high crystallinity (which refers to the degree of structural order in a solid crystal) (Hamilton, 2008).

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Metal-doped TiO_2 solutions and films are prepared using a sol-gel method (the simplest method observed). Other case studies have used copper, ferric, and aluminum ions as dopants to be introduced into titanium dioxide crystal lattice. In this system design, however, a heterogeneous solution of nano-sized titanium dioxide photocatalysis is doped with chromium (III) ion [Cr(III)]+). Chromium doping of TiO_2 has been reported to yield an increase in photoreactivity (Hussain, 2011). Dopant studies have reported a red shift in the absorption spectra of the doped chromium and titanium dioxide material, which means the material can display photo absorption with increased wavelengths of radiation, but this is dependent on how the material is structured; whether grown in nano tubes, thin films, or other coated applications (Hussain, 2011). However, this does not necessarily correlate with an increase in photoactivity, but chromium has a crystal body-centered cubic structure and can be well structured to stabilize the anatase tetragonal crystal structure (Hussain, 2011).

2.2.2   Secondary Catalysis

The photo-cleavage (hydrolysis) of water is a difficult process to control and involves the formation of many chemical intermediates, which can react with each other, short-circuiting the specific process. The basic process is summarized below in Equation 4.

$$2H_2O \xrightarrow[hv \geq Ebg]{H_2\ catalyst\ |\ Semiconductor | O_2\ catalyst} O_2 + 2H_2. \tag{4}$$
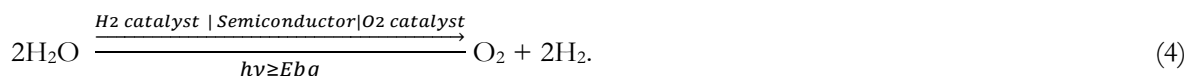
The main problem associated with this photoreaction is the very low quantum yields (a radiation-induced process which measures the number of times a specific event occurs per photon absorbed by the system) associated with photo- or chemically-induced reactions. This is caused by factors such as the electron recombining with the semiconducting hole, low photostabilities on the semiconducting surface, and high overpotentials of H_2O and O_2 in reacting with the conductance band of the photogenerated hole; thereby eliminating the possibility for the hydroxide ion to form the hydroxide radical (Mills, 2004).

To further the photoreduction of water, certain research groups have used a platinum group catalyst (PGM) catalyst, (such as Platinum Pt), in the system, which is usually integrated into the semiconductor particles (Mills, 2004), but such metals are very expensive and not readily available for environmental engineering applications. Silver Ag^+ is a transitional metal, and is known to have localized surface plasmons, (LSPs), which are charged density oscillations confined to metallic nano-particles that have absorption bands in the near-UV region, which cause strong light scattering and an enhancement of the local electromagnetic field (Awazu, 2008). Silver Ag^+ has been found to have the enhanced photocatalytic behavior of titanium dioxide, if enhanced with near UV range field amplitudes (Awazu, 2008). A considerable enhancement of the UV field in the vicinity of silver (Ag+) ions can increase the photogeneration of the electron hole and therefore increase the reduction of O_2. This then increases the overall oxidative state of water by forcing the conductance band in transpiring the H+ cations into the sacrificial electron acceptor, generating hydrogen gas H_2 (g) or a reduction of oxygen gas O_2 (g) into the oxide ion (O_2-). This process is illustrated in Equation 5:

$$\text{SED } [O_2(g)] + 2H+ + 2H_2O \xrightarrow[hv \geq Ebg]{Ag+ \ | \ Semiconductor \ TiO2} O_2\text{-} + H_2(g) \tag{5}$$
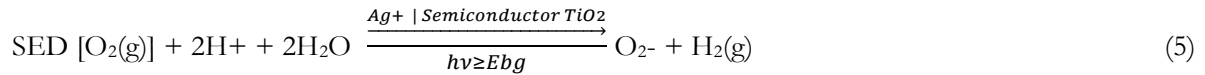
2.3 Electrolysis of Water

The electrolysis of water is the decomposition of water (H_2O) into oxygen (O_2) and hydrogen gas (H_2) caused by an electric current being passed through the water. An electrical power source is connected to two electrodes, (or two plates), typically made from an inert conductive material such as platinum, stainless steel, or graphite, which are then placed into a volume of water. Hydrogen appears at the cathode (the negatively charged electrode, at the point where electrons enter the water), and oxygen appears at the anode (the positively charged electrode). Assuming an ideal faradic efficiency, the amount of hydrogen generated should be twice the number of moles of oxygen, and both are proportional to the total electrical charge

conducted by the solution. However, in many types of cells, competing side reactions dominate; resulting in different products. When conduction is less than ideal, this is related to factors such as the electrolyte used in the water, the pH of the solution carrying the current, and any secondary contaminates that may react to the voltage charge. Electrolysis of pure water requires excess energy in the form of an overpotential, which overcomes various activation barriers. To counter any problems, the efficiency of electrolysis is increased through the addition of an electrolyte (such as a salt, an acid or a base, termed "electrocatalysts"), which then carries the current ampere through the voltage cells more efficiently. The electrolytic cells require electrocatalysts, which are obtained by the addition of a salt. Pure water has an electrical conductivity of about one/millionth of that of seawater, (sea water has a conductivity value of 50 mS/cm), and there is typically 50 g/L of sodium chloride found in most high saline water sources (Electrolysis).

An example of the REDOX reaction occurring in electrolysis:

Anode (oxidation): $2\ H_2O(l) \rightarrow O_2(g) + 4H + 4e^-$ (6)

E_o (oxid.) = -1.23 V, Eo (red.) = 1.23 V

Cathode (reduction): $[2H + 2e^-]_{(aq)} \rightarrow H_2(g)$ (7)
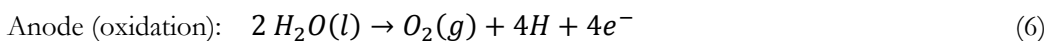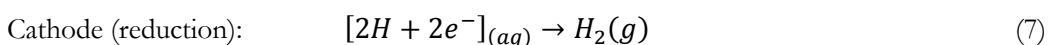
E_o (red.) = 0.00 V

2.3.1   Electrolytic Cell

By applying an electric current through an external circuit, voltaic cells submerged in solution are used to drive spontaneous chemical reactions. These cells are important because they are the basis for the batteries that fuel modern society. However, they are not the only type of electrochemical cell in existence. It is also possible to construct a cell that works in a chemical system by driving an electric current through the system. These cells are called electrolytic cells. Electrolysis is used to drive an oxidation-reduction reaction in a direction in which it does not occur spontaneously (Electrolytic, 2012).

As mentioned in the previous section, pure water is a very poor conductor of electricity. An addition of an electrolyte (in this case sodium sulfate) is therefore added to water to provide ions, which can flow

through the solution, thereby completing the electric circuit. The electrolyte must be soluble in water and should also be relatively inexpensive. Most importantly, it must contain ions that are harder to oxidize or reduce than water. When an aqueous solution of Na_2SO4 is electrolyzed, H_2 gas collects at the surface of one electrode and O_2 gas collects at the other, (which can be observed during experimentation). Within the photocatalytic reactor, a source of direct current (a DC voltage generator) is connected to a pair of inert electrodes (99.9% pure compressed graphite plates) immersed in sodium sulfate solution. The concentration of sodium sulfate is 50 g/L, with a conductivity of 50 mS/cm. The salt is stirred in a 4 liter cylinder for 1 hour, and is assumed to be fully homogenous, with no clustered particles observed within solution.

This experiment uses 3 electrolytic cells in a series, composed of graphite, within a fiber glass container which is exposed to the atmosphere. The electrodes are then connected to a DC voltage source for electric current.

It would be dangerous to use a sealed design to collect the H_2 and O_2 gas given off in the reaction, and a pressurized cell, for the separation of the gases, would be more expensive to construct, (therefore, these were not taken into account when designing the photocatalytic reactor).

2.3.2   Electrolytic Cell to Assist in Oxidation

Titanium dioxide under UV irradiation can create hole–electron pairs in an aqueous solution. The holes react with the hydroxyl group in water, acting as an electron donor, to produce the hydroxyl radicals. The electrons simultaneously react with the dissolved oxygen in water, and act as an electron acceptor to yield super oxides such as O_2^- (Mills, 2004). However, at times the generated electron hole pairs do not participate in the redox reaction with water or oxygen, and disappear as heat through the recombination of electrons holes. This recombination of holes and electrons is therefore known to be one of the most important factors affecting a decrease of photocatalytic efficiency (Kima, 2003). Transmitting photogenerated electrons through an external circuit (electrolytic cell) with an electrochemical bias (an electrolyte) into a cathode (Kima, 2003) can be considered to suppress the recombination effect. A catalytic oxide electrode such as TiO_2, known as a dimensionally stable anode (DSA), is capable of generating hydroxyl radicals under an electrochemical

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potential to evolve oxygen gas (Kima, 2003). The photogenerated electrons on the electrode surface can be forcibly taken out into a cathode by the oxidation function of the anode, suppressing the recombination of hole–electron pairs, while the photocatalytic anode is under UV irradiation; with the potential of generating oxygen evolution and applied oxidation. Previous research shows that this system can assist the photocatalytic enhancement to about 90%, due to the suppression of the recombination of holes and electrons, and by forcibly generating electrons through an external bias into a cathode, (with the oxygen generated by the electrolytic reaction acting as an acceptor to the electrons) (Kima, 2003). To conclude, if an electrode is combined with a photocatalyst, (the TiO_2 substrate on an electrode), can simultaneously act as an electrolytic anode and a photocatalyst. The anode of an electrolytic–photocatalytic cell therefore has increased potential for oxygen evolution using irradiating UV and a voltage potential. The electrode generates the hydroxide radicals (OH-) in both electrolytic and the photocatalytic reactions.

2.4   Combined Theories

The principles of design of the photocatalytic oxidation reactor for the purpose of decomposition of organic solute are based on 3 main processes and 2 main applications. The 3 main processes used to satisfy the photocatalytic oxidation reactor are:

- The adsorption of photons on the surface of a semiconductor (Titanium Dioxide). Ultraviolet radiation (UV), which acts as the active energy agent on the semi-conductive surface and as a photo-reactive agent, produces the hydroxyl radical by an integration of these processes, and the hydroxyl radical can then decompose organic molecules into the simple forms of carbon dioxide, water, and mineral acids.

- The enhancement of the redox reaction of water and oxygen with electrolytic cells controlled by the process of electrolysis. This can provide a favorable oxidation-reduction reaction in a direction which minimizes the counterproductively of the semiconducting surface to prevent the recombination of the holes and electrons.

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- The photo-enhancement and reactivity of titanium dioxide with the addition of a secondary catalysis. This is provided using the process of doping the titanium dioxide with a transition metal chromium (Cr III) and a highly photocatalytic transitional group metal, such as silver (Ag). There are two main applications which allow an integration of these processes in an experimental reactor, so as to efficiently drive chemical decomposition and enhance purification process of contaminated solution. They are as follows:

- The coating of the graphite plates with doped Titanium Dioxide using annealing heat treatment, wherein a material is altered, causing changes in its properties such as hardness and ductility (Process Annealing, 2013). The dopant TiO_2-CrIII-Ag+ is annealed to graphite plates at a high temperature, whilst the coat is simultaneously atomized to increase the effect of diffusionless transformation. This transformation affects the electrochemical behavior of annealed samples initial characteristics, by improving conductive potentials, and the resulted change in crystal structure, and to increase the stability of the semiconductor resistance to corrosion (Mazăre1, 2011).

- The integration of graphite plates into an electrolytic cells structure within the batch reactor volume. Small portions of the plates must be exposed to the atmosphere and kept dry in order not short the circuit flow of the electrolysis process.

3   PREPARATION FOR EXPERIMENTAL TRIALS

3.1   Design of Batch Reactor

Experimental design of the photocatalytic oxidation batch reactor aims to produce and optimize the process of organic degradation. The design sought needs to accomplish three separate goals:

1. To rapidly degrade the initial contamination concentration over a short period of time, and then sustain the reactor process of degradation efficiency over an extended period using stabilizing photoactivity.

2. To extract solution samples for accurate and precise data on total organic carbon (TOC), chemical oxygen demand (COD), pH, and conductivity.

3. To be able to be re-used for repeated experiments with similar initial concentrations and parameters to show consistency in results with similar trials.

The type of reactor used and designed therefore dictates the parameters used in the reaction operations and it should be capable of increasing the solution dissolution with surface catalysis, produce a fully mixed, homogenous environment, and provide all necessary and available modifications in favor of photo-chemical reactions.

The reactor design incorporates these fundamental parameters:

- The graphite-plate reactor has a 3-cell electrolysis configuration.

- The batch reactor is assumed to be <u>unsteady-state</u>, since isothermal conditions change as well.

- The reactor is open to atmospheric pressure and temperature.

- The reactor is fully mixed by a recycled flow provided by a single submerged pump (at a flow rate of 3.78 liters per minute).

- Constant energy input is provided by a DC power supply.

- The reactor has a custom- designed mirrored ceiling to reflect UV light into the reactor solution.
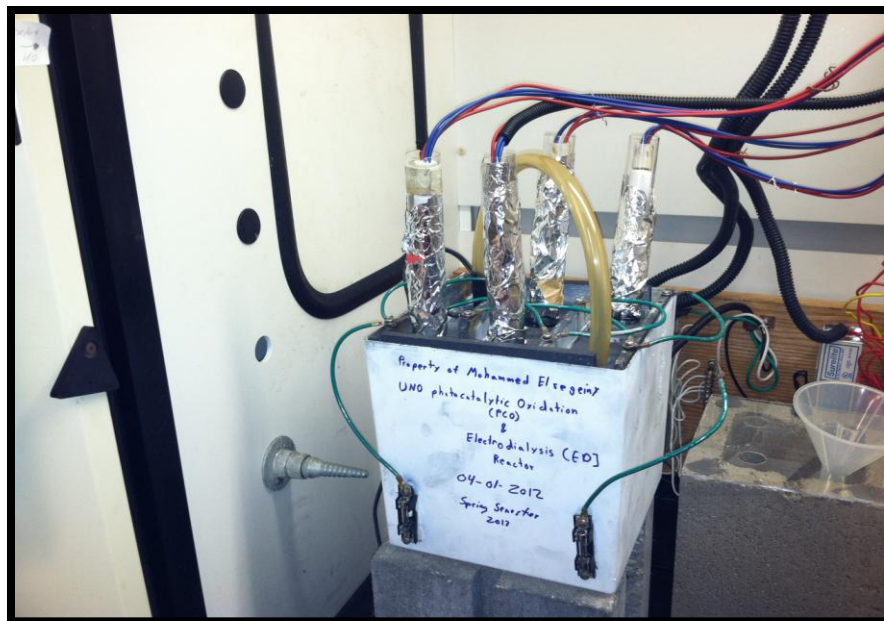
Figure 3. Assembled photocatalytic reactor ready for experimental trial

The photocatalytic oxidation reactor uses simplified materials and techniques that can be reinstated in a larger-scale pilot reactor. The parameters consist of using pure 98% graphite plates (with a chemical binder), which are electrically conductive. Five plates are used as conducting anodes and cathodes for electrolysis. The compressed graphite can up hold a temperature of 800° C. The reactor has a volume of 3.8 liters, (approximately 1 gallon) and dimensions of 16,5 cm (height) by 17.8 cm (length) by 17.8 cm (width). A fiber glass skeleton is interlocked inside the reactor and fabricated to contain the graphite plates. The reactor has a built in drainage for solution removal. The design includes a mirrored ceiling attached to the bottom end of the cover, to reflect UV light into the solution. Within the reactor, three 40 watt UV~lights ($\lambda \leq 365$ nm) as used in UV disinfection technology, are structured between the 3 electrolysis cells. The graphite plates are supplied with a DC voltage power supply. A plain visual of the rector seen in Figure 3
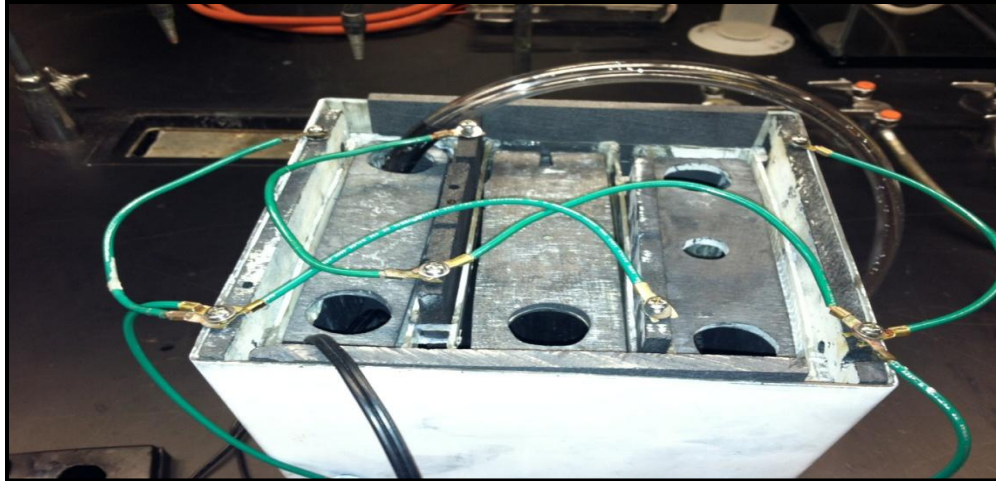
Figure 4. Visual of the electrolysis cells with cut and fitted graphite plates.

3.1.1 Summary of Alternative Photocatalytic Reactors

There have been many attempts to produce a photocatalytic reactor for the purpose of water purification. Some attempts have produced inspiring results, and some have initiated further research into their design-perfection. However, most designs have not been economically feasible. There are typically two types of photocatalysis reactor:

1) Fixed Catalyst (F.C.)

This reactor fixes the catalysis on to a specified surface area and uses an adsorption process to effectively degrade organic compounds by circulating fluid flow through or around the surface area of the integrated catalysis, while the surface is irradiated with radiation (Wang, 2008).

2) Powderized Catalysis (P.C.)

This reactor introduces and disperses the catalysis into a solution volume and uses an absorption process to effectively degrade organic compounds by circulating contamination and catalysis into a homogeneous solution, while the entire volume is irradiated with radiation (Wang, 2008).

It has been concluded from various research (Wang, 2008) that when titanium dioxide is used in powder formula it has a higher degrading efficiency than a fixed catalysis because of the increased dispersion between the waste water and the catalysis producing the oxidative hydroxide radical, resulting in a more rapid interaction between the hydroxide radical and the organic compound needing to be oxidized. In pilot plant studies conducted over the past few years, titanium dioxide powder has been commonly used as a photocatalysis, which illustrates its effectiveness within processes used to degrade harmful organic material. Titanium dioxide is cheap and insoluble in water. However there are operational flaws in its use as a powderized catalysis, due to the need for additional technology to separate the catalysis from the waste water after photocatalytic degradation. This introduces a dilemma: the introduction of titanium dioxide particles within a solution increases the photocatalytic efficiencies, but results in increased separation difficulty, which results in additional costs for catalysis removal technology; the usefulness of the technology is therefore overshadowed.

Listed below are some reactors used in analyzing fixed and powderized catalysis (Wang, 2008):

- Annular Photoreactor (F.C)
- Packed Photoreactor (F.C)
- Photo Catalytic Taylor-Vortex Reactor (P.C)
- Titanium Dioxide Fluidized Bed Reactor (F.C)
- Titanium Dioxide Coated Fiber Optic Cable Reactor (F.C)
- Falling Film Reactor (F.C)
- Thin Film Fixed Bed Slope Plate Reactor (F.C)
- Swirl-Flow Reactor (P.C)
- Concrete Reactor (P.C)
- Batch Reactor (F.C) and (P.C)
- Flat-Plate Reactor (F.C) [An example of a Flat-Plate Reactor, (Appendix A)]
- Tube Reactor (F.C) and (P.C)
- Bell Reactor (F.C)

For the purpose of simplicity, a batch reactor is used in this experiment to acquire degradation data and to make an analysis of the modifications necessary for the increase of photocatalytic efficiency, can be found.

3.1.2   Construction Phases

In research, the construction and design phases of an engineering project can take months or even years to perfect and complete, at times with less than satisfactory results. Guidelines for design are fundamental, but even so flaws can be found in data results, experimental errors, or even process misconceptions. Most of the material used in the construction of the reactor was purchased from industrial and local hardware stores. Construction began by stripping a fiberglass fish tank and adding a drainage system and graphite holding skeleton. No plastic or organic binders, such as epoxy, were used within reactor, in order to prevent organic carbon cross contamination during photocatalytic exposure. A fiber glass skeleton was constructed using 3.1 mm thick fiber glass strips welded together to form a holding skeleton for all graphite plates to interlock and to prevent the plates from touching, (so as not to short the circuit of the electrolysis process during experimentation). A total of 12 custom cut graphite plates were used within the reactor. They were cut to tightly fit the fiberglass skeleton, and by doing this five x 15.2 cm by 15.2 cm plates, two x 16.5 cm by 16.0 cm plates, two 10.2 cm by 2.5 cm plates, one x 10.2 cm by 3.8 cm plates, and one x 14.0 cm inch by 14.0 cm inch plate were produced. The reactor was placed and operated under a laboratory ventilation hood to prevent toxic or harmful fumes from entering the laboratory work space during experimentations.
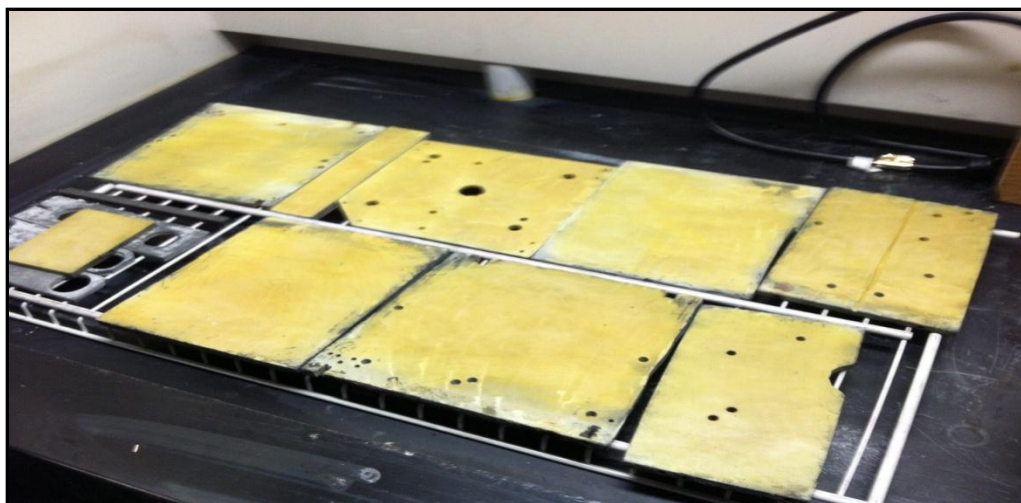
Figure 5. Custom cut graphite plates with fresh doped titanium dioxide coat.

3.1.2.1   Redesign from Failed Results

After the initial construction of the reactor, many experiments were made to establish prominent results. However, a lack of resources and equipment failure lagged the experimental progress and hindered many objectives defined in the initial phase of experimenting. Trial and error were the main sources of development in integrating and modifying major and minor improvements in design and experimental operations. A list of the experimental trials is presented to show the evolution of the experimental analysis and the reason for the modifications of the design and procedure, which then produced relatively accurate results.

Table 1 Details of the trials and applied enhancements during design and analysis of the photo-electro catalytic reactor. Explanations of reactor modifications and reformulation of reactor procedures to insure proper degradation analysis and the evolution of the final reactor design are included.

Trial Date	Graphite Coat	Analysis	Initial Concentration in ppm/C Measured	Contamination	Trials	Electrolysis	Detention Time
03-20-12	TiO$_2$	TOC	250	Tween 40	1	No	Approx 24 h, Samples taken

							continually within 24 hour mark.
Results of Experiments with Modifications	Degradation of Tween 40 was reduced to 170 ppm C, however, severe fowling and precipitation accrued, which permanently stained the TiO_2 coat, leaving experimental apparatus damaged. The use of Tween 40 was discontinued, and the graphite plates were recoated with a new TiO_2 coat.						
03-25-12	TiO_2	TOC	100	Phenol	3	No	Approx 1 hour, samples taken every 7 minutes
Results of Experiments with Modifications	Analysis of TOC sampling degradation was sporadic and revealed inconclusive data. The cause was determined from using phenol which **[1]** damaged the combustion chamber during TOC sampling. The use of phenol was discontinued. The TOC analyzer was fitted with a new combustion chamber.						
03-31-12	TiO_2	TOC	100	Rhodamine	3	No	Approx 1 hour, samples taken every 7 minutes
Results of Experiments with Modifications	Results showed a limited or no form of solid degradation - one trial had a sinusoidal function in degradation, with increased contamination levels during experimentation. Color of Rhodamine sample was relatively also unchanged. It was concluded that the cell chambers were not fully mixed because of apparent dead zones where the Rhodamine accumulated into a gel above the submerged pump. Proceeded with applying electrolysis to a second solution sample. Also increased laminar flow within reactor *[2], and removing apparent dead zones.						
04-01-12	TiO_2	TOC	100	Rhodamine	1	Yes	Approx 1 hour, samples taken every 7 minutes
Results of Experiments with Modifications	After the first trial, there was visual degradation where the final 9th sample was almost clear. However, an error accrued during TOC sampling process, causing severe damage to the combustion chamber. These two *[3] results were both caused by the use of Sodium Chloride (NaCl) during electrolysis. Discontinued the use of NaCl as electrolyte, because it was oxidizing the Rhodamine and replaced it with sodium sulfate Na(SO4). Replaced the combustion chamber of the TOC analyzer						
04-03-12	TiO_2	TOC	100	Rhodamine, 4-Nitrophenol	2	No	Approx 1 hour, samples taken every 7 minutes
Results of Experiments with Modifications	Slight degradation from the Rhodamine after the first trial, around 3% within final sample, and no degradation from the second trial. No forms of degradation for either trial form the 4-nitrophenol. Halted the final trail to conserve remaining DI water. Proceeded to use the electrolysis for the same containments of Rhodamine and 4-nitro phenols at same initial concentrations						
04-05-12	TiO_2	TOC	120	Rhodamine, 4-Nitrophenol	1	Yes	Approx 1 hour, samples taken every 7 minutes
Results of Experiments with Modifications	No forms of degradation from either contaminate, with sporadic increase of concentrations up to 3 mg/L during final 20 minutes of sampling time. Data analysis has errors and unproductive results. Restructured experimental procedure, reducing initial contaminations and applying enhanced TiO_2 coat with Chromium Ion and stripping old coat of pure TiO_2						
04-10-12	TiO_2-CrIII	TOC	25	Rhodamine, 4-Nitrophenol	1	No	Approx 2.5 hours, samples taken every 10 minutes
Results of Experiments with Modifications	In all trials, a sudden rise of contamination levels, up to 5 mg/L from initial concentration, with no degradation below initial concentration. Previous sampling points were taken from below the reactor, from the drainage. Sampling point now taken from pump outlet on solution surface. It was assumed precipitation caused increased contamination levels, even though it was not necessarily visual						
04-10-12	TiO_2 – CrIII	TOC	25	Rhodamine, 4-Nitrophenol	1	No	Approx 2.5 hours, samples taken every 10 minutes

Results of Experiments with Modifications	Three percent degradation was observed with Rhodamine and no degradation with 4-nitrophenol. Graphs show stagnation in degradation after 40 minutes of experimental sampling. Next experiment will use electrolysis and observe results.						
04-12-12	TiO$_2$–CrIII	TOC	25	Rhodamine, 4-Nitrophenol	2	Yes	Approx 2 hours, samples taken every 7 minutes
Results of Experiments with Modifications	Both reagents had around 5-7% reduction from initial concentration within the first trial and below 5% degradation on the second trial. With each trial, efficiency within the reactor decreases. However, there is much improvement in comparison to non-electrolysis. The TiO$_2$-CrIII may have fouling which was visual. Application of backwashing is applied every 35 minutes, by removing reagent solution to 4 liter containers and washing coated plates by introducing purified water from drainage outlet, and reintroducing same reagent solution into reactor.						
04-13-12	TiO$_2$-CrIII	TOC	25	Rhodamine, 4-Nitrophenol	2	Yes	Approx 1 hour, sampling time is every 5 minutes, first 7 samples taken then reactor is backwashed for about 1 min, with the last 6 samples taken in the last 30 minutes.
Results of Experiments with Modifications	No more than 5% degradation before backwashing for Rhodamine with no degradation for 4-nitro phenol. After backwashing, 3% degradation of Rhodamine, with no degradation in 4-nitro phenol samples. Large spikes in organic carbon after backwashing occurred. Tween 40 contaminate was reintroduced. Better anti fowling procedure was introduced by using high pressure water upon coated graphite plates after drainage.						
05-14-12	TiO$_2$-CrIII	TOC	30	Tween40	1	Yes	Approx 1.5 hours, sampling time is every 10 minutes, backwashing occurs every 30 minutes for about 1 min.
Results of Experiments with Modifications	Only max of 3% of degradation from the initial concentration to time of backwashing. Operation was observed from the initial concentration after backwashing to the final concentration after 30 minutes of reactor operation. The analysis was only averaged at 8% degradation since only one trial was used to conduct the experiment. To increase photocatalytic operations, a secondary catalysis (Ag+) was introduced to help increase degrading efficiency. Tween 40 concentration was lowered. COD analysis was introduced to observe degrading efficiency to that of TOC, even though it is understood that it is less accurate than the TOC analysis.						
06-18-12	TiO$_2$-CrIII-Ag+	TOC/COD	80	Rhodamine	2	Yes	Approx 3.5 hours, sampling time every 10 minutes, backwashing occurs every 30 minutes for about 1 min.
Results of Experiments with Modifications	Apparent degradation of the samples, with no change of dye discoloration. With increase and decrease of samples concentrations, an average result was calculated, showing a reduction of 10 ppm C from initial concentration after final sample. No degradation visually, but analytically apparent. Conducted next experiment with 4-nitrophenol *[4]						
06-20-12	TiO$_2$-CrIII-Ag+	TOC/COD	80	4-Nitrophenol	1	Yes	Approx 3.5 hours, sampling time is every 10 minutes, backwashing occurs every 30 minutes for about 1 min.
Results of Experiments with Modifications	Apparent degradation with 1st trail. Random increases in concentration generated with the TOC analyzer with 2nd and 3rd trial sample analysis. The reactor coat also to seem to darken to a black transparent coat where light intensity is the strongest. Experiment failure seems to be attributed to the modification of TiO$_2$-CrIII coat with the silver ion, and visually, the black tarnish on the coat seems to be caused by the photo-decomposition, which can be blamed the by production of silver sulfide. *[5] The next experiment with the Tween 40 would conclude whether or not the Ag+ caused the experimental failure.						
06-22-12	TiO$_2$-CrIII-Ag+	TOC/COD	80	Tween 40	1	Yes	Approx 3.5 hours, sampling time is every 10 minutes,

							backwashing occurs every 30 minutes for about 1 min.
Results of Experiments with Modifications	Degradation with some and not of others. Relatively constant after 2nd backwashing. During experimentation, increased foaming was observed on the surface of solution. It was concluded that the Ag+ ion caused the failure of degradation. Coats were remade with silver mass concentration within coat solution from 40% to 5%. In addition sodium sulfate was no longer used and sodium bicarbonate was used instead to save on sodium sulfate						
06-23-12	TiO$_2$-CrIII - Ag+	COD	25	Rhodamine, 4-Nitrophenol, Tween 40	1	Yes	Approx 2.5 hours, sampling time is every 10 minutes, backwashing occurs every 30 minutes for about 1 min.
Results of Experiments with Modifications	During the experiment of the 4-nitrophenol, sodium bicarbonate reacted with the mercuric sulfate causing the COD vials to foam and overflow. COD analysis failed because of the sodium bicarbonate. Sodium sulfate was reintroduced, and detention time increased to visualize a more dynamic change in degradation, with decreased initial concentrations to create more realistic parameters for experiments						
06-24-12	TiO$_2$-CrIII -Ag+	COD	50	Rhodamine, 4-Nitrophenol, Tween 40	1	Yes	Approx 4 hours, sampling time is every 10 minutes, backwashing occurs every 30 minutes for about 1 min.
Results of Experiments with Modifications	Sudden shifts of concentration levels increasing and decreasing from initial concentrations were seen in all contaminates of the first trial. There was too much sporadic change in concentration. COD had inaccurate shifts in concentrations during extent of backwashing, some concentrations recorded to be too low in some cases. Decided not to implement backwashing in the final experiments since samples shifts were dramatically inconsistent after backwashing.						
07-17-12 to 06-20-2012	TiO$_2$-CrIII- Ag+	COD/ TOC	70	Rhodamine, 4-Nitrophenol,Tween 40	3	Yes	Approx 4 hours, sampling time is every 15 minutes, with no backwashing
Results of Experiments with Modifications	Forms of degradation in all experimental trials, with consistence in all trials with specific contaminate. Over 15 samples were taken. However, with a limited number of COD vials, only 5 main samples were taken in the course of 4 hours, so as not to stricken other lab members needing them for other use. Used as Final Data analysis						

*[1] Phenol forms a carbon char residue polymer at high temperatures. (Sykes, 1967)
*[2] Modified the graphite plates by drilling holes of 1 cm throughout upper water level of plates.
*[3] Chlorine is a powerful oxidizer and can oxidize the catalyst within the TOC analyzer, damaging the analyzer.
*[4] The addition of mirrors for increased illumination within reactor.
*[5] Research shows the tarnishing effect of silver sulfide (http://www.vam.ac.uk/content/journals/conservation-journal/issue-18/tarnishing-of-silver-a-short-review).

3.2   Preparation of Coat

A number of reactions can occur during experimentation with the photo oxidizing surface, (as stated in previous chapters) in order to find the best conditions in which to generate the hydroxyl radical. In theory, photogenerated electrons upon layers of TiO$_2$ doped with Cr (III) and the addition of Ag+ can have more favorable reactions and outcomes in the production of oxidizing agents within solution. This can be visualized in Figure 6 (Dvoranová, 2002).
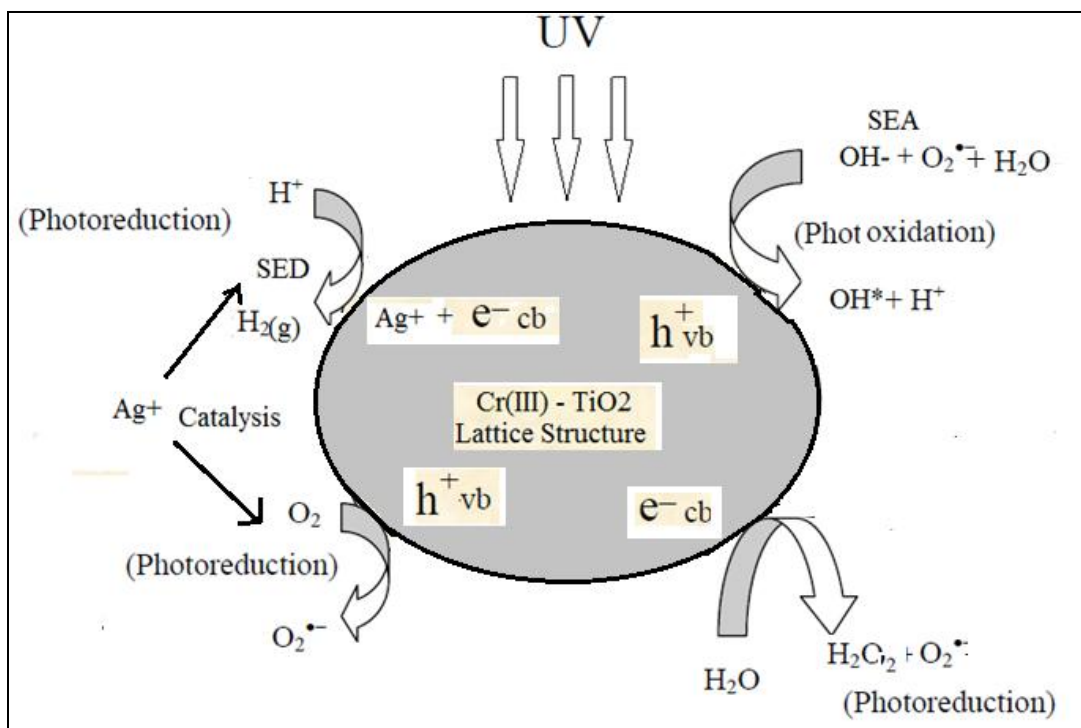
Figure 6. Visual cumulative of photoactivity reactions within the Crystallized CrIII-TiO₂ coat during photodegradation process. **(**Adapted from Auffan (2009))

In this experiment, low-cost methods were used in the layering of the semiconductor doped titanium oxide (TiO_2) chromium III (Cr III), and silver ion (Ag+) coat upon inorganic graphite plates, which necessitated the use of a laboratory setting. The first phase involved the development of the TiO_2 nano-particles laced with Cr(III), and the second phase involved the application of the silver ion coat.

3.2.1   Chromium Ion Placement within Titanium Oxide Lattice

The main process in doping the TiO₂ coat is the addition of impurities. The purchased Titanium Oxide (TiO₂) Nanopowder Dispersion (US Research Nano-Materials TiO₂ Nanoparticles Aqueous Dispersion, Anatase, 15 wt%, 5-15 nm) was stored in an aqueous solution where its solubility was dependent on the solution having a pH of below 1. Carbolic acid was used and an extremely stable surfactant (poly-vinyl-pyrrolidone) which helped stabilize the nano sized TiO₂ within the solution. Anatase TiO₂ was chosen because it has strong photocatalytic properties. The higher potential of its positive electron holes in oxidizing

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water can increase the production of the hydroxyl radicals, in comparison to rutile, (discussed in a previous chapter, and which is another widely used crystal form of TiO_2)(Carp, 2004). One theory suggests that anatase is more photoreactive because it has an extension of its steeper crystal structure along the vertical axis of the crystals, which is longer than the rutile crystalline structure. This keeps anatase predominantly unstable during photoactivity, while always trying to achieve kinetic stability (Yeredla, 2008).

To insure durability of the coat when binding with the graphite plates, (which have nano- size particles ranging from 80 nanometers to 200 nanometers), the coat is heat treated to $500°$ C in order to obtain a successful diffusionless transformation. To obtain a permanent order of the lattice structure of the titanium dioxide to the surface planar structure of the graphite, it is necessary to obtain the formation of an amorphous graphite molecular structure by binding polymerized chains of the TiO_2 solution using thermal metamorphism. In order to achieve this, high temperature and pressure is used to form the hardened lattice structure. However, the anatase structure is still unstable and highly photosensitive to light and has the potential to reduce with air particles and weaken the binding particles with the amorphous graphite structure (Carp, 2004). Therefore, to keep a higher and stable photo-electro-chemical activity during the degradation process in water, the anatase 5-15nm polymorphism crystal structure is doped with the Chromium III ion. Chromium III has a body-centered cubic crystal structure that can integrate in to the tetragonal crystal system of the TiO_2 (Carp, 2004). Synthesis begins using chromium chloride in preparation with a slow-gel process to form the Cr (III) to the TiO_2 lattice. Research shows that the sol-gel methods are simple and highly effective in creating singly-doped TiO_2 samples.

The procedure of synthesizing (Cr (III) - TiO_2) samples began by first extracting chromium III+ ion from chromium chloride. In order to effectively prepare the sample, the TiO_2 nano-dispersion anatase 5-15 nm was magnetically stirred at $150°$ C for 2 hours. TiO_2 clumps started to form as water evaporation began and pH rose, and to prevent this a few drops of phosphorous acid was added. The solution was considered ready when 20% of the water volume had evaporated. The weight ratio of TiO_2 to the purchased solution was 15%. (A 250 ml sample contains around 13 grams of pure TiO_2). The effective doping level of

Chromium has a 0.3% mole ratio, so to be effective it is necessary to place 336 mg of Chromium (III) into crystal lattice of 13 grams of TiO_2 (Park, 2009).

To separate the chromium ion from chromium chloride, 750 mg of Chromium chloride was added to 70 ml of ethanol, until fully dissolved and then 25 ml of 10 mol/l of sodium hydroxide aqueous is added to a dark green chromium solution. The solution showed a color change from dark green to light blue. The remainder of the solution was integrated into 200 ml of the nano-dispersed titanium dioxide. Once fully mixed, the addition of 100 ml of distilled water was integrated until no precipitation in the TiO_2 solution was observed, and then 2 -3 drops of phosphoric acid was added to retain the pH at below 1.5. Re-measuring the mass weight of the TiO_2 laced with Cr(III) showed an effective weight ratio increase from 0.15 to 0.187 within the suspended nano-dispersed solution.
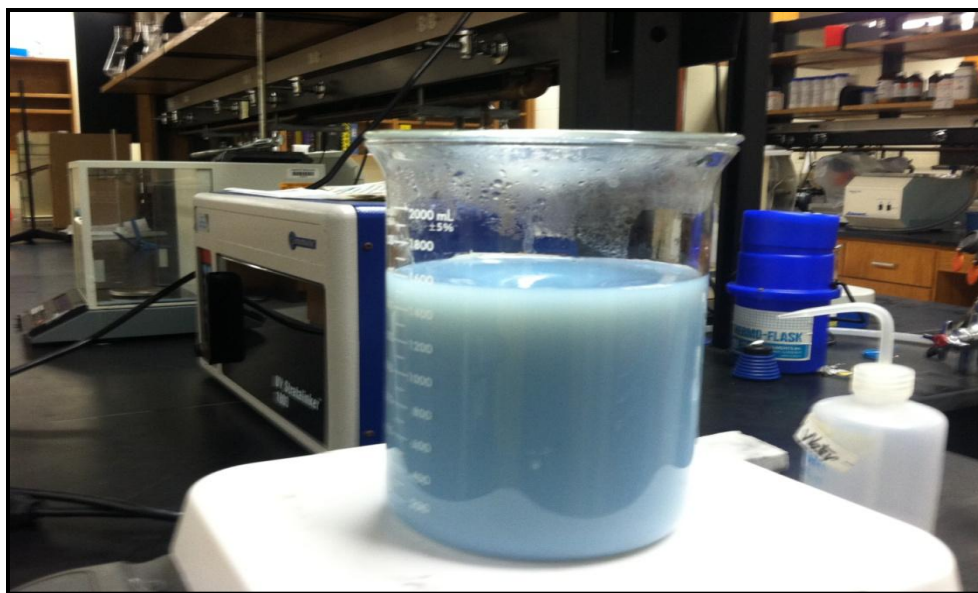
Figure 7. Prepared doped chromium titanium dioxide solution

The formation of the coat upon graphite entails the consideration of three important factors:

1) Anatase transforms to the equilibrium rutile phase between temperatures of 700°C to 1000°C, increasing its specific gravity. A maximum temperature of 500°C is used to minimizing any transformations that depend on the temperature and crystal structure stability of TiO_2 lattice during morphology (Bakardjieva, 2005).

2) The heat treatment of the TiO$_2$ crystal structure goes through an oxygen annealing process, where the TiO$_2$ chemical properties are distorted because of an oxygen vacancy between the molecular chains of the TiO$_2$ crystal structure (Barnard, 2004). This gives the TiO$_2$ a dark yellow appearance, indicating increased optical absorption spectra of photons, which then delivers increased light-harvesting abilities. However, during the cooling process the coat returns to a pure white layer which has a lower photoactivity than the yellow coat. To counter this effect, the Cr(III) acts as a focal molecular inheritor to the absent oxygen molecule during the annealing process, so as the structure cools the yellow tint is retained, indicating a higher potentiality of excepting photons during photocatalysis (Wang, 2012).

3) The coat to be applied to the surface of graphite must be atomized before layering on the graphite plates, so to have uniform consistency. This is accomplished using high pressure or oxygen removal technologies.

3.2.2   Application of Silver Ion

The procedure aims to integrate 5% by weight of aqueous silver within a solution of doped titanium dioxide. Based on an estimate of the total molecular mass of solution, silver is 64% of the total mass of silver nitrate. Therefore, it was necessary to add a total of 0.77 g of silver to the solution, corresponding to 13 g of titanium dioxide. While the solution was kept at a temperature of above 100°C, 1.2 g of silver nitrate (Ag(NO3)) was added, to increase the solubility of the silver nitrate within the solution. The amount of Ag(NO3) required for doping was based upon research recommending 5% wt for the doping of Ag+ to the TiO$_2$ solution. Once added, the solution must be kept hot, in order to keep the silver nitrate soluble within the solution (Barakat, 2011).

3.2.3   Coat Application

A ceramic oven was heated to 500° C, the graphite plates were placed within it for 10 minutes, while a pressure spray paint gun was calibrated to 100 psi. Once the graphite plates reached the recommended temperature, the application of the coat began. After the momentary removal of the plates from the oven, the

coat of atomized doped TiO_2 solution was applied with a slow, constant stroke. The application continued until a color change from dark gray to yellow was observed on the plate. The plate was then inserted back into the oven to reheat to the set temperature, and the coat was reapplied in the same manner. Once the coat had been reapplied 3 times, the plates were set aside to air-cool until at room temperature. It was necessary to apply 2-3 coats to obtain an effective, uniform coat on the graphite plates. The plates were then inserted into the reactor to run tests for contamination levels.

3.3 Analysis of Organic Degradation

In order to simplify analysis, total organic carbon (TOC) was used initially as the sole analysis in many experiments. However, after repeated failures and the inconsistency of the analysis, the chemical oxygen demand analysis was also used as an indirect measurement of the organic compound degradation within reactor samples. The analysis was not used to observe the direct effect of the hydroxyl radical on contaminates, but to show significant forms of organic decomposition within set detention. It was believed that using two systems of analysis would reveal similar or divergent forms of effective degradation within the reactor samples. This would assist in an understanding of the effect of the primed coat, and the improvements made to the coat surface through the course of experimentation.

3.3.1 Total Organic Carbon (TOC) Analysis

TOC is the amount of carbon bound in an organic compound and often used as a non-specific indicator of water quality or the cleanliness of pharmaceutical manufacturing equipment. A typical analysis of TOC measures both the total carbon present and the so-called "inorganic carbon" (IC), the latter representing the content of the dissolved carbon dioxide and carbonic acid salts. Subtracting the inorganic carbon from the total carbon yields the TOC amount, usually measured in parts per million of carbon (ppm C). The TOC analyzer used was the Torch Combustion TOC/TN Analyzer. A measurement of TOC is accurate, but

complex equipment and procedure are required, as is the use of computers to analyze and maintain TOC operations.
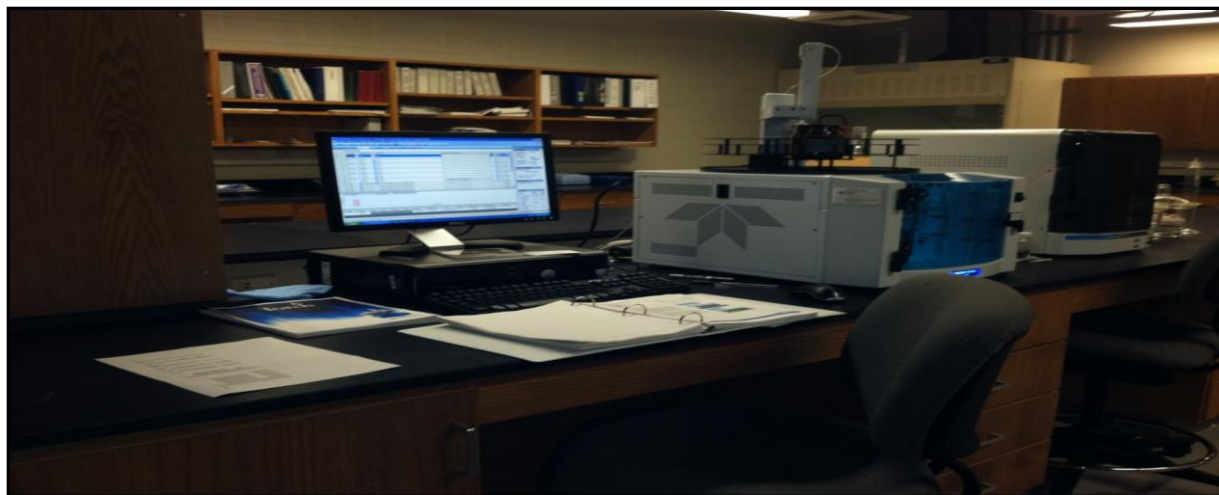
Figure 8. Torch Combustion TOC/TN Analyzer

3.3.2   Chemical Oxygen Demand (COD) Analysis

COD tests are commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers) or wastewater, making COD a useful measure of water quality. The amount of COD is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution.

The COD analyzer used was the HACH DRB 200 Reactor. The COD analyzer is fast and simple, but is less accurate on a sensitive scale for measuring pollutant concentrations.

Figure 9. The HACH DRB 200 COD Reactor

3.3.3 <u>Secondary Variables (pH, temperature, and conductivity)</u>

Analyses of pH, temperature, and conductivity were carefully evaluated as to the role each plays in the quality of water and which variable significantly influences photodegradation, (or how photodegradation influences these variables).

To determine the effects of pH, temperature, and conductivity, A Thermo Scientific Multiparameter Meter with probes was calibrated and inserted into the reactor during each trial of photodegradation operation. This was to show how effective the photoactivity and electrolysis were within a fully mixed solution.

Detailed analysis can effectively predict the limitations and values for operational objectives and the correlations between changing variables within sampling points. With future research, non-equilibrium thermodynamic models could be created to assist in accurately controlling and advancing photocatalytic reactors.

To elaborate, a brief summary is included as to how each variable can affect the conditions of the system from the beginning to the end of the experimental run. The most important variable to be taken into account is pH, which is the measurement of molecules of quantified ionization of hydroxyl anions (OH-) and hydrogen cations (H+). From previous research, highly acidic solutions (pH $\cong$ 3) have been found to assist in the degradation of some molecules such as chlorobenzene, that were found to have an optimum pH of 3.5 (Holmes, 2003). A high pH (pH $\cong$10) has also been found to help in the oxidation of ammonia and a trace

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low pH preference has been explained for the ability of hydrogen peroxide to create hydroxide radicals (Holmes, 2003). A high pH has also been credited with providing adequate amounts of hydroxyl ions necessary for making hydroxyl radicals (Holmes, 2003). It was necessary, therefore to assess how the design would affect the pH in the analysis of photocatalysis as an effective means of treatment and practicality, from the initial to the final readings.

The effect of temperature on photocatalysis has been cited in literature as having both positive and negative aspects. Previous research shows a linear increase in degradation with an increasing temperature up to 90°C, however this is not effective with all contaminates (Holmes, 2003). It would appear that the diffusion of $\overset{\cdot}{O}H$ from the surface of the TiO_2 to the pollutant at a higher temperature increases the photocatalytic reaction rate (Holmes 2003). However, higher temperatures may have negative effects on the concentration of dissolved oxygen in the solution and dissolved oxygen levels below a certain point may allow for electron-hole recombination at the surface of the TiO_2 (Holmes, 2003). Electron-hole recombination is dominant unless there is an electron acceptor such as oxygen available to absorb the excited electron.

The measurement of conductivity shows the decrease in the quantity of inorganic salts from start to finish during electrolysis. The use of inorganic salts assists in the forming of a complete circuit in the electrolysis operations (simulating sea water conduction), and is not designed to assist in the degradation process. However, previous studies show that, depending on their nature, concentrations and the pH of the solution, inorganic salts can more or less decrease the photocatalytic efficiency (Guillard, 2005). One hypothesis suggests that there are inhibiting effects due to the hydroxide radical scavenging for some other anions, such as Nitrates ($NO3-$), Chlorine ($Cl-$), Sulfates (($SO4)2^-$), Phosphates (($PO4)3^-$), and carbonates (($CO3)2-$). These anions can be competitive in reacting with oxidative particles throughout a solution (Guillard, 2005).

3.4   Experimentation and Sampling

3.4.1   Preparation of Organic Contaminants

Organic chemicals are found in: pesticides, industrial chemicals, disinfection by-products, and medicinal products. Contaminants chosen were based on ideal usage of the photocatalytic technology implemented in known industrial and commercial treatment applications. Depending on the region and treatment operation, specific treatment operations exist to target specific organic compounds. To show the effectiveness of the photocatalytic technology on a range of typical contaminates, 3 organic compounds found commonly within waste and commercial treated waters were used to verify whether the photocatalytic technology worked, independent of organic contaminant type. These organic compounds are water soluble and are very difficult to remove with standard water treatment technologies, and require more advanced treatment such as reverse osmosis or activated carbon. The compounds used were as follows:

- Rhodamine - a fluorine dye which is generally toxic and is soluble in water, methanol and ethanol. It is typically used for dye tracing within water systems, and is used as a method of tracing in tracking various flows (using dye added to a liquid current). This organic compound is used in leak detection, natural waterflow analysis (rivers, lakes, ocean currents, and also sewer and stormwater drainage analysis (Rhodamine, 2013)

- 4-NitroPhenol - a phenolic compound (water soluble hydrocarbon of 10 g/L at 15°C) that belongs to a nitro group at the opposite position of the hydroxyl group on the benzene ring. This type of phenol is a genotoxic and carcinogenic substance with fatal and devastating mutagenic properties. It is derived from gas and oil industries manufacturing and the stabilization of plastic polymers, and can be found in oil industrial waste runoffs (4-Nitrophenol, 2013)

- Tween 40 - A polysorbate, which is a class of emulsifiers, it is a non-ionic detergent used for cell lysis, nuclei isolation and cell fractionation, mainly in pharmacological applications. Its water solubility and relative non-toxicity. (Tween 40, 2013).

Figure 10. Organic compounds used: 4-nitrophenol, Rhodamine; and Tween40.

The initial concentration of contaminants used:

- 100 mg/L of 4-NiroPenol

- 240 mg/L of Tween 40

- 100 mg/L of Rhodamine

In developing the contaminated solutions, the initial concentrations of each contaminant equated to approximately 70 parts per million of carbon (ppm C), measured using the TOC analyzer. Four liters of deionized water were added with 50 g of sodium sulfate, (which has a conductance of 50 mS/cm, - the conductance of seawater). Each contaminant was added to 4 liters of the stirred solution, then fully mixed. When the contaminant solution was ready, the solution was poured into the reactor, and closed with a lid.

Figure 11. Trial preparation of contaminants and sodium sulfate

Figure 12. Fully mixed 4 liter Rhodamine solution with 50 grams of sodium sulfate

3.4.2   Charging Cells, Voltage, and Current Monitoring

Before the initial experiment, it was necessary to charge the graphite plates, by applying a DC voltage to generate the highest current the reactor could carry, for a period of 10 minutes. The current was typically in the order of 0.3 Amps through all the cells, and 0.133 through each cell. Approximately 30 volts was needed to stabilize the current. Once the cells were charged, visible bubbles of a mixture of hydrogen and oxygen gas could be seen forming on the submerged graphite plate surface, which lasted throughout the entire detention time of 4 hours. The current relatively changed in the order of -0.002 Amps every hour, which could have been caused by the separation of the electrolyte into its own cations and anions; thus decreasing conductivity. The voltage increased and decreased slightly during the experiment, but had a relative voltage drop of 3 volts throughout the entire experimental trial.
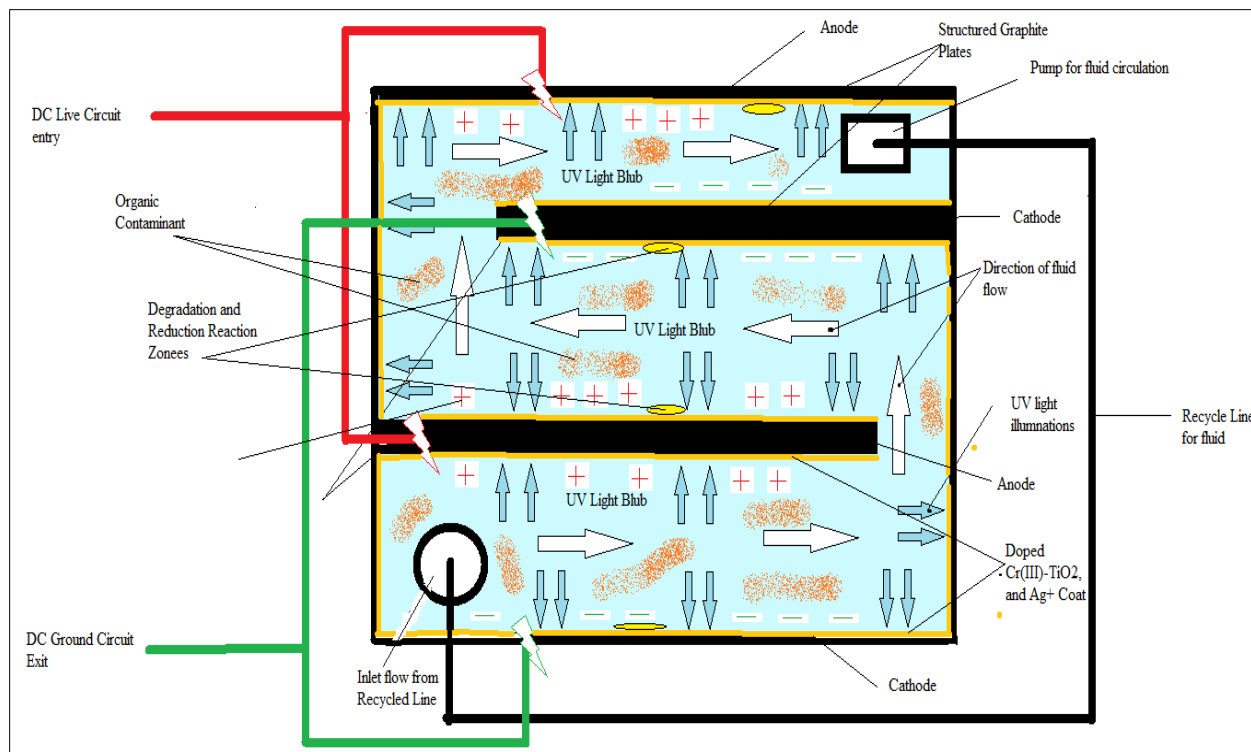
3.4.3   Sampling of Photocatalytic System

Figure 13. Plan view of the reactor mechanisms during photodegradation.

Figure 13 shows a plain view of the photocatalytic reactor during active operation. By limiting the detention time to 4 hours, an average of 16 samples were taken per experimental trial. The setup was sought to effectively show the combination of the technologies and how the system flows interacted with the surface coat. The effective surface area of the $Cr(III)$-TiO_2 and $Ag+$ coat needed to treat approximately 3.8 liters of contaminated water, was approximately 1626 cm^2. Samples were collected using 10 ml lab pipettes, and taken from the discharge of the recycling pump provided in the system. Total organic carbon (TOC) vial[[gs were used to collect the samples, which were kept airtight. Each vial contained 20 mL of sample solution. These vials were used in providing samples for COD analyzer vials, and inserted into the TOC analyzer. Each sampling vial was reused after being placed into 15% nitric acid solution before reuse. The experiment required 1 hour of preparation time, and 8 hours for the analysis of the samples.

Figure 14. Photocatalytic operation of 3 cell reactor

4 RESULTS AND ANALYSIS

4.1 Kinetic Study

The Langmuir-Hinshelwood (L-H) equation has been shown to appropriately model the kinetic reaction rates of catalytic reactions, and can be used to define the rate constant for photocatalysis in an oxidation reaction (Holmes, 2003). In this model, the rate of reaction (r) in equation (9), and the fraction of surface covered by the substrate, or fraction of the adsorption sites occupied on the substrate is (θ) in equation (10). All variables cannot be held constant though, which makes this order a non-constant because of unsteady state conditions. However, the main objective is to relate the consistency of the K_1 Langmuir constant and the K_2 rate of reaction in a numerical range based upon contaminates used in the analysis, for the final derived design of the photocatalytic reactor (Holmes, 2003).

The Langmuir-Hinshelwood (L-H) model is defined using a combination of equations (9) and (10):

$$r = \frac{-dC}{dt} = K_2\theta \tag{9}$$

$$\theta = \frac{k_1 C}{(1+K_1 C)} \tag{10}$$

When substituting the fraction of the adsorption sites θ into equation (9), gives equation (11):

$$-\frac{dC}{dt} = \frac{K_2 K_1 C}{1+K_1 C} \text{ (\textbf{Langmuir-Hinshelwood Equation})} \tag{11}$$

After reforming the algebraic equation and integrating both sides using the identities of integration, we derive equation (12):

$$-\frac{dC}{dt} = \frac{K_1 K_1 C}{1+K_1 C} \quad \rightarrow \quad \frac{1+K_1 C}{K_1 K_2 C} = \frac{dt}{dC} \quad \rightarrow \quad \frac{dC\,(1+K_1 C)}{K_1} = dt\,K_2$$

$$\rightarrow \int_{C_o}^{C}(1 + K_1 C)(-dC) = \int_0^t K_2 K_1 dt \,,$$

$$\ln\left(\frac{C_o}{C}\right) + K_1(C_o - C) = K_2 K_1 t \tag{12}$$

Where C_o is the initial concentration, C is the concentration at time t, (the time of reaction sample), K_1 is the Langmuir constant and is the equilibrium adsorption constant for a particular contaminant to the photocatalyst (which cannot be derived numerically and is difficult to derive experimentally), and K_2 is the true rate constant, which is experimentally derived.

It is important to note that Langmuir–Hinshelwood (L–H) law is used in four possible reaction scenarios (Konstantinou, 2004):

(1) That the reaction takes place between two adsorbed substances.

(2) That the reaction occurs between a radical in solution and an adsorbed substrate molecule.

(3) That the reaction takes place between a radical linked to the surface and a substrate molecule in solution.

(4) That the reaction occurs with both of species being in solution.

In all cases, the expression for the rate equation is similar to that derived from the L–H model, which has been useful in modeling the process, although it is not possible to determine whether the process takes place in the bulk of the solution or at the surface interface (Konstantinou, 2004).

However, there are two problems in using the L-H model. Firstly, the assumption that contaminants are completely oxidized by the hydroxyl radical photo degradation process is not true, because the mineralization and oxidation process creates secondary byproducts of both inorganic and organic substances. This therefore cannot be ignored during experimentation. The use of additional mathematical transformations is therefore needed to accurately depict the kinetic model for the particular reactor. To facilitate this, highly diluted initial concentrations of Co (mol/l) < $(1 \times 10^{-3}$ mole/l $)$ are used. The molar concentration of the byproducts formed would therefore be much greater than the molar concentration of the solute within the reactor and throughout reactor operations. Because none of the initial concentrations of 4-NitroPhenol, Rhodamine, and Tween 40 exceeded $((1 \times 10^{-4}$ mole/l $)$, the term "$(K_1)*(C)$" in equation

(11) becomes much smaller than 1, and the denominator is neglected, and the L-H equation becomes equivalent to a first order reaction in equation [4-4]. In this case, the reaction rate is consistent with a steady state logarithm. This is assumed because the TiO_2 will be saturated at the surface, (where the reaction will predominately take place), and why low K values are therefore expected.

The second problem is that the rate of photocatalytic degradation depends on several factors, including: illumination (L), oxygen concentration (O), pH levels (pH), temperature (T), inorganic concentration (IC), and secondary reduction reactions of acids (Rc). However, if these variables are not constant, then K2 **cannot** be integrated into the true rate constant, and its value is more or less dependent of the Langmuir-Hinshelwood kinetic model used to describe kinetics mineralization process, (which is the most important part of the analysis). To simplify this dilemma, the following assumptions on the parameters used are made:

1) Since the UV lamps are within close proximity to the majority of the graphite plates (1 cm distance), UV illumination is kept constant and is independent of the contaminate concentration used.

2) The oxygen produced from the photocatalytic reaction is significantly less than the O_2 generated from the electrolysis. Throughout experimental operations, the system is open to the atmosphere and fully mixed. The O_2 saturation level depends on temperature, and to simplify the process O_2 saturation is ignored.

3) The increase in pH levels is the result of the sulfates produced by the hydrolysis of sodium sulfate salt, and the sulfate is assumed to be neutral to the reaction from either the oxidizing radical or the contaminant. The rise in pH is mostly attributed to the electrolysis rather than the photocatalytic activity, and the experimental trials with no contaminant support this conclusion.

4) Sodium sulfate is the predominant inorganic mineral and is significantly higher than, and remains almost constant, in comparison with any inorganic substance produced from the degradation process.

5) Temperature is kept under 60° C. In some literature, temperatures between 20°C and 60°C have a minimal effect in supporting photocatalytic reactions, and it is therefore assumed that the influence of temperature is minimal (Moiza, 2005).

6) Since low K values are assumed, the organic acids produced should be significantly lower than the bulk reactor concentration during all times of the experimental trial.

With these assumptions, the K_1 Langmuir constant and the K_2 rate of reaction are integrated into a single constant. This can then be written as: $K_1K_2 = K$, and (Equation 12) can be simplified to (equation 13):

$$C = C_o e^{-kt} \qquad\qquad (13)$$

where, k is equal to the rate constant application for the desired photocatalytic system.

This equation can be used to study many photocatalytic oxidations, and is a pseudo first-order kinetic equation, which successfully describes the process for concentrations under 100 ppm C.

4.2 Analysis of Non-electrical Photocatalysis

The first trials performed with no electrolysis operation were predominantly unsuccessful, with almost no degradation both analytically or visually. Organic compounds were almost unaffected by UV operations alone, even after the doping of the TiO_2. The only exception to this oxidizing parameter was during the first trial with Tween 40, where initial concentrations were well over 1000mg/L, which halted experimentation due to the secondary reaction precipitants that fouled the TiO_2 coat beyond repair. With low concentrations, the experiments were unsuccessful and the oxidation process was not prevalent with Tween 40, Rhodamine, or 4-nitrophenol samples. (It should be also noted that experimentation without UV irradiation also showed no degradation.)

4.3 Results of Final Stage of Research

The performance of the photocatalytic reactor using the heterogeneous doped Cr(III)-TiO2-Ag+ coat has certain limitations, and these limitations can be attributed to the simplicity of reactor design. The thickness (3-layer coat) of nano-titanium dioxide catalyst doped with chromium and silver ion was no more

than 1/10 of a mm thick; the equivalent thickness of a double-coat of wall paint. The UV irradiation time and the current through the system were constant throughout the majority of experiments. The only two key parameters that changed during analysis were: 1) the type of contaminant used; and 2) the initial concentration of the specified organic compound. The enhancement of the semiconducting coat is a sensitive parameter, and was only suggested as an improvement for the photoactive coat after increased degradation results were shown in data from research analysis. An increase in photodegradation was, however, observed during the activation of the electrolytic cells, thus showing some clear effects that may have a supporting theory as in chapter 2.3.2. Advanced measuring equipment was not used, however, in relation to why the enhancements improved the reactor design, (such as measuring the reactivity of the TiO_2 coat, and if other organic substances were formed during the degradation process). The surface application of the photoactive coat was basic, but effective in forming a strong ductility TiO_2 recrystallization bind to the graphite. Perfecting the technology needs an understanding of a more complex material science process in doping and stabilizing the TiO_2 coat, so to achieve the highest photoactive coat possible.

4.3.1   Visual Observations

With all contaminants, the oxidation process can be described as having unusual effects, such as multiple cluttering of a thin chemical film over the water surface of the reactor, (which appeared almost gel-like), as well as a thick chemical film over the doped TiO_2 coat after the end of the experimental trial, which was dubbed as chemical fouling. Contaminants did appear to cluster around dead zones, preventing the compounds from interacting with the photoreactive layer.

As described in 3.2.2, when silver is exposed to high frequency light, it carries a negative charge, and it tends to form a black metallic substance. During experimentation, highly transparent black stains were observed over time, where the light intensity was closest to the graphite plates.
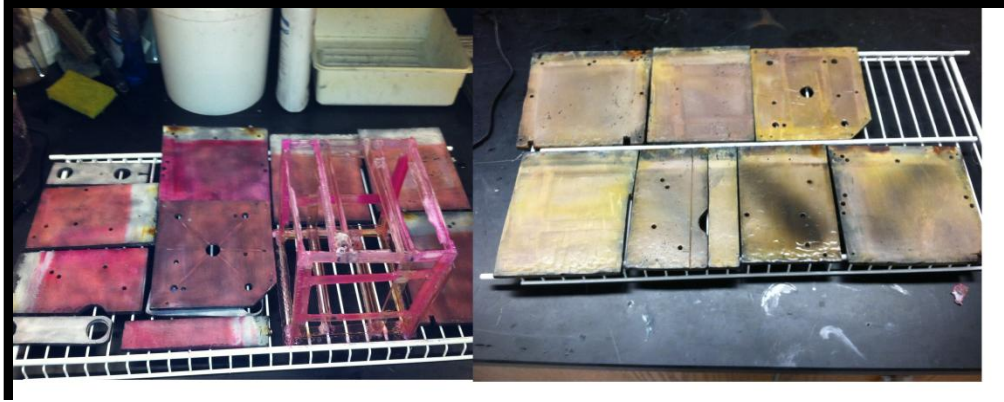
Figure 15. The left-hand photo shows the effect of fouling caused by the Rhodamine compound. The right-hand photo shows the accumulation of black silver stains, which increased during every experimental trial.

Observations showed an increase in pH values and temperature while conductivity decreased by 5 mS/cm after the final sample was taken. There was no significant visual change in the sample coloring with Rhodamine, 4-nitrophenol, or Tween 40. Foaming was observed with the Tween 40. Precipitation, even though not apparent during experimentation, did appear to adhere to the doped TiO_2 coat during washing of the plates.

4.3.2   Data Analysis

Using the data from the final trial of experiments, the rate constants of three organic materials were calculated from the degradation charts. The initial concentrations of Tween 40, 4-nitrophenol, and Rhodamine were constant throughout each trial, but each showed varied rate constants depending on the contaminant type. Measurements of pH, temperature, conductivity, and concentration were transferred to an Excel file, and patterns were observed between the COD and TOC analyses for each containment sample. Data from each trial was summed and averaged, and applied in Equation 13 to derive rate constants by the type of contaminate and the type and analyzer used. The secondary dependent variables are described in (Figures 16 - 18). Results show linear progression in all the variables, after repeated experimental acquisitions.
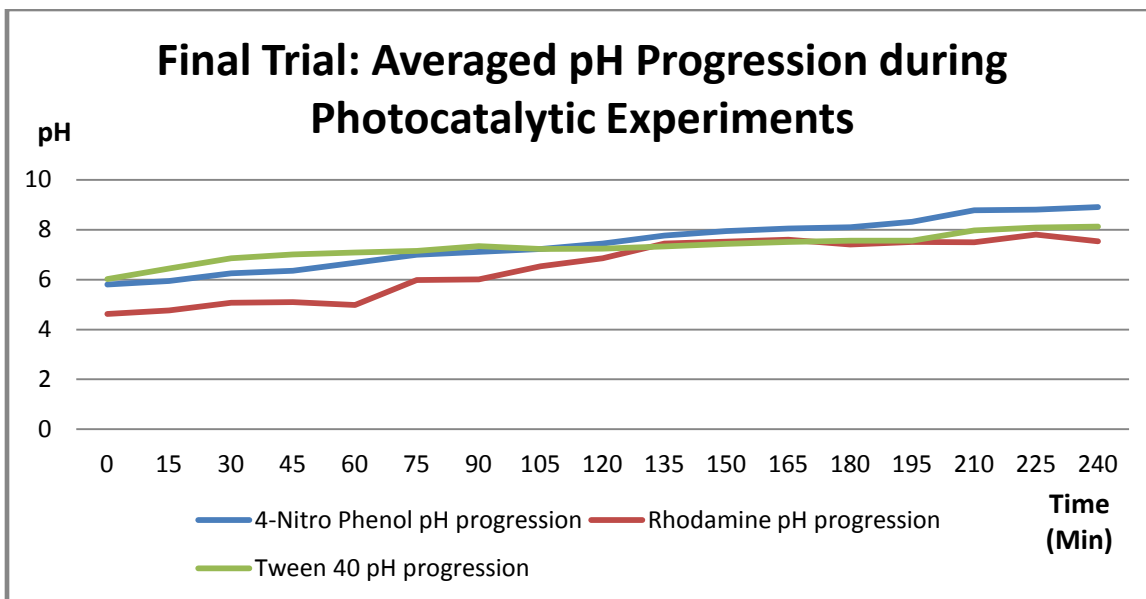
Figure 16. Linear progression of increased pH values for all organic contaminants with time. This progression can be the result of the dissociation of sodium sulfate into its respective ions, causing increased pH values over time. The sulfate ion anion is often associated with alkali, alkaline earth, or transition metals through ionic bonds.
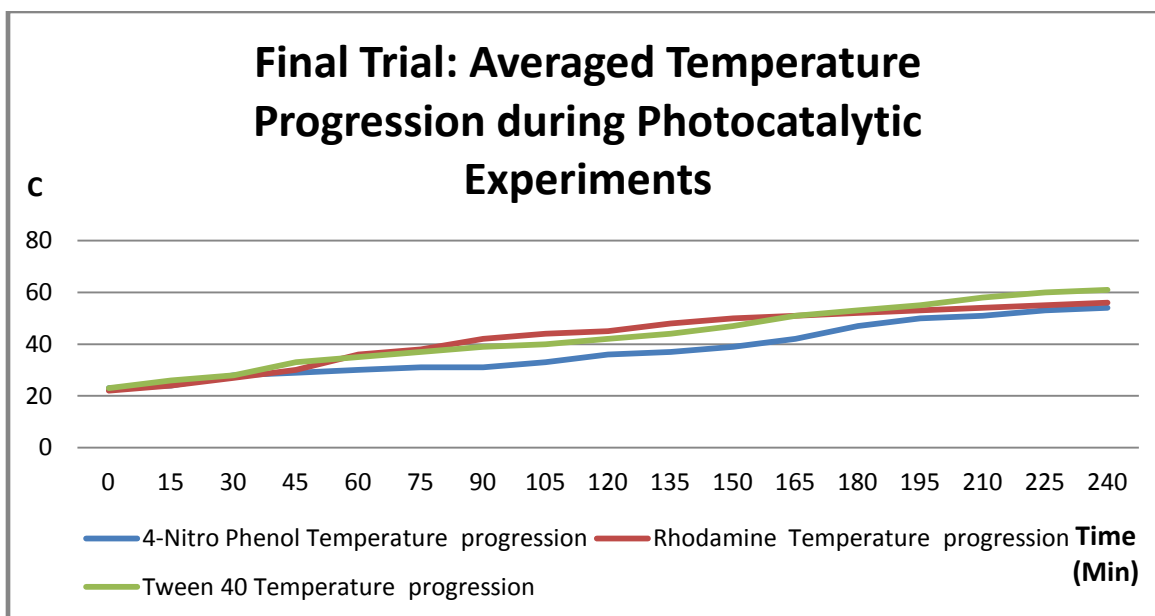

Figure 17. Linear progression of increased temperature for all organic contaminants with time. This progression can be mainly attributed to the release of heat from the UV lights during photocatalytic reactions.
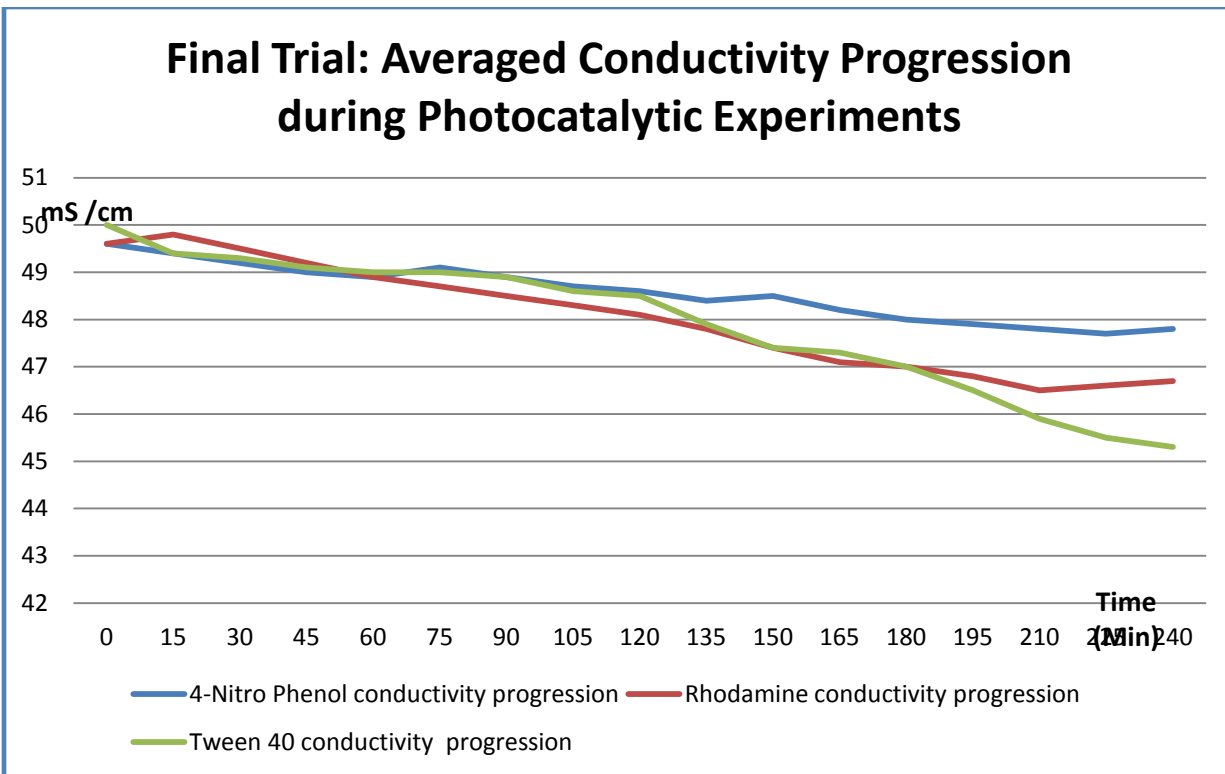
48

Figure 18. Linear progression of decreased conductivity for all organic contaminants with time.

In Figure 18, the decreased conductivity for all organic contaminants with time results from the depletion of the electrolyte as it is diminished during the maintenance of electrolysis, which is also the reason for the voltage shifts during experimentation.
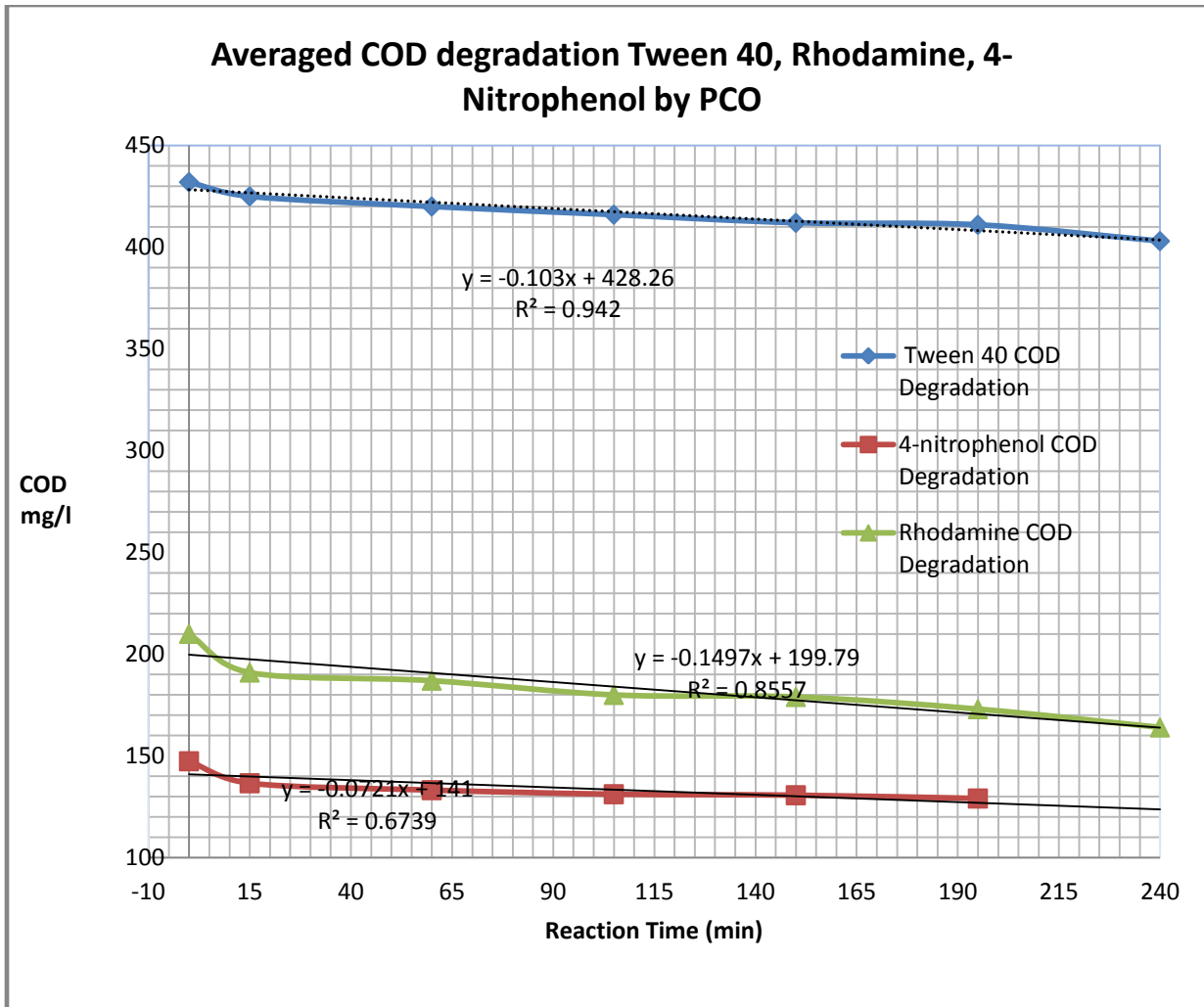
Figure 19. Analyses of the COD degradation of 240 mg/L Tween 40, 100 mg/L of 4-NitroPheno, and 100 ng/L of Rhodamine by PCO.

Figure 19 is based upon the first two hours of reactor time. The COD analyses show a slight rate of degradation, with almost no declination of contaminate substrate for the remainder of the experiment. However, it was difficult to accurately depict the rate of degradation with only 6 points in the analysis; this is because the number of vials needed for the COD analysis was limited.
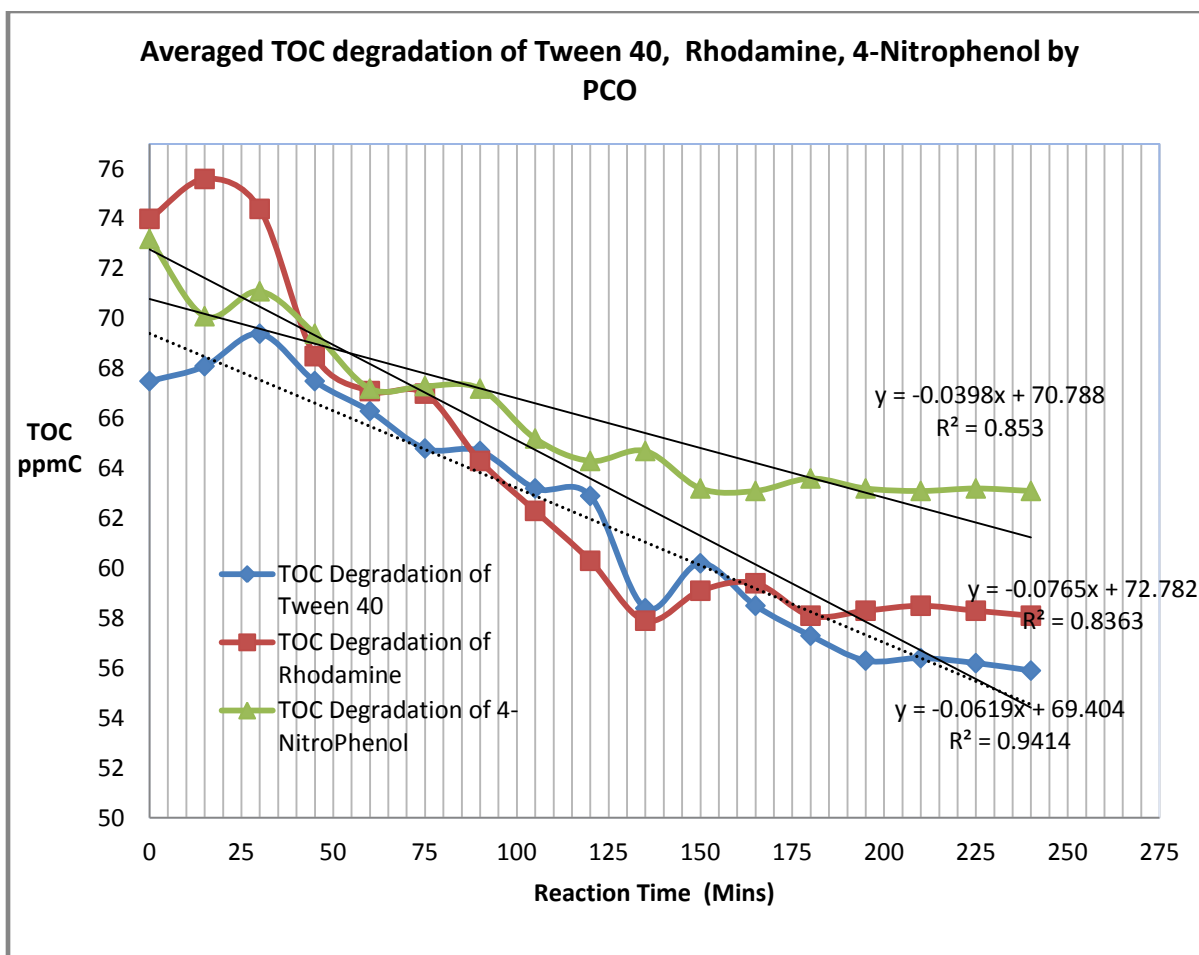
Figure 20. Analysis of TOC degradation 240 mg/L Tween 40, 100 mg/L of 4-NitroPheno, and 100 ng/L of Rhodamine by PCO

Figure 20 displays a visual interpretation of the data extracted from the TOC analysis from 16 sampling points. These graphical observations with respect to time, reveal a tendency for the removal of the contaminants and show random shifts of organic carbon within the first half hour of reaction time, followed by an increase in the reaction rate within 30 to 150 minutes of operation and then a final stabilization and lower degradation rate for the reminder of the experimental trial. It is difficult to explain why the concentration increases and then levels off, or why there is a decrease in the degradation rate at certain sampling points, but there is clearly a visible overall degradation within the system, albeit a very slow one.

The data from Figures 19 and 20 were used to assess the overall percentage of contaminant removal for each contaminant and the form of analysis used, as shown in Figure 21.
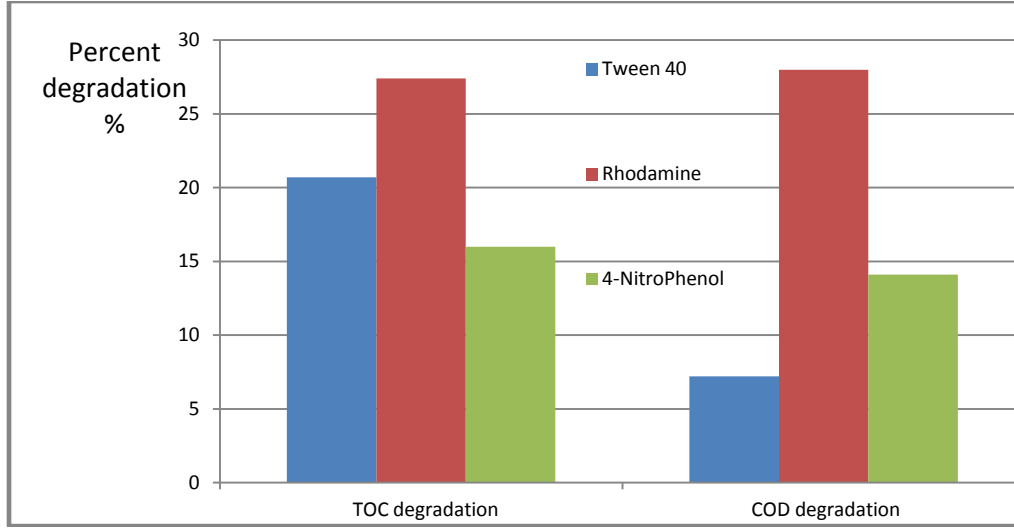
Figure 21. Average results of final photocatalytic experiments. Averaged degradation percentage of organic concentration within total detention time of 4 hours. The columns represent a comparison of total degradation between TOC and COD analyses based on identical trials and samples.

The results of Figure 21 demonstrate the ability of the reactor to remove between 10 to 30% of the targeted contaminates within trial sessions. Importantly, Rhodamine and 4-nitro phenol had similar percent degradations within both TOC and COD analysis. Evidently the same cannot be said for Tween 40, which has a standard deviation of about 7 in both analyses.

The Langmuir-Hinshelwood (LH) equation has been simplified into (equation 14):

$$C = C_o e^{-kt} \tag{14}$$

This equation is used by many researchers to model the degradation rates in photocatalytic oxidation reactors. The LH equation shown represents: the actual rate of reaction of the photocatalysis, k; the bulk concentration of contaminant in the solution, C; the initial bulk concentration, C_o; and the mean detention time, t. (Holmes, 2003).

During this research, the concentrations were kept below 100 ppm C for the ease of modeling oxidation kinetics in the reactor using first-order kinetics.

Figure 22. The TOC target analysis represents the kinetic rates of degradation in first-order for each recalcitrant. These data is experimentally derived from values in figure 20. Most of the compounds show a value of $R^2 > 0.8$.
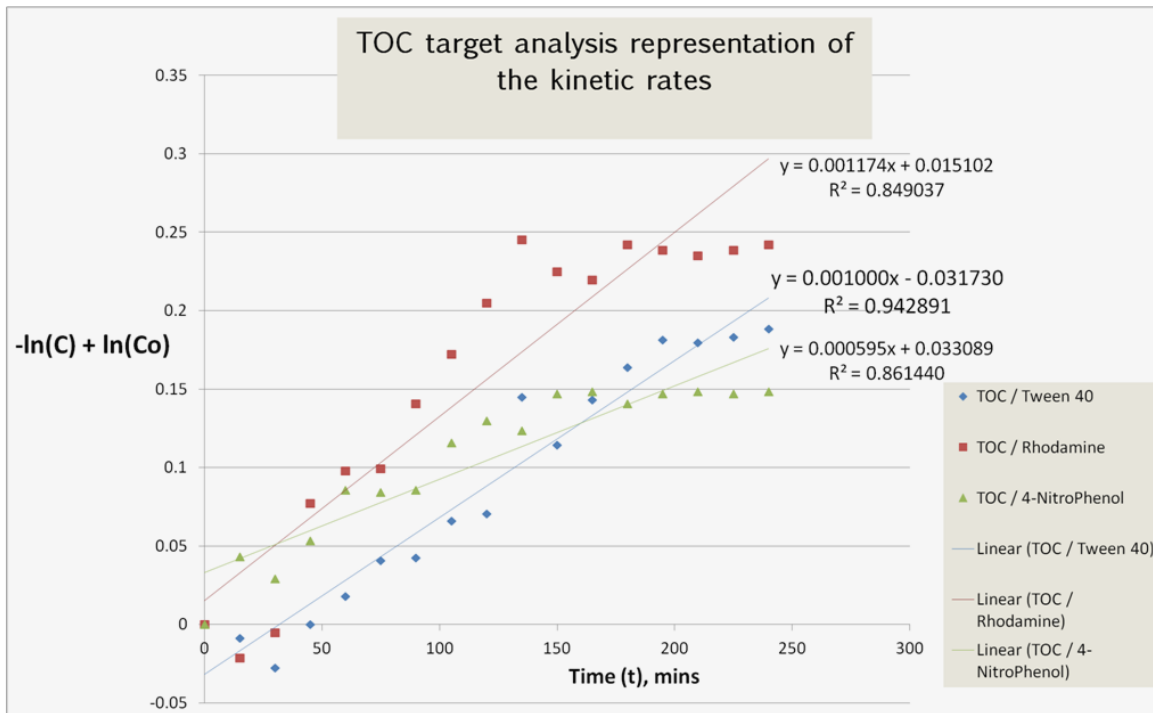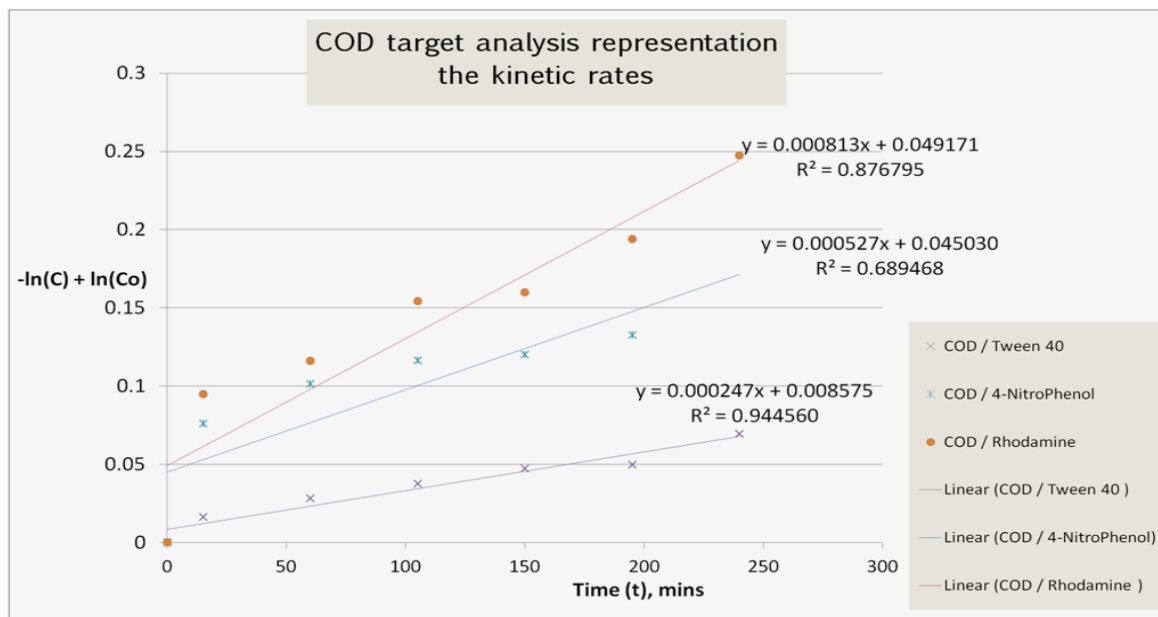

Figure 23. The COD target analysis represents the kinetic rates of degradation in first-order for each recalcitrant. These data is experimentally derived from values in figure 19. Most of the compounds show a value of $R^2 > 0.8$, except for the COD / 4-Nitro Phenol.

Observed reaction rate constants analytically derived in Figures 22 and 23 are not similar to those seen by other researchers for a fixed TiO_2 catalyst (Holmes 2003). In the experiments conducted for this study first order rate constants had average values of less than 0.005 (min-1) for all organic compounds used. The pH in the reactor increased to a pH of 8 (approx), and there was a temperature increase of 30° C for all organic compounds, which could explain the low rates derived. The first order rate constants for each compound had slight variations between the TOC and COD analyses, Rhodamine and 4-nitro phenol had a similar rate constant, which confirms that the analysis of degradation is precise and accurate. However, Tween 40, had significantly different values in both the COD and TOC analyses, and in all three trials the degradation values were quite inaccurate. Tween 40 is a complex polysorbate and possibly reacts differently to the mercuric sulfate found in the vials of the chemical oxygen demand analysis. One theory is that polysorbate tends to form peroxides during ionic breakdowns. This could also be the reason why the COD readings for Tween 40 were well over 400 mg/L, compared to the lower values found in Rhodamine and 4-nitrophenol. (Ha E, 2002)

A comparison of these reaction rate constants poses complications in the understanding of what influences their discrepancy. In cases previously reported in literature, UV energy, pH, and reaction temperature, if controlled, are capable of influencing degradation, and of manipulating TiO_2 photocatalytic properties within experimental apparatus (Holmes, 2003). The parameters are not set to be controlled within the photocatalytic reactor, but are restricted by the design parameters of the basic photocatalytic degradation, in simplifying the reactor for use in water treatment applications. The rates compromised are influenced by dependent variables within the reactor characteristics, and it is important to associate the data gathered with the type of contamination, and by the analysis used to derive slope formations shown in Figures 22 and 23.

The reaction rate constants (k) shown in Table 3 are first order rate constants for each of the listed target contaminants.

Table 3. Reaction rate constants "k" (min^-1) corresponding to the analysis and contaminate used

Organic Chemical	Rhodamine	4-Nitrophenol	Tween 40
TOC	0.001174	0.000595	0.001
COD	0.000813	0.000527	0.000247

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4.3.3 Bases for Langmuir-Hinshelwood

At low bulk concentration values, the LH equation becomes equivalent to a first order reaction equation because the TiO_2 is saturated at the surface. In deciphering the rate constant dependency, both types of analyses produced statistically significant results. The outcome clearly shows dependency on the contaminant type and the method of analyzing the degradation. Combining the results obtained more accurate parameter estimates, and the results could actually provide evidence that initial molar concentrations (based upon the molar weight of the contaminant) affect the effectiveness of the photocatalytic reactions. The results need to be followed-up by experiments using various initial concentrations and additional types of contaminates, if to prove statistically significant.
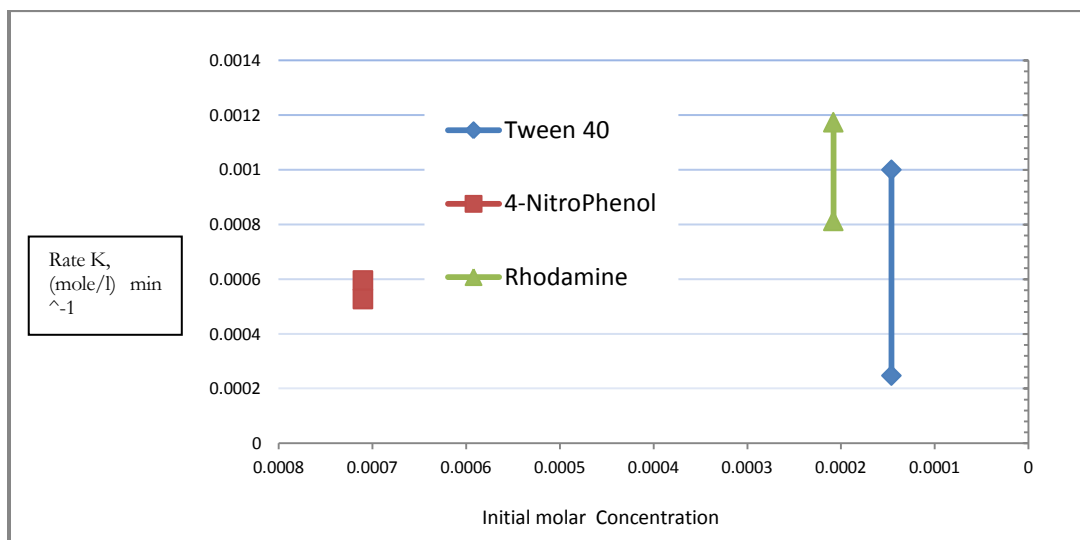

Figure 24. Observation of reaction rates on the initial molar concentrations for each contaminate and the precision of the rate constant to the type of analysis.

5 CONCLUSIONS

Higher efficiencies were achieved in redesigning the reactor by: creating a more photo-active coat, applying a secondary catalyst, and introducing mirrors to reflect the UV light to increase luminosity within flow volume. Photocatalytic degradation depended strongly on the initial molar concentrations. It appears probable that lower molar concentrations produce higher rate constants within the analysis. The escape of oxygen and hydrogen ions from the system into the atmosphere could be one of the causes for the extremely low degradation.

A graphite-coated batch reactor arranged in an electrolysis style cell design is possibly not the best design for photocatalytic oxidation. In these experiments, effective photocatalytic analysis of contaminant degradation in the reactor was limited by:

1) The UV radiation intensity, which could not be recorded without the necessary equipment to do so.

2) The basic methods used in applying the photocatalysis coat. The porosity and measured nano-thickness of coat were not investigated, as this would have required advanced application methods, which may not prove to be cost-effective.

3) Repeated equipment malfunctions. It was not possible to measure the dissolved oxygen level to see if this also influenced the reactors photoactive reactions. Rhodamine had an average of 27% degradation in an extended reaction period of 4 hours, while 4-nitrophenol had 15%, and Tween 40 had 20%, (neglecting the readings from the COD analysis).

First order rate constants for the photocatalytic degradation of Rhodamine and Tween 40 had the highest rate constant (ignoring the Tween 40 analysis of the COD), and also had the lowest molar concentrations. The 4-nitrophenol had the highest molar concentration, with similar results from both analyses of TOC and COD, but it also had the lowest derived rate constants. One possible reason for this could be the molarity of the solution. Molarity for this research was not initially a concern; however, there is a correlation between the molar mass of a substance (average molecular mass) and its rate of degradation. From this research, it appears that the substance with the lowest molar concentration (mole/l) can be effectively oxidized at a higher rate of photodegradation, based upon the batch reactor design. The electrolysis also has

an effect in assisting the degradation process; but the reason for this is not clear. One theory is that electrolysis produces overpotential reactions. This relates specifically to the polarization of organic chemicals, and whether a specific solute can have variations of redox potentials that are activated during photocatalytic activity. To relate the molar concentration of a substance to the electron transfer, it is necessary to investigate the electrochemical reaction rate, oxygen evolution, adsorption rates, and how these variables dictate the kinetics of the photocatalyst to the type of substrate; which is a difficult task. One theory, the hydrophobic effect, seems to support the reason why the contaminants appear to clutter during operational conditions. The hydrophilic effect (hydrophobic if describing more inorganic colloidal) is the observed as spontaneous rupture of soap-films and of thick water films relatively in aqueous solutions in presence of dilute amounts of cationic surfactants (Israelachvili, 1981). Agglomeration of hydrophilic colloids typically involves polarization of organic compounds by the addition of significant amounts of ions, which compete with the colloids for water molecules (Chaplin, 2012). These large colloidal organic molecules are thermodynamically stable, and become hydrated, resulting in the colloidals simulating low-density water formation, and thus appearing to coagulate within the solution (Armenante, 2012).

Over time, adsorption of contaminants to the TiO_2 coat surface may drastically increase fouling, and reduce efficiency. Proper automatic pressurized washing may be required during operations to reduce adsorption of contaminates to the surface of the TiO_2 coat. This also implies that a treatment process train is needed, consisting of more than one photocatalytic reactor in a series. Pressurizing the reactor may also increase the effect of fouling, but this must be tested to be determined. However, pressurizing the reactor may play a part in reducing these effects and enhance degradation, but to efficiently control these factors using a wide range of concentrations and flow rates well-known challenges need to be overcome. The requirement of an advanced reactor system is needed, with real-time data acquisitions, fouling prevention technologies, a higher degree of material analysis of the TiO_2 coat, and with current research advancements used to detect hydroxide ions through the solution flow of a photocatalytic reactor. Research into photocatalytics belongs to a combination of scientific fields, and researchers need to create a set of combined proposals to find the exact design necessary to achieve proper degradation.

5.1   Recommendations

Closing the system to atmospheric pressure may increase gas solubility and bring optimum conditions for achieving increased oxygen evolution. However, although a completely closed and pressurized system could increase efficiencies, these needs' to be tested to be proved effective. The process could also be improved in other ways; such as placing higher intensity UV blubs, using fouling prevention technologies such as back washing, and/or advanced nano-layered coat applications.

5.2   Design Task for Continuous Flow Reactor

To enhance the performance limitations, two parameters, if measured, could enlighten future research into the technology:

1) Chromatography of the solute adsorption to the photocatalytic coat. This would be useful in determining whether the fouling is caused by by-products of degraded organic compound or by the adhesion of organic compounds to the photocatalytic coat.

2) The measurement of the hydroxyl radical reactivity during photoactivity is another important variable, which could be accomplished by pulse radiolysis. This would determine the degree of reactivity between the TiO_2 coat, doped TiO_2 coat, and the doped TiO_2 coat with secondary catalyst.

With these advancements it would be possible to pursue a reactor design for the better photo degradation of organic material, which could then be applied to a continuous flow, photocatalytic reactor. A potentially formidable design would be a series of pressurized cylindrical tubes coated with a similar doped TiO_2 photoactive composition and a non-expensive secondary catalyst, together with electrolyses mechanisms. Better rate constants could then be expected for any type of contaminate, and could take place within a limited detention time.

5.3   Feasibility within Water Treatment Technologies

A feasibility of developing a photocatalytic reactor for water treatment is only limited by the potential of grasping the limitations of photocatalytic research and its innovative uses. A reactor using a doped titanium dioxide coat arranged in an electrolysis cell could be the first step in significantly developing a well-defined treatment for the degradation of hazardous and soluble organic compounds in water or waste water effluents.

This research needs to be taken to further levels, and needs to include key points such as the detailed analysis of molar concentrations and semiconductive material reactivity, using a more sophisticated reactor. The photocatalytic reactor may not be suitable for the degradation of wastewater, but it could be used as an advanced disinfectant. It may be necessary to produce several designs to assess the fundamental uses of the photocatalytic reactor with practical flow rates and detention times. Trial and error method was used to show the progression of the photocatalytic treatment in this study; it may also be best way to create such a technology option within water and wastewater treatment facilities.

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