IMPROVEMENTS IN PHOTOCATALYTIC OXIDATION:
PHOTOCATALYST COMPOSITION AND REACTOR DESIGN

By
WILLIAM L. KOSTEDT, IV

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To my mother
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Advanced oxidation processes including UV/H₂O₂, ozone, and photocatalysis have demonstrated the ability to solve complex environmental problems. These processes derive their power to oxidize recalcitrant organic compounds and microorganisms from powerful hydroxyl radicals. For the case of photocatalysis, hydroxyl radicals are generated when a wide-bandgap semiconductor like titanium dioxide (TiO₂) is exposed to ultraviolet light of sufficient energy to generate an electron-hole pair. A favorable reaction occurs when the electron reacts with oxygen to form a superoxide radical and the hole reacts with water or a hydroxide ion to form a hydroxyl radical. Oxidation of organic compounds by hydroxyl radicals can lead to complete mineralization, i.e., conversion to carbon dioxide, water and mineral acids. First photocatalysis, it has the potential for complete conversion of a compound to non-toxic inorganic products. This is in contrast to other technologies that simply transfer the compounds to another phase, like distillation or adsorption. Second, the oxidant is generated in-situ by a catalyst so storage or purchase of a possibly hazardous and expensive oxidant is not necessary.

Photocatalytic oxidation of organic contaminants has received much attention in academic literature, but commercial implementation has been slow due to several factors, including the difficulty in scaling up photocatalytic processes for water treatment from a laboratory scale to an
industrial scale. One particular difficulty is reactor containment of highly photoactive nanoparticulate titanium dioxide, which is popular due to its low-cost and stability relative to other photocatalysts. Nano TiO$_2$ is putatively nontoxic, however, this property is a current topic of active research. A solution proposed by Purifics, a Canadian engineering company, utilizes a patented separation device utilizing a backpressure cycled membrane and automated system (Photo-Cat®). It was imperative to examine the performance and successful implementation of this technology and compare this to the alternative approaches. Another popular approach has been to immobilize the nano-sized titanium dioxide, which will likely decrease the mass transfer of contaminants to the photocatalyst with respect to slurry, but avoid the separation difficulty. A more effective approach, and that used in this research, was to immobilize the titanium dioxide on magnetic core particles that could be both agitated and contained using a two-component magnetic field. This provided increased mass transfer seen in slurry-based systems and provided a potential option for avoiding photocatalyst separation altogether. A magnetically agitated photocatalytic reactor (MAPR) has been developed and assessed for oxidation of aqueous organic contaminants. While using phenol and organic red dye to simulate waste components is consistent with past literature and important to explore, it ignores factors that may hinder a photocatalytic performance including competitive adsorption of various organic compounds and their oxidation byproducts and the demonstrated detrimental effect of inorganic compounds such as ammonium bicarbonate on photocatalytic oxidation. To assess these effects, this work looked at photocatalytic oxidation of air evaporation subsystem (AES) ersatz water while modifying the photocatalyst mass magnetic field current and frequency to find the optimal conditions. After performing these preliminary experiments, several proposals were formulated to improve the performance of the MAPR involving both the photocatalyst synthesis and the reactor design.
CHAPTER 1
INTRODUCTION

Drinking water supplies are becoming increasingly polluted with biological and chemical compounds by anthropogenic activities including inadequate or improperly designed water and wastewater treatment facilities, industrial waste, and the result of trying to mediate other environmental problems. For example, in Milwaukee, a waterborne Cryptosporidium outbreak affecting 403,000 people was implicated in the deaths of many immunocompromised residents [1]. Domestic industry is regulated by the EPA to prevent human and environmental exposure to known hazards when they are discharged into the potential water supplies. This approach has likely prevented a great deal of hazardous discharge as well as reducing the negative environmental effects when an accidental discharge occurs. Unfortunately, some hazardous waste includes organic compounds that were of unknown hazards during discharge, or that were discharged before regulations were established. Endocrine disrupting compounds represent a class of chemicals difficult to eliminate using traditional biological or thermal oxidation although their health risk has been proven [2]. Another source of water pollution is the result of trying to reduce air pollution by adding methyl tert-butyl ether (MTBE) to gasoline. The addition to gasoline in high population density areas was intended to reduce emissions of carbon monoxide and ozone [3], but ultimately caused widespread contamination of groundwater supplies due to leaking underground storage tanks [4]. While searching for the most effective technology to overcome these environmental hazards, it is important to consider the robustness, or ability to handle unforeseen requirements without sacrificing performance.
Several technologies offer effective solutions for complex water treatment problems, but have significant weaknesses. One of the most widely used solutions is sorption to activated carbon or zeolite surfaces. These materials function by transferring the pollutant from solution to relatively high surface area materials that can be tailored to remove the most high priority pollutants [5]. The primary drawback to this method is that the pollutant still needs to be disposed of once the adsorbent is exhausted. Additionally, the process of manufacturing activated carbon may contribute pollution [6], yet this must be weighed against alternatives that may pollute more including titanium dioxide. Another option is thermal oxidation, which is very robust yet energy intensive. Finally, biological treatment provides a low-energy approach to treat a variety of challenging pollutants [7]. The disadvantages are that the microbial community may be difficult to maintain and may not be effective in treating a fluid stream with large transient fluctuations in nutrients or pollutants. Furthermore, biological treatment may not be effective for certain compounds [8] and may not be effective for low, yet environmentally significant concentrations.

Advanced oxidation allows mineralization (conversion to carbon dioxide, water, and mineral acids) of almost all organic compounds and inactivation of pathogenic microorganisms [9]. The key component to advanced oxidation is the production of highly reactive hydroxyl radicals at ambient temperature using one of several approaches [10]. One approach involves using ultraviolet (UV) light to irradiate a dissolved oxidant including ozone, hydrogen peroxide, or both. The UV photons have sufficient energy to initiate chemical reactions that lead to the formation of the hydroxyl radicals [11]. Another approach is to mix hydrogen peroxide and ozone. Although this chemistry has
been studied for at least 40 years [12], the commercial technology for application is nascent. Several companies including Hydroxyl Industrial Systems and Calgon Carbon Corporation have developed commercially successful technologies to generate and utilize the power of hydroxyl radicals for treatment of water. Hydroxyl Industrial Systems has successfully demonstrated the efficacy of their design for inclusion in municipal wastewater treatment as well as industrial treatment of MTBE and cyanide. Calgon Carbon Corporation has licensed their UV systems to inactivate \textit{Cryptosporidium}, \textit{Giardia}, and other pathogenic microorganisms in three municipal water treatment plants. This thriving commercial activity is indicative of an advanced oxidation industry that is able to provide unique solutions to challenging problems.

During long-term space missions, access to safe water is a key component to success. A unique advanced life support system is being developed to close the loop between water and wastewater. Hence, graywater is collected from shower, food preparation, humidity condensate and urine waste sources and treated to potable water quality standards. The process typically consists of several subsystems including a primary treatment technique that will be either a physical-chemical process or biological and a post-processor that will likely involve a catalyst or some other physical-chemical treatment. The challenge of a closed-loop water recovery system for long-term space missions has motivated the development of some cutting-edge technology that has applications beyond providing safe drinking water for space inhabitants. The engineering specifications involve an optimization of power, mass, volume, and crew time that are unlike typical terrestrial requirements. The primary mission of these explorations will be to conduct experimentation; hence, anything that detracts from this mission such as an
unnecessarily power intensive advanced life support process should be avoided. Many of the technologies developed have focused on regenerative systems that use a catalyst, or microbes to treat water. These types of systems are advantageous because they have the potential to reduce the mass and volume necessary with respect to a system that uses consumables. Additionally, systems that use ultraviolet (UV) light to drive chemical reactions in water can utilize solar UV, thus reducing power requirements with respect to a system that uses a powered light source. A water recovery solution that combines the advantages of a catalytic system with the utilization of UV is photocatalysis. Photocatalytic systems for a water post-processor have been developed for space applications [13], but also have been commercially successful for terrestrial applications [14].

In photocatalysis a wide bandgap semiconductor such as titanium dioxide (TiO₂) is irradiated with UV light. The TiO₂ acts as a photocatalyst by generating hydroxyl radicals on its surface when it is exposed to UV light of sufficiently low wavelength (380 nm) [9]. The process occurs when a UV photon excites an electron from the valence band to the conduction band creating an electron-hole pair. In order to induce photocatalysis this electron-hole pair must migrate to the surface of the TiO₂ crystal. If during this migration the electron and hole recombine, thermal energy will be released and the photocatalytic reaction will not occur. The hole is a powerful oxidant and can react with water or a hydroxyl ion to form a hydroxyl radical. At the same time, dissolved oxygen can react with the electron to form a superoxide radical. This reaction between oxygen and the electron is important because it follows slower kinetics than the reaction at the hole and thus can prevent electron-hole recombination.
The titanium dioxide used for photocatalysis is typically in slurry (aqueous suspension of fine particles) or immobilized on a substrate. The most photoactive form of titanium dioxide is nanometer sized primary particles that form slightly larger agglomerates in solution. Degussa P25 is particularly effective commercially available TiO₂ that consists of 30 nm primary particles [15]. It is advantageous to use slurry because it allows maximal utilization of the available specific surface area, though the small particle size makes separation challenging, but not impossible. Purifics ES, Inc. has developed and patented a slurry separation device that solves this problem and applied their technology to military and industrial markets [14]. Immobilization of the TiO₂ on a substrate prevents the need for a complex separation device, but suffers from a mass transfer disadvantage that negatively affects the photocatalytic performance. This mass transfer limitation can be mediated, but not eliminated, by immobilizing the TiO₂ on a high specific surface area substrate such as amorphous silica prepared using an acid catalyzed sol-gel procedure [16].

To combine the advantages of the slurry-based and immobilized photocatalytic systems a magnetic photocatalyst has been used in the past [17, 18]. The magnetic photocatalyst is synthesized by coating small magnetic particles (nm or μm) first with silica (SiO₂) and then with TiO₂. The silica layer acts as an insulator to prevent photodissolution or separation of the TiO₂ from the magnetic particle when irradiated by UV light [17]. Additionally, the titanium dioxide has a high affinity for the silica, making the particle more mechanically robust. The magnetic property has been used in the past to provide a simple, effective method of separation, but this requires the photocatalytic reactor to be operated in batch.
It has been demonstrated that a dynamic magnetic field can be used to agitate and confine the catalyst within a magnetically agitated photocatalytic reactor (MAPR) such that its exposure to UV light and thus photocatalytic oxidation is optimized [19]. The general principle is that a magnetic catalyst particle experiences a force due to the magnetic field gradient. The magnetic field consists of two components. First, a permanent magnet is located above the reactor to apply a force opposing gravity thus distributing the photocatalyst more evenly in the vertical direction. Second, an alternating magnetic field is generated by feeding a sinusoidal signal to a solenoid located below the reactor. This alternating magnetic field generates a magnetic field gradient of alternating direction that induces agitation of the catalyst, which has been proven to increase the extent of photocatalytic oxidation of phenol [13, 19].

Adsorption and absorption are imperative processes to consider for a magnetically agitated photocatalytic reactor (MAPR). The process of adsorption involves transferring a pollutant (sorbate) material from solution to the catalyst (sorbent). Both the physical and chemical characteristics of the system, including the chemical nature of the sorbent and sorbate, the particle size, and motion of the sorbent with respect to the bulk, will determine the extent and kinetics of adsorption. The motion of the catalyst is determined not only by the magnetic field, but by the inherent magnetic properties of the catalyst. This motion will determine whether there is significant film or bulk diffusion limitations for adsorption. In order to understand these magnetic properties, it will be important to examine their origin from an atomic perspective. Several authors have used oscillating magnetic field gradient induced motion of particles for applications other than photocatalysis [20-23], but their knowledge is pertinent to understanding why the chaotic
rotation and translation of particles might be useful for a photocatalytic reactor – particularly for enhancing UV light absorption. Similarly, several authors have used magnetic photocatalysts in the past for their simple separation capability using a magnetic field [17, 18, 24-33]. They have synthesized these photocatalysts using a wide variety of materials and methods, each of which can influence their applicability for a MAPR.

Additional work combines the advantages of the silica coating with the synergistic impact of a high surface area silica support material with an easily modified pore size distribution. Past research has indicated a synergy between high surface area silica support materials and titanium dioxide for photocatalytic oxidation [34]. In addition, the use of magnetic materials for photocatalyst supports is widespread, but until now the two concepts have not been combined. By first coating barium ferrite with silica, it is possible to disperse it in a high surface area silica-titania composite developed previously [34] while avoiding adverse impacts to the magnetic properties due to the corrosive environment. When ground, sieved, and rinsed, this material is a highly versatile particulate magnetic photocatalyst.

Hypotheses:

- Substantial improvement in magnetic photocatalyst synthesis can be achieved, resulting in higher rates of photocatalytic oxidation.
- A photocatalytic reactor with slurry separation device and/or a magnetically agitated photocatalytic reactor can act as a secondary or post-processor for treating graywater during long-term space missions.
- Improvements to the magnetic field in a magnetically agitated photocatalytic reactor will result in a greater reaction rate of photocatalytic oxidation.
- An optimal ZnO-TiO2 composite composition and heat treatment will result in an increased reaction rate of photocatalytic oxidation.
- A high surface area magnetic photocatalyst can be designed with a modifiable pore size distribution.
Objectives:

- Determine the impact of magnetic core material and repeated coating on photocatalyst performance.
- Improve the magnetic field in a way that counteracts gravity and induces confinement while improving photocatalytic oxidation kinetics.
- Assess hydrothermal and calcination heat treatment of various compositions of a ZnO-TiO2 composite and understand the impact of primary particle size and bandgap energy.
- Incorporate a magnetic material and a photocatalyst into a high surface area silica support material while maintaining both the magnetic and photocatalytic properties of the material.
Magnetism: Source and Properties

Magnetic materials have properties that are both fascinating and useful. As children, many of us are captivated by the apparently magical forces of attraction and repulsion between two materials possessing the proper magnetic characteristics. However, the explanation of the source of these magnetic characteristics is better left to scientific experts. These experts have discovered that microscopic current loops, much like the series of current loops in a solenoid, also occur within magnetic materials. This current is due to the electron motion and spin [35]. The macroscopic behavior of materials within a magnetic field can be simply defined by equation 2-1.

\[ M = \chi_m H \]  

(2-1)

Where \( M \) is the magnetization density, \( \chi_m \) is the magnetic susceptibility and \( H \) is the applied magnetic field. This relation allows us to quantify the ability to manifest magnetic changes within a material using an external magnetic field. When \( \chi_m \) is low (± 10\(^{-4}\) to 10\(^{-6}\)), the material is considered paramagnetic or diamagnetic, which means that much more powerful external magnetic fields are necessary to induce changes in the magnetization density [35]. For ferromagnetic materials, equation 2-2 is used instead to define the relationship between external magnetic field and magnetization density to make the coefficient a more reasonable value.

\[ M = (1 + \chi_m)H = \mu_r H \]  

(2-2)

Where \( \mu_r \) is defined to be the relative magnetic permeability of the material.

Antiferromagnetism occurs when a couple of atomic moments oppose each other in a
magnetic field such that the net magnetization density is zero. An interesting variant are ferrimagnets in which a similar behavior occurs with opposing, but unequal magnetic moments leading to a net magnetization that is typically lower than ferromagnetic materials. Magnetite is an example of a ferrimagnetic material where the iron is found in the crystalline structure as Fe$^{2+}$ and Fe$^{3+}$ depending on the lattice location [36]. This net magnetic moment of magnetite has been used for compass designs for at least the last thousand years.

For ferromagnetic materials, there are several other important quantitative parameters that define the material and thus its applicability for engineering solutions. First, there is a temperature above which the ferromagnetic behavior disappears, which is referred to as the Curie temperature. It is quite evident that if the ferromagnetic behavior is important to the function of an engineered device, then the operating temperature range should be well below the Curie temperature. The parameters of coercivity, remanent magnetization, and saturation magnetization can be best understood by examining the hysteresis loop plot (Figure 2-1). By following the series of events on the curve starting with the origin and moving to the right, the magnetic flux density of the magnet (B) increases as the applied magnetic field (H) increased until it reaches a saturation magnetization value ($M_S$, not shown). Subsequently, the applied magnetic field direction is reversed and the flux density decreases, but not at the same slope as it increased. At the point where the applied magnetic field is zero, the magnetic flux density is still present as a remanent magnetization ($B_R$). As the applied magnetic field is reversed further, the magnetic flux density continues to decrease until it reaches zero at the value referred to as the coercivity ($H_C$).
For the magnetic photocatalyst, each of these parameters has a potential impact on performance. First, the coercivity for hard magnetic materials like barium ferrite is has a relatively high magnitude whereas for soft magnetic materials like magnetite it is correspondingly low. This determines both how difficult it is to magnetize the material and likewise how difficult it is to demagnetize the material. For a magnetically agitated photocatalytic reactor (MAPR) application, it is critical that this coercivity be relatively high to assure that the oscillating magnetic field does not demagnetize the magnetic particle. The MAPR uses a combination of oscillating and static magnetic fields to induce agitation and confinement. Additionally, if this value is too high it will not be possible to magnetize the magnetic particles by moving a magnet near them – a more powerful electromagnet may be necessary. The remanent magnetization determines what magnitude of magnetic flux density remains after the particles have been magnetized. If this value is too low, the magnetic particle will not be agitated within the magnetic field. If the remanent magnetization is too high, the interparticle attraction might be large.
enough that the photocatalyst will form clusters that will not be broken apart in the presence of an oscillating magnetic field gradient.

**Photocatalysis and Motion**

For successful photocatalytic oxidation a very distinct series of events must occur involving the almost simultaneous absorption of light and adsorption of contaminants or oxidant precursors. Perhaps the simplest way to understand the phenomenon is to follow the energy through the process. Light is the source of energy necessary to oxidize organic contaminants. This energy is transferred from a photon to a valence band electron in the titanium dioxide crystal. If the photon energy is sufficient, the electron is promoted to the conduction band. The electron and the vacancy it left behind, the electron-hole, can migrate to the surface of the crystal. If, on the way to the surface the electron and electron-hole recombine, the energy is released in the form of heat. If the electron electron-hole pair successfully makes it to the surface, they can participate in reduction and oxidation reactions respectively. The electron can reduce adsorbed oxygen to form a superoxide radical and the hole can oxidize adsorbed organics or oxidant precursors like water or hydroxyl ions to hydroxyl radicals [9]. It is possible that the hydroxyl radical may migrate into solution, but its high reactivity will likely prevent it from traveling far [9].

When applying these principles to a MAPR system, it is clear that the motion of the photocatalyst can play a significant role in enhancing both the absorption of light and the adsorption of contaminants. First, the light absorption is related to the distribution and motion of the catalyst within the reactor. Since the magnetic core is prone to absorb light (no UV transparent hard ferromagnetic material is known although a composite core could be semi-transparent), light will not likely reach a photocatalyst particle if its path is
blocked by another particle. Given this information, and that the photocatalyst itself or the agglomerates formed in solution are large enough to have a diffusion limitation, it is clear that the ideal situation for maximum light absorption is for the photocatalyst to be moving and well distributed within the reactor. This ideal motion and distribution will, of course, depend on the geometry of the reactor and the light source. Adsorption of contaminants will be affected similarly by both the distribution and motion of the photocatalyst. To be adsorbed, the contaminant must first diffuse through the bulk solution then through any boundary layer before it can reach the surface of a non-porous solid [37]. If the photocatalyst resides in a stationary heap on the bottom of a reactor, diffusion will be impeded by both the diffusion distance and boundary layer contribution to diffusion resistance. The reactor conditions can be optimized for increased adsorption by distributing the catalyst more evenly throughout the reactor to reduce diffusion distance and by increasing its motion to reduce the film diffusion resistance. Ideally, this motion would be chaotic to increase the probability of a successful photocatalytic oxidation event.

**Applications of a Magnetic Field Gradient for Particulate Systems**

Applied magnetic field gradients have been used in a diverse group of magnetic particulate system applications. These applications typically fall into one of two categories: confinement or agitation. The first category includes a magnetic field gradient induced stabilized fluidized beds while the second category comprises particle coating, particle deagglomeration for powder flow and fluidized beds and finally a magnetically agitated photocatalytic reactor and utilizes an oscillating magnetic field gradient.

A magnetic field gradient can be utilized to provide an additional force for a fluidized bed that can be useful for both terrestrial and microgravity conditions.
Jovanovic et al. have developed the Gradient Magnetically Assisted Fluidized Bed (G-MSFB) to perform this task [38]. Their design utilizes a series of Helmholtz rings supplied with direct current that increases from coil to coil as one moves up the column such that the coil at the bottom of the column has the highest current and the coil at the top has the lowest current. This variation in coil current gives rise to a magnetic field gradient which acts much like gravity. They found that they could both enhance fluidization under normal gravity conditions and induce fluidization in microgravity conditions (aboard a NASA KC-135 aircraft) where it does not normally occur due to the absence of gravity because the media can not be contained within the reactor [39]. For a MAPR application, this gradient induced force using a direct current could be useful for both improving the distribution and containment of the photocatalyst. In fact, the versatility of the electromagnetically generated field gradient will allow tailoring of the field to a specific gravitational environment or flowrate.

An oscillating magnetic field gradient can cause small magnetic particles to spin and fluidize [20], which is a useful type of motion for several applications. The discharge of powders from hoppers is a relatively simple matter as long as the particles are not small or cohesive. However, cohesion between the particles can cause arching or rat-holing, which occurs when the powder flows more quickly down the sides or middle respectively. To combat the adhesion, typical means include vibrating (vibrating hopper wall or vibrating outlet), pneumatic (air blasts, aeration, etc.), and mechanical methods (rotating screw). Dave et al. proposed the use of a magnetically assisted powder flow (MAPF) system, which consists of 0.85-3 mm barium ferrite particles that were agitated within the hopper near the outlet by an oscillating magnetic field gradient. The particles
were contained by a 635 μm wire mesh at the outlet. By using the MAPF they were able to achieve a controlled discharge of a 15 μm mean diameter cornstarch powder, which is known to be a very cohesive and hence difficult powder to deliver accurately using a hopper.

Another application used by the same research group who developed the MAPF was to effect dry particle coating using a magnetically assisted impaction coating (MAIC) technique [21]. The general concept was to coat larger core (host) particles with fine particles (guest) to prevent cohesiveness and hydrophilicity by causing intraparticle collisions as the magnetic particles were agitated in an oscillating magnetic field. They chose to coat cornstarch and cellulose with silica particles and polymethylmethacrylate (PMMA) with alumina particles. They were successful at reducing hydrophilicity and flowability of cornstarch and cellulose and attributed this success to a thorough coating by silica particles. The SEM evidence suggested that the magnetically agitated particles were not only effective for the impaction coating process, but also breaking up larger agglomerates of guest particles to form a more thorough and uniform coverage. They noted that surface coverage was most thorough at 45 Hz and between 80 and 100 Hz, but there was a decrease in coverage between 60 and 70 Hz. Additionally, they found that as they increased current between 1 and 5 A there was a corresponding increase in surface coverage. A similar magnetically agitated system was used to enhance fluidization of silica nanoparticles was developed by Yu et al. using an oscillating magnetic field gradient and millimeter sized barium ferrite particles [23]. They found that the chaotic spinning and translation of the particles was able to break up the soft nanoparticle agglomerates enough to allow enhanced fluidization even after the magnetic particles
were removed. A follow-up article was also recently published that went into a more
detailed explanation of the dry particle coating procedure using the MAIC method and
comparing it to other conventional dry particle coating techniques [22].

Both of these oscillating magnetic field gradient applications demonstrate that a
chaotic spinning and translation particle motion can be induced. Even though this motion
was not developed with the intent of enhancing photocatalytic oxidation, it is likely that it
will have this effect due to the enhanced absorption and adsorption expected as explained
in the Photocatalysis and Motion section and seen in previous work [13].

**Magnetic Photocatalyst Synthesis**

Magnetic titanium dioxide-based photocatalyst synthesis has evolved since the first
conference proceedings by Beydoun et al. [26] in 1998 (Figure 2-2), yet the basic core-
shell structure has remained the same. This structure consists of a magnetic core material
that is coated with titanium dioxide and possibly an electrically insulative material
between the two. The motivation for the magnetic photocatalyst developed by Beydoun
et al. was to provide a simple method of catalyst separation using a magnet. Their
photocatalyst design also allowed them to take advantage of the high specific surface area
and diminished film diffusion resistance of a particulate catalyst with respect to an
immobilized photocatalyst.

The magnetic core materials used by past researchers include both hard and soft
magnetic materials. The most common core material is magnetite (Fe₃O₄), a soft
ferrimagnetic material that can become oxidized to maghemite (γ-Fe₂O₃), which is also
ferrimagnetic if the particles are heated over 150-170°C according to Beydoun et al.
Fortunately, the saturation magnetization of maghemite is decreased by only 12% (from
84 to 74 emu g⁻¹), yet at higher temperatures of about 550°C and depending on the
particle size and shape the maghemite is converted to hematite, which is so weakly ferromagnetic that it is no longer practical to separate using a magnet [17]. Beydoun et al. attempted to reduce the length of the heat treatment and added a silica insulating layer [17] to prevent this core oxidation from adversely affecting the separation capability. Hard magnetic materials are more difficult to magnetize, but once magnetized can maintain their magnetic characteristics as opposed to the spontaneously induced magnetic behavior of soft magnetic materials. However, they may suffer from some of the same oxidation-related decrease in magnetic properties [40]. Materials that are hard magnets can be recovered using a magnet just as soft magnets, but they have the additional capability of being agitated using an oscillating magnetic field gradient. Two hard magnetic materials, barium ferrite and zinc-nickel ferrite have been used by several researchers with the intent of magnetic agitation [19, 41, 42] and magnetic recovery [43, 44].
Figure 2-2. Comparison of magnetic photocatalyst synthesis procedures.
The magnetic core sizes found in literature range from 4 to 2000 nm and many were produced in the lab. The smallest measured core was developed by Beydoun et al. in 1999 using a coprecipitation of iron (II) and iron (III) chloride with ammonium hydroxide, which produced a particle size range of 4-10 nm [28]. The same group of researchers also produced 40-70 nm magnetite particles by oxidizing Fe(OH)₂ gels with potassium nitrate at 90°C [26]. In contrast to the predominantly wet chemistry methods, Chung et al. chose to use an ultrasonic spray pyrolysis method to produce 720 nm nickel ferrite core particles [45]. Other researchers produced cobalt (26-74 nm) and zinc-nickel (1200 nm) ferrites using a hydrolysis and precipitation method [43, 44, 46]. The researchers who chose barium ferrite purchased their core materials from Arnold Engineering [41, 42] and Alfa Aesar [19]. Possibly the most elaborate core synthesis method was that developed by Rana et al. utilizing a microemulsion technique [47]. Essentially, this technique involves making a mixture of nanometer sized water droplets in oil using a surfactant that act as individual chemical reactors. Two of these microemulsions were prepared: one containing the metal chlorides and the other containing ammonium hydroxide. The microemulsions were mixed allowing the contents to slowly react with each other as the micellar structures periodically rupture and transfer contents to another water droplet thus slowing the rate of particle nucleation. In this case, the particle size was approximately 10-20 nm including the titanium dioxide shell.

The first use of a silica insulating layer in a magnetic photocatalyst was described by Chen and Zhao in 1999 [48] and later elaborated by Beydoun et al. in 2001 [17]. Chen and Zhao found that they could increase the photocatalytic activity of their magnetic photocatalyst by adding a silica membrane deposited using a pH adjusted sodium silicate solution. They proposed that this increase in photocatalytic activity was due to the prevention of electron-hole recombination at
the γ-Fe₂O₃-TiO₂ interface. Shortly thereafter Beydoun et al. published a series of articles describing the negative impact of the γ-Fe₂O₃-TiO₂ junction on photocatalytic activity due to the same electron-hole recombination effect and the occurrence of photodissolution, which causes titanium dioxide particles to be ejected from the surface of the magnetic substrate [28]. Beydoun et al. also proposed to solve this problem using a silica insulating layer, but instead performed this coating using the Stöber method with a tetraethylorthosilicate (TEOS) silica precursor [17]. Lee et al. [42] and Kostedt et al. [19] used the Stöber method as well, but chose to use isopropanol instead of ethanol as a solvent, which is likely to produce larger silica particles. Additionally, Lee’s method indicated a single coating of silica whereas Kostedt coated twice using the same procedure. Along the same lines as their aerosol core synthesis method Chung et al. produced a silica coating using ultrasonic spray pyrolysis of TEOS [45].

Titanium dioxide nanoparticles have been predominantly deposited using a wet chemistry approach with an alkoxide TiO₂ precursor. Chen and Zhao [48] were the only authors to use Degussa P25 to coat their magnetic photocatalyst. They did so by first abrading the mixture of magnetic particles and TiO₂ then sonicating and annealing the dried particulate mixture. Over half of the authors who synthesized magnetic photocatalysts used a method involving the hydrolysis and condensation of titanium n-butoxide (TBOT). This typically involves heating a mixture of water and TBOT in an ethanol solvent to produce a slightly crystalline TiO₂ sol. These titanium dioxide particles can be deposited on the magnetic substrate surface using agitation by a magnetic stir bar or by sonication. Since the titanium dioxide particles deposited using this method are only slightly crystalline, and the crystallinity and crystalline phase are critical to high photocatalytic activity, a subsequent heat treatment is necessary to generate primarily anatase phase nanoparticles.
Most authors have used temperatures between 450-550ºC for between 30 and 180 minutes to accomplish this increase in crystallinity and phase change to anatase. The positive effects of the crystalline phase change may be offset by decreases in surface hydroxyl group density or particle size increase if the temperature is too high or the treatment duration is too long. Additionally, Gao et al. [49] found that heat treating to between 700 and 900ºC caused a phase change to rutile and formation of pseudobrookite (Fe₂TiO₅), which decreased photoactivity as well. It should be noted that Gao’s study did not utilize any silica insulating layer. Another approach was that developed by Watson et al. [18] to directly deposit anatase phase using a titanium isopropoxide precursor with a high water to alkoxide ratio and acidified with nitric acid. This direct deposition avoids the necessity of the heat treatment step, which was shown by their previous work to decrease the magnetic properties and increase the cost and time required for synthesis.

The synthesis procedures can have a dramatic impact on both the adsorption and absorption properties of the magnetic photocatalyst. The core size and material will determine its adsorption properties. Silica was used by many researchers as a membrane to prevent unfavorable electronic interactions with the core material, but it also has some promising properties for adsorption due to the surface silanol functional groups [50]. Additionally, the size of the core material as well as the size of the titanium dioxide particles will influence the specific surface area of the photocatalyst. Generally, smaller core material will lead to a greater specific surface area, but it is important to consider the possibility of several core particles being included in a single silica membrane [19, 42].

In light of the concepts presented in this work, it is apparent that the optimization of a MAPR requires knowledge of adsorption and absorption. Specifically, it is important to consider
the properties of the photocatalyst and its behavior in an oscillating magnetic field gradient. The impact of photocatalyst distribution and motion on oxidation was elucidated. It was also demonstrated that the magnetic characteristics of the material used for the core has an impact on its ability to be fluidized.

**Dye Removal Using a ZnO-TiO₂ Composite**

Textile dyes represent a significant environmental hazard to aquatic biota and humans due to their toxicity [51] and tendency to cause eutrophication [9]. Improvements in chemical structure have led to increased longevity of dyed fabrics, yet make the textile wastewater more difficult to treat. Traditional biological methods often fail due to the increased stability of highly aromatic dye molecules. Additionally, methods such as adsorption, reverse osmosis, coagulation, etc. simply transfer the dye from one phase to another leaving a secondary waste problem.

Several options for advanced oxidation exist including wide-bandgap semiconductors. These materials have the ability to generate hydroxyl radicals when exposed to sub-bandgap energy photons (typically in the ultraviolet range). Frequently used wide-bandgap semiconductors include TiO₂ [52-54], ZnO [52, 55, 56], CdS [57], and others. However, TiO₂ is most popular due to its relatively low toxicity, low cost, and resistance to photocorrosion [58]. The other materials function as photocatalysts, but exhibit photocorrosion in the presence of UV light that drives the photooxidative reactions. This is particularly troublesome for compounds such as CdS as photocorrosion leads to pollution with a heavy metal [57]; however several studies have reported superior performance by using ZnO instead of TiO₂ [59, 60].

While the most frequently used photocatalyst materials are composed of a single semiconductor, other authors have found benefits of using mixed oxides with TiO₂ and one of the following: ZnO, WO₃, SiO₂, or ZrO₂ [61-68]. Some explanations for this phenomenon include increased surface acidity and favorable electronic interactions between the different
metal oxide materials. This study included a comparison between two heat treatment methods, hydrothermal and calcination after co-precipitation of ZnO/TiO$_2$ and explored the role of surface area, heat treatment, and zeta potential, and bandgap energy on photocatalytic oxidation and adsorption of Procion Red MX-5B, an azo dye.
CHAPTER 3
MATERIALS AND METHODS

Common Methods

**Magnetic Photocatalyst Synthesis Method**

**Silica coating**

Several barium ferrite core materials were used. For “Incorporation of a Permanent Magnet and Influence of Ball Milling on MAPR Performance” the raw material for the magnetic core was ball-milled barium ferrite with an average particle size of 2.2 μm. For all other studies, the barium ferrite was a powder obtained from Alfa Aesar. Barium ferrite was coated with silica using a base catalyzed sol-gel procedure [17, 42, 69] to provide insulation between the magnetic core and the photocatalyst layer for the purpose of preventing photodissolution and corrosion of the core. The silica coating procedure is as follows: 300 mg of 2.2 μm barium ferrite particles were dispersed in 25 mL of isopropanol (Acros Organics) and sonicated for 5 min. After sonication, 1.1 mL of tetraethylorthosilicate (TEOS, Aldrich), 4 mL of deionized (DI) water (18.2 MΩ•cm, Nanopure), and 0.147 mL of ammonium hydroxide (Aldrich) were added to the sonicated solution. The prepared solution was vigorously stirred for 3 hr at room temperature. The silica-coated barium ferrite particles were recovered from the solution by magnetic separation, washed with isopropanol and DI water, and finally dried at room temperature for 2 days. This was a single coating for “Incorporation of a Permanent Magnet and Influence of Ball Milling on MAPR Performance” and a double coating was performed for all other work.

**Titania coating**

An amorphous layer of titanium dioxide was deposited using a hydrolysis and condensation technique [18, 70]. The prepared silica-coated barium ferrite particles were dispersed in a mixture of 100 mL of ethanol (Aldrich) and 2.7 mL of DI water and sonicated for
10 min. Next, 0.47 mL of titanium n-butoxide (TBOT, Acros Organics) was dissolved in 10 mL of ethanol and this solution was gradually added with a pipette to the mixture of particles, ethanol, and water. The solution was vigorously stirred for 10 min at room temperature and then heated to 90° C at a rate of 5° C/min, where it stayed for the next 2 hr while stirring vigorously. The prepared sample was recovered from the solution by magnetic separation and washed with ethanol and DI water. The wet sample was then dried in an oven at 60° C for 2 days. The dried sample was heat-treated in a box furnace with a 5° C/min ramp to 500° C, then held for 1 hr in an ambient atmosphere to develop the anatase crystalline phase of TiO2, which was verified by XRD [42]. The particles were magnetized by passing a magnet over them several times. Presence of the silica layer was verified via energy dispersive x-ray (EDS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) [42]. TiO2 mass loading using the double coating technique was determined to be 28.0% by digesting and comparing dried sols prepared with and without silica-coated barium ferrite particles. The digestion method was adapted from Korn et al. [71] and the samples were analyzed with a Perkin Elmer 3200 inductively coupled plasma optical emission spectrometer (ICP-OES). A Brunauer, Emmett, and Teller (BET) surface area analysis using a Quantachrome Nova 2200e revealed a specific surface area of 31.3 m²/g.

**Incorporation of a Permanent Magnet and Influence of Ball Milling on MAPR Performance**

**Experimental Setup**

The experimental setup consisted of three primary components: a magnetic field generation system, a curved quartz reactor (to increase transmission of UV wavelength light with respect to the previously work with a Pyrex reactor), and three ultraviolet lamp fixtures. The magnetic field generation system consists of a function generator whose signal is fed to an audio
amplifier and finally to a series of two solenoids (Figure 3-3). In addition, a 2.54 cm³ permanent magnet is suspended on a sheet of plexiglass above the reactor as can be seen in Figure 3-1. This addition of a static magnetic field counteracts the gravitational field that causes the catalyst to remain clumped near the bottom of the reactor thus increasing UV irradiation of the catalyst. It is important to note that this static field may need to be modified depending on the gravitational requirements of the application. For instance, on the moon, where the gravity field is weaker, a weaker magnet could be used to generate the static field. The reactor is constructed of three quartz segments oriented at right angles to each other with the middle segment curved to follow the polar symmetry of the alternating magnetic field. The three UV lamp fixtures are located above and on both sides of the reactor.

Figure 3-1. Magnetically agitated photocatalytic reactor.

**Photodegradation of Phenol and Procion Red MX-5B Dye**

Phenol and reactive red were chosen as simulated pollutants for their ease of testing. Stock solutions were prepared with liquid phenol (Fisher) or Procion Red MX-5B powder (Aldrich) diluted with 18.2 MΩ/cm Barnstead E-Pure water. An 8-watt 254 nm UV lamp (Spectronics Corp.) was chosen to test the hypothesis of previous work [72] that the lack of photocatalytic
activity with the 254 nm lamp was due to sub-visible wavelength light absorption by the Pyrex reactor. To prevent this problem, a quartz reactor was used instead. All experiments were performed in batch with 10 mL of simulated pollutant, 100 mg of catalyst unless specified otherwise and the reactor was sealed with rubber caps (fluid was not in contact with the caps and adsorption was found to be negligible). Analysis of phenol concentrations was performed with a GC/MS (Varian 3900/2100T) and non-purgeable dissolved organic carbon (nDOC) with a Tekmar Dohrmann Apollo 9000. Procion Red dye was analyzed using a Hach DR4000U spectrophotometer with a 1 cm quartz cell to measure the maximum wavelength absorbance of 538 nm.

Enhanced Photocatalyst Synthesis and Reactor Parameter Exploration

Photocatalytic Test Stand

The experimental setup consisted of a magnetic field generation device, UV lamps and a batch reactor. The 10 mL curved reactor was constructed of 3 fused quartz tubes as can be seen in Figures 3-2 and 3-3. The straight upright segments have an inner diameter of 1.27 cm and the curved segment has an inner diameter of 1.05 cm. The 8-watt UV lamps had a 365 nm wavelength peak output and were manufactured by Spectronics Corp. (Westbury, NY). During experimentation, the reactor was sealed with Teflon caps that were not in contact with the solution.
Figure 3-2. Two-dimensional drawing of quartz reactor.

Figure 3-3. Three-dimensional drawing of quartz reactor.
The magnetic field was generated with an alternating current signal fed to a series of two solenoids (Figure 3-4). Each solenoid consisted of 152 m of 18 AWG wire wound around an 8.9 cm diameter wire spool. The wire was wound in 20 layers with 23 turns per layer as a result of modeling to maximize the magnetic field gradient [72]. The signal was generated by a BK Precision 4011A function generator. The output from the function generator was delivered to a Guitammer BKA 1000-4 power amplifier with outputs attached to the leads of solenoids in series (Figure 3-4). Solenoid A was used to increase the impedance of the amplifier load to prevent overloading while solenoid B was used for the magnetic field generation beneath the reactor as seen in Figure 3-2. Finally, a 2.54 cm³ permanent magnet was suspended on a sheet of plexiglass above the reactor to provide a magnetic field that counteracted gravity. With the permanent magnet in place, the catalyst within the reactor was both horizontally and vertically dispersed. During all experiments the test stand was covered with a black box to prevent UV light from entering or leaving. A fan assisted in transferring heat generated by the solenoid and UV lamps to maintain a steady state sample temperature of 29 ± 5 °C.

Figure 3-4. Alternating magnetic field generator.
Gas Chromatograph/nDOC Analysis of Phenol

Liquid phenol from Fisher Chemicals (90.9%) was used to simulate aqueous organic pollutants. All experiments treated 10 mL of an 11 mg/L phenol solution prepared for each experiment by diluting the concentrated liquid phenol with Barnstead E-Pure 18.2 MΩ/cm water. The initial dissolved oxygen was found to be 7.5 ± 0.2 mg/L using a YSI 52 dissolved oxygen meter (used according to manufacturer guidelines) and was not augmented with an external oxygen supply during experiments. The reactor was operated in batch such that data for each time represents a discrete experiment. Samples for GC and nDOC (non-purgeable dissolved organic carbon) analysis were obtained by separating the catalyst from solution with a magnet and storing it in a VOA vial with Teflon septa at 4 °C until testing. Non-purgeable dissolved organic carbon was measured on a Tekmar Dohrmann Apollo HS 9000 with autosampler. Purging and mixing was accomplished by sparging the sample, which had been pH adjusted with phosphoric acid, with zero grade air for 3 minutes. Analysis of phenol concentrations was performed with a GC/MS (Varian 3900/2100T) using a solid phase microextraction (SPME) sampling technique with an 85 µm polyacrylate coated fiber assisted by an addition of reagent grade sodium chloride. The column was a PTE-5 and the temperature profile included maintaining 40°C for 4 minutes, then elevating to 260°C at a rate of 12°C/min The relative standard deviation for (RSD) for replicate analysis of samples was less than 5% for both reported phenol concentrations and nDOC values.

Magnetic Photocatalyst Characterization and Reactor Performance Using AES Ersatz Water

Characterization of the Magnetic Photocatalyst

The magnetic photocatalyst was characterized for both crystalline size and to determine what type of assembled structures formed during exposure to the magnetic field. Crystalline size
was determined by performing an x-ray diffraction (XRD) analysis using a Phillips APD 3720
then using the Scherrer equation to estimate the size (eq. 3-1). Assembled structures were
examined using a JEOL 6400 scanning electron microscope (SEM) with an accelerating voltage
of 5 kV before and after exposing the sample to the magnetic field at 1 A at 60 Hz with the
permanent magnet present.

\[
t = \frac{k \lambda}{B \times \cos \theta}
\]  

(3-1)

**Photocatalytic Test Stand**

The photocatalytic test stand consisted of components to generate the magnetic field and
provide UV light to the curved quartz reactor. The oscillating magnetic field was generated using
a solenoid powered by an amplified sinusoidal wave function while the static magnetic field was
the result of a permanent magnet located above the reactor. By using a function generator to
modify the solenoid frequency, and an audio amplifier to alter the solenoid current, the magnetic
field was altered to determine its effect on photocatalytic oxidation of AES (Air evaporation
system). All experiments were performed with 100 mg catalyst, 10 mL of AES ersatz and an
oscillating magnetic field provided at 60 Hz with 1 A current for 1 hour in batch unless specified
otherwise. Also, all experiments used three-254 nm peak output lamps.

**Analysis of Photocatalytic Oxidation**

Air evaporation system ersatz water was prepared using the procedure developed by
Verostko et al. [73] and dilution water was provided by a Nanopure Diamond Analytical TOC
water purifier. Because the oxidation byproducts are numerous and not easily identifiable, non-
purgeable dissolved organic carbon (nDOC) was used to assess the extent of photocatalysis. The
nDOC was measured with a Tekmar Dohrmann Apollo 9000 HS. The nDOC analyzer first
adjusted the pH of the sample with phosphoric acid, then purged with air to remove inorganic
carbon. Subsequently, a sample was injected into a furnace filled with a platinum doped alumina catalyst at 680ºC to convert organic chemicals to carbon dioxide (CO₂) and water. The water was removed by cooling to condense some of the water, then by a Nafion membrane to remove remaining water. Finally, a scrubber was used to remove corrosive gas before the stream was directed through a non-dispersive infrared detector (NDIR) to quantify the amount of CO₂ produced.

**Photocat Experiments Using Graywater Formula**

**Simulated NASA Graywater Preparation**

Several simulated wastewater types were prepared for testing in the Photo-Cat®. The first type, simulated transit mission wastewater was prepared using the chemicals listed in Table 3-1. The chemicals were quantitatively transferred to the reservoir of the Photo-Cat® after it had been filled with 15 L of tap water (containing typical organic and inorganic materials at acceptable levels for potable water) and titanium dioxide. Mixing took place as the water was re-circulated through the system.

**Biological Water Processor Effluent Preparation**

Biological water processor effluent (BWP) was prepared according to the NASA Ersatz [73]. The 1 L concentrated solutions were prepared with the specified chemicals and allowed to remain at room temperature in sealed containers. To prepare a working solution, the specified quantity of each concentrate was transferred to the Photo-Cat® reservoir and allowed to mix as the system re-circulated (Table 3-2).
Table 3-1. Simulated graywater formula.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Amount Per Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium bicarbonate</td>
<td>2726 mg</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>850 mg</td>
</tr>
<tr>
<td>Potassium bicarbonate</td>
<td>378 mg</td>
</tr>
<tr>
<td>Hippuric acid</td>
<td>174 mg</td>
</tr>
<tr>
<td>Potassium dihydrogen phosphate</td>
<td>173 mg</td>
</tr>
<tr>
<td>Potassium bisulfate</td>
<td>111 mg</td>
</tr>
<tr>
<td>Citric acid</td>
<td>92 mg</td>
</tr>
<tr>
<td>Glucuronic acid</td>
<td>60 mg</td>
</tr>
<tr>
<td>Johnson’s Baby Shampoo</td>
<td>1.2 g</td>
</tr>
<tr>
<td>Ammonium hydroxide (14.8 N)</td>
<td>1 mL</td>
</tr>
<tr>
<td>Vegetable oil</td>
<td>667 μL</td>
</tr>
<tr>
<td>Water (Tap)</td>
<td>868.4 mL</td>
</tr>
</tbody>
</table>

Table 3-2. Biological water processor formula

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Amount Per Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium bicarbonate</td>
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</tr>
<tr>
<td>Amonium chloride</td>
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<tr>
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<td>Potassium bisulfate</td>
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<tr>
<td>Potassium chloride</td>
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<td>Hydrochloric acid (37%)</td>
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<tr>
<td>Glucuronic acid</td>
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<tr>
<td>Creatinine</td>
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<tr>
<td>Urea</td>
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</tr>
<tr>
<td>Ethanol</td>
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</tr>
</tbody>
</table>

**Photocatalyst/UV Lamps**

Degussa P-25 (particle size approximately 30 nm) was chosen as the photocatalyst and was used as received. For each experiment, 10 grams of catalyst was added to the reservoir after it was filled with 15 L of tap water providing a TiO₂ slurry concentration in the system of 667 mg/L. The UV source was 8-64” 75 watt bulbs with a peak output wavelength of 254 nm.

Figure 3-5. Supervisory control and data acquisition schematic of photocat. SLP = slurry loop pump, DPCV = discharge pressure control valve, SLCV = slurry loop control valve, SFCV = slurry feed control valve, BPD = backpulse device, PWSV = purge water solenoid valve, DSV = drain solenoid valve, ISV = influent solenoid valve.
Supervisory Control and Data Acquisition Interface, Control Systems, and Programmed Operation Modes

The supervisory control and data acquisition (SCADA) interface allowed complete control of system functions including UV lamp operation, pump speed, and solenoid valves (Figure 3-5). A programmed purge mode was used to clean the system between experiments. In this mode, all portions of the Photo-Cat® were flushed with tap water at least 3 times. The interface also monitored temperature, pH, and various flowrates in real-time. Programmed operation modes were used for batch mode, where the slurry separation device was bypassed and default mode where it was not. Finally, a programmed low-flow mode allows a low flowrate of contaminated water to be delivered to the reactor via an externally-controlled pump.

Effluent Sampling and Testing

Samples were collected in 40 mL acid-washed glass vials with Teflon septa and were promptly refrigerated at 5 °C. An initial sample was taken to verify the effectiveness of cleaning between experiments. A portion of each sample was analyzed with a Hach DR4000U for absorbance at 254 nm using a 1 cm path length quartz cell. Using this value as an estimate of non-purgeable dissolved organic carbon (nDOC), the sample was diluted with Barnstead E-Pure water (18.2 MΩ/cm) to maintain a nDOC level below 10 mg/L. The diluted sample was analyzed for nDOC using a Tekmar Dohrmann Apollo 9000 HS TOC analyzer.

Photocatalyst Comparison Using the Photocat Reactor

Biological Water Processor and Air Evaporation System Effluent Ersatz Preparation

Biological water processor effluent (BWP) and air evaporation system effluent (AES) were prepared using the NASA ersatz definition [73] developed by Verostko et al. To prepare a working solution, the specified quantity of each concentrate was transferred to the Photo-Cat®
reservoir and allowed to mix as the system re-circulated. Dilution water was from a Nanopure Infinity water purifier.

**Photocatalyst/UV lamps**

Both Degussa P25 and silica-titania composite photocatalysts were used. Degussa P25 was used as received. Silica-titania composite photocatalyst was synthesized using the procedure described previously for 140 Å mean pore size and 30% TiO₂ by mass [16]. Instead of making pellets in 96 well assay plates, the gel was aged as a monolith in a 3 L beaker. After aging, the xerogel was dried at 103°C for 18 hours then ramped to 180°C where it dwelled for 6 hours. Once dry, the gel was heat-treated with a 5°C/min ramp to 500°C to remove any residual organics were it remained for 1 hour. After the heat treatment, the gel was ground with a mortar and pestle and the 45-90 µm fraction was used for experimentation. A Brunauer, Emmett, and Teller (BET) surface area analysis using a Quantachrome Nova 2200e revealed a specific surface area of 400 m²/g. The UV source was 8-64” 75 watt bulbs with a peak output wavelength of 254 nm.

**Scanning Electron Microscopy (SEM)**

SEM images and energy dispersive x-ray (EDS) spectra were obtained using a JEOL JSM 6400 with an accelerating voltage of 15 kV. Backscatter electron (BSE) images were obtained using a solid-state detector located on the polepiece. All specimens were coated with a conductive carbon layer prior to analysis using a vapor deposition technique.

**Effluent Sampling and Testing**

Samples were collected in 40 mL amber glass vials that had been soaked in 10% sulfuric acid for 24 hours and subsequently heated to 550°C for at least 1 hour. The samples were promptly refrigerated at 4 °C. An initial sample was taken to verify the effectiveness of cleaning between experiments. A portion of each sample was analyzed with a Hach DR4000U for
absorbance at 254 nm using a 1 cm path length quartz cell. Using this value as an estimate of non-purgeable dissolved organic carbon (nDOC), the sample was diluted with Nanopure Dlamond (18.2 MΩ/cm) to maintain a nDOC level below 10 mg/L. The diluted sample was analyzed for nDOC using a Tekmar Dohrmann Apollo 9000 HS TOC analyzer.

Impact of Heat Treatment and Composition of ZnO-TiO2 Nanoparticles for Photocatalytic Oxidation of an Azo Dye

Materials

All chemicals used in this study were analytical grade reagents. Zinc nitrate hexahydrate Zn(NO₃)₂·6H₂O and titanium tetrachloride TiCl₄ (Fisher) were chosen as precursors of ZnO and TiO₂ respectively. Procion Red MX-5B was used for photocatalytic oxidation and adsorption experiments.

Synthesis

Zn(NO₃)₂·6H₂O and TiCl₄ solutions were mixed at room temperature using magnetic stirring. The samples were synthesized at different compositions, which will be referred by the percentage of TiO₂ with the balance ZnO followed by C for calcined or H for hydrothermal (95H corresponds to 95% TiO₂ that was hydrothermally prepared). The pH was adjusted to 8.5 by slowly adding an ammonium hydroxide solution and continuing to stir for two hours. White Zn(OH)₂/ Ti(OH)₄ precipitate formed instantaneously. The precipitated samples were divided into two portions to study the effect of direct calcination and hydrothermal techniques. One portion was separated by filtration and washed by water several times until the pH reached 7. The first part was dried overnight at 110 °C and calcined at 500 °C for 5 hours. The second portion was hydrothermally treated (high pressure water vapor environment) in a Teflon-lined autoclave at 150 °C for 10 hours. The powder was then filtered, washed and dried at 110 °C for 24 hours.
Characterization

Material characterization including specific surface area was estimated using nitrogen adsorption isotherms measured on a Quantachrome Nova 2200e and modeled using the Brunauer Emmet and Teller (BET) model, x-ray diffraction (XRD) \( 2\theta \) patterns were derived with a Phillips APD 3720, zeta potential was determined using a Brookhaven ZetaPlus, and diffuse reflectance spectra were estimated using a Labsphere PELA-1000 integrating sphere module in a Perkin-Elmer Lambda 800 UV/Vis spectrophotometer.

Dye Photocatalytic Oxidation

Performance of the photocatalyst materials was assessed by measuring both adsorption and photocatalysis of Procion Red MX-5B dye. All experiments were conducted using a Glas-Col Rugged Rotator. Teflon sealed borosilicate vials were prepared with 20 mg of photocatalyst and 40 ml of 15 mg/l Procion Red MX-5B (RR) dye solution (Figure 1) where pH was unadjusted and measured to be 6.8 ± 0.2. Photolytic degradation of this dye was found to be negligible in previous work by Khan [74]. Dye adsorption was quantified by preparing vials and rotating for 24 hours in a dark black box before analysis. Photocatalytic oxidation experiments involved preparing samples in Teflon sealed borosilicate vials in the same manner as in the adsorption experiments except that an array of four-8 watt 365 nm peak output UV bulbs were placed 7.6 cm from the rotator for 3 hours. Ferrioxalate actinometry determined the total flux to be \( 1.01 \times 10^{-5} \) einsteins/min. RR concentration was measured by first vacuum filtering the samples using a 0.2 \( \mu \)m nitrocellulose membrane filter, and then determining the absorbance of the sample using a Hach DR/4000Uspectrophotometer at 538 nm.
A High Surface Area Magnetic Photocatalyst with Controlled Pore Size

High Surface Area Magnetic Photocatalyst Synthesis

Barium ferrite (Alfa Aesar) particles were coated with silica using a Stöber technique [33]. Specifically, 4000 mg of BaFe$_{12}$O$_{19}$ were dispersed in 500 ml of 0.51:0.79:15:0.037 mol ratio of H$_2$O:NH$_4$OH:EtOH:TEOS. The particles were stirred for 24 hr with a PTFE overhead mixer at 475 RPM. The resulting particles were dried at 65 °C for 24 hr resulting in a total mass of approximately 4.40 g. The silica-coated barium ferrite particles and 18.9 g titanium dioxide (Degussa P25) were then dispersed in an acid catalyzed silica sol-gel [75]. The sol-gel consisted of 113 ml of Nanopure water (18.2 MΩ·cm), 225 ml ethanol, 156 ml TEOS, 18 ml 1M HNO$_3$, and varying volumes of 3% hydrofluoric acid. The volume ratio of HNO$_3$ to HF was used to denote the 3 types of high surface area magnetic photocatalyst (HSAMP) explored in this work. For example, HSAMP8 indicates that a volume ratio of 8:1 and a volume of 2.25 ml HF. The gelation time varied by hydrofluoric acid concentration between 7 and 24 hrs. This time was determined as the time necessary to reach a viscosity such that visible particle movement was negligible and the vortex near the overhead mixer paddles was no longer apparent. The gel was then poured into plastic specimen containers, sealed and aged at 25 °C for 48 hrs then 60 °C for another 48 hrs. To dry the gel and evaporate residual ethanol, the aged gel was dried in a PTFE container with a small hole on the top. The drying followed a 3 °C ramp to 103 °C, held for 18 hr, then followed another 3 °C ramp to 180 °C and was held for 6 hr. After drying, the xerogel was heat treated with a 5 °C ramp to 450 °C, held for 1 hour and cooled naturally. The resulting xerogel was ground with a mortar and pestle and wet sieved to retain the 45-90 μm fraction. The powder was dried at 180 °C and stored under vacuum until use.
Characterization

Characterization techniques included scanning electron microscopy (SEM), x-ray diffraction (XRD), diffuse reflectance, vibrating sample magnetometry (VSM), and inductively coupled plasma (ICP) analysis. Scanning electron microscope images were obtained with a JEOL JSM 6335F with a field emission element at a 5 kV accelerating voltage. X-ray diffraction patterns were found using a Phillips APD 3720 with Cu Kα radiation with 2Θ of 20-80° with a step size of 0.02°. Particle size comparisons were made using the Scherrer equation [76]. Vibrating sample magnetometry was performed using a Princeton Measurements Corporation MicroMag 3900. Finally, a Perkin-Elmer Plasma 3200 with optical emission spectrometer (OES) was used for ICP analysis of the HSAMP.

Assessment of Photocatalytic Oxidation

Phenol was chosen as a surrogate contaminant due to its extensively studied reaction mechanism and the widespread use for assessment of photocatalytic oxidation. A 6.5 mg/l phenol solution was prepared with Nanopure water (18.2 MΩ/cm) and reagent grade phenol (90%, Fisher). The dissolved oxygen was measured to be 7.5 ± 0.2 mg/l using a YSI 52 dissolved oxygen meter and was not augmented with an external oxygen supply during experiments. The solution pH was unadjusted and measured to be 6.8 ± 0.2 prior to use during experimentation. Phenol adsorption experiments were carried out by preparing Teflon sealed borosilicate vials with specified masses of HSAMP and 40 mL of phenol solution and rotating for 24 hours in a dark black box. Vials were prepared the same manner for the photocatalytic oxidation experiments except that an array of four-8 watt 365 nm peak output UV bulbs were placed 7.6 cm from the rotator for various times. Ferrioxalate actinometry determined the total flux to be $1.01 \times 10^{-5}$ einsteins/min. Subsequent to recovering the HSAMP using a magnetic decantation technique, phenol concentration was determined with a GC/MS (Varian
3900/2100T) using a solid phase microextraction (SPME) sampling technique with an 85 µm polyacrylate coated fiber assisted by addition of reagent grade sodium chloride. Non-purgeable dissolved organic carbon (nDOC) was measured on a Tekmar Dohrmann Apollo HS 9000 with autosampler. Purging and mixing was accomplished by sparging the sample, which had been pH adjusted with phosphoric acid, with zero grade air for 3 minutes. The relative standard deviation for (RSD) for replicate analysis of samples was less than 5% for both reported phenol concentrations and nDOC values.
CHAPTER 4
INCORPORATION OF A PERMANENT MAGNET AND INFLUENCE OF BALL MILLING ON MAPR PERFORMANCE

The magnetic core of a magnetic photocatalyst forms the basis for the structure and growth of subsequent coatings with silica and titania. Ball milling provided a method for reducing the size of larger particles. In addition, while the magnetic field initially consisted of only an oscillating component for agitation, experimentation with other external magnetic fields including electromagnets and several types of permanent magnets resulted in the discovery of the enhancement effect possible with a permanent magnet located above the reactor.

**Phenol Photodegradation**

In contrast with previous experiments [72], the current fed to the solenoids in series was held constant and the corresponding photocatalytic activity was also found to remain relatively constant (Figure 4-1). The composite catalyst, irradiated by the 8-watt 254 nm lamp, was able to decrease the 10 mg/L initial phenol concentration by an average of 92.2% after one hour. The frequency range was from 0 to 80 Hz in increments of 10 Hz. The nDOC decrease was an average of 50.0% by carbon. The lower removal of carbon than phenol is thought to be the result of formation of oxidation byproducts from incomplete mineralization. Since the treatment objective is defined in terms of a final nDOC goal of 0.5 mg/L, the nDOC value is most important.

![Normalized Concentration Decrease vs Frequency](image-url)
Additional experiments were performed to determine if the consistent photocatalytic activity was due to a high concentration of catalyst, so 50 mg was used for a 30 minute experiment instead. As expected, the decrease in the phenol concentration was significantly reduced, but the photocatalytic activity remained relatively constant through the frequency range (Figure 4-2).

Ball-Milling Impact on Catalyst Performance

The raw material for catalyst synthesis is ball-milled barium ferrite according to the procedure described in previous work [72]. The process involves rolling a jar filled with water, large barium ferrite particles and zirconia grinding media. Collisions between the media, walls of the jar, and barium ferrite break the material into progressively smaller pieces. If the barium ferrite loading is too high, the milling process will be incomplete and both the particle size distribution and morphology will be drastically different. In the past, 3 grams of barium ferrite was used for each ball-milling batch. To increase output, 7 grams of barium ferrite was used with the same ball-milling and catalyst manufacturing procedure. The resulting change in
photocatalytic activity was quantified by decolorizing a 10 mg/L solution of Procion Red dye with catalyst synthesized using both the 3 gram and 7 gram ball-mill batches (Figure 4-3).

![Figure 4-3. Normalized color decrease (1-C/Co) by catalyst synthesized using barium ferrite ball milled in different quantities.](image)

There is clearly a dramatic impact of the raw material on the photocatalytic activity of the composite catalyst with an average increase of 70% for the material ball-milled in smaller batches. Scanning electron microscope images of the finished catalyst show a more angular morphology indicating a lack of coating by silica and titania on the 7 g batches (Figure 4-4).

In support of the supposition that the change in morphology indicates a lack of coating by silica and titania, EDS spectra indicated a decrease in silicon and a slight decrease in titanium on the surface of the catalyst using the different raw material (Figure 4-5). Previous work has shown that the silica layer is critical to prevent photodissolution at the titanium dioxide – magnetic core junction [17] thus the decrease in silicon indicated by the EDS spectra could mean that there is an increase in photodissolution, which might explain the decreased performance shown in Figure 4-3.
Figure 4-4. Scanning electron microscope images of catalyst prepared using different ball-milling procedures 7 g batch, A and 3 g, B NOTE: the magnification is different for each image.

Figure 4-5. Energy dispersive x-ray spectroscopy spectra of catalyst prepared using different ball-milling procedures 7 g batch (upper) and 3 g on (lower).

**ESM Estimation**

The NASA Specialized Center of Research and Training (NSCORT) at Rutgers University in New Jersey provides an example calculation for a subsystem based on the ISS data from
mission documents. Although the data are presented for a 6-member crew for a 3650-day mission, one can calculate the equivalent systems mass (ESM) for a 4-member crew for 100- and 1000-day missions. Similarly, based on reasonable estimations for the MAPR one can calculate the ESM for these units.

The ESM of the MAPR was estimated to be 289 and 380 kg for 100- and 1000-day missions (Table 4-1). Since the small mass, small volume, and essentially no requirement for crew time or consumables (except potentially UV lamps) significantly reduce the MAPR’s ESM, a method to control power consumption could further accent the benefits of this technology.

It is difficult to compare a single water recovery system to an entire water treatment train with respect to ESM because the calculation for the post processor alone does not account for systems integration. Since this task is not simplified by the data provided on the NJ-NSCORT website, the ESM for an Integrated PhotoCatalytic Water Recovery System (IPCWRS) based on Honeywell’s cascade distiller and the MAPR is provided for comparison purposes. This system consisted of a urine preprocessor, cascade distiller, and MAPR. These data are presented in Table 1 and clearly show that the IPCWRS ESM is anticipated to be considerably less ESM than the ISS baseline. Although all of these calculations were estimates, it was proposed that the major difference between the ISS and IPCWRS was that the IPCWRS significantly reduced logistics, mass, volume, and power consumption.

Table 4-1. Equivalent systems mass (kg) for international space station baseline and photocatalytic systems.

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<th>100 Day mission</th>
<th>1000 day mission</th>
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<tr>
<td>ISS Baseline</td>
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<tr>
<td>MAPR</td>
<td>289</td>
<td>380</td>
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<tr>
<td>IPCWRS</td>
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CHAPTER 5
ENHANCED PHOTOCATALYST SYNTHESIS AND REACTOR PARAMETER EXPLORATION

While the previous chapter introduced improvements in basic parameters including photocatalyst synthesis and magnetic field configuration, this chapter is focused on a more detailed assessment of reactor parameters and further explores the influence of photocatalyst synthesis including double coatings and titanium dioxide particle size.

Catalyst Synthesis

The surface morphology of the barium ferrite core indicated sharp edges and a dominant flat hexagonal shape. The magnetic property caused the particles to agglomerate into stacks. After the catalyst was coated with double layers of silica and titania, the sharp edges are less evident. In addition, the agglomerates are more irregularly shaped possibly due to silica necking between the particles of barium ferrite.

A superconducting quantum interference device (SQUID) analysis of the barium ferrite core and the composite photocatalyst demonstrated several important features of the catalyst [72]. First, the catalyst and barium ferrite had a clear hysteresis loop indicated by the lag in magnetism of the sample with changes in applied magnetic field intensity. This hysteresis loop is indicative of a ferromagnetic material possessing a remanent magnetization as was expected for barium ferrite. This remanent magnetization was approximately 23 emu G/g for the composite photocatalyst and 24 emu G/g for the barium ferrite core. The SQUID analysis confirmed that coating the barium ferrite caused only a slight decrease in remanent magnetization and the ferromagnetic property was preserved.

Phenol Photolysis

Previous studies have indicated that phenol undergoes photolysis when exposed to 185 or 254 nm irradiation [77]. Similarly, 254 nm has been found to be more effective for mineralizing
phenol [13]. In our experiments, phenol showed no photolytic mineralization during seven hours of exposure from three 365 nm lamps using a quartz reactor. Therefore data shown herein are a result of photocatalysis and not photolysis. Indeed, a full-scale MAPR system may take advantage of photolytic degradation, yet it is important here to distinguish between photolytic and photocatalytic effects because the two reaction mechanisms may produce different byproducts.

**Phenol Adsorption**

It is important to quantify the extent of adsorption to the catalyst in the absence of UV to isolate what phenol and nDOC concentration changes may be due to oxidation. For this experiment, 100 mg of catalyst was agitated with 1 A current at 60 Hz signal frequency. The data indicate that phenol concentration and nDOC did not change over a period of 7 hours.

**Phenol and nDOC: Effect of Lamp Number and a Permanent Magnet**

Initial experiments employed 100 mg of the composite photocatalyst, 1 A current, and 60 Hz solenoid frequency. When the permanent magnet was present, the phenol concentration after 5 hours was not detected via GC analysis (Figure 5-1), while close to 70% of the nDOC remained (Figure 5-2). Without the permanent magnet (NPM) and with one 365 nm lamp (1L) the nDOC concentration decrease was less than the variation in replicate analysis of samples (Figure 5-2), but the phenol concentration at 7 hours decreased to 29% of its original value (Figure 5-1). Therefore, a large fraction of the phenol was simply being converted to byproducts. In order to increase the rate and efficiency of photocatalysis, two 365 nm lamps were added (i.e., for a total of 3 lamps or 24 W). Although the decrease in phenol concentration after 7 hours was approximately the same with and without the permanent magnet (Figure 5-1), the initial pseudo-first order rate constant for phenol oxidation was 3 times greater (0.80 min\(^{-1}\) vs. 0.27 min\(^{-1}\)) with the permanent magnet. Data for nDOC (Figure 5-2) indicated that after 7 hours, 0.6 mg/L C
remained with a permanent magnet whereas when it was not present during the experiment, 3.1 mg/L was still remaining. The improvement in photocatalytic degradation from the fixed magnet is believed to be due to its ability to counteract gravity with a magnetic field gradient. Under the influence of this magnetic field gradient, the catalyst was more effectively spread throughout the reactor thus increasing its exposure to UV.

Figure 5-1. Comparison of number of UV lamps and presence of permanent magnet for degradation of phenol in the MAPR (WPM = with permanent magnet, NPM = no permanent magnet, 1L = 1-365 nm lamp, 3L = 3-365 nm lamps).

Figure 5-2. Non-purgeable dissolved organic carbon concentration as a function of number of lamps and presence of permanent magnet in the MAPR (WPM = with permanent magnet, NPM = no permanent magnet, 1L = 1-365 nm lamp, 3L = 3-365 nm lamps).
Catalyst Mass Optimization

The quantity of catalyst in the reactor was optimized for phenol and nDOC reduction using 2 hours of exposure with one 365 nm lamp. With a 365 nm lamp, which was shown earlier not to cause photolytic mineralization, the phenol removal was greater than nDOC removal for the entire range of catalyst mass (Figure 5-3). This was most likely an indication that several oxidation byproducts remain in solution after 2 hours of irradiation. The trend in phenol removal showed a slight increase as mass increased up to 400 mg and remained constant at higher mass loadings. The nDOC trend demonstrated an increase in removal with mass until 400 mg where there was a peak and then a descent as the mass increased further. This optima is believed to be the result of two phenomenon. An increase in phenol and nDOC removal is expected with an increase in TiO₂ concentration (as a function of catalyst mass increasing) due to an increase in the number of reaction sites and thus the quantity of hydroxyl radicals produced. A competing phenomenon is expected as the catalyst concentration reaches a level where the UV light is blocked, reducing the proportion of catalyst receiving photons of sufficient energy to generate hydroxyl radicals [78].
Figure 5-3. Catalyst mass effect on phenol photocatalysis in the MAPR (Normalized Concentration Decrease $= \frac{C_0 - C}{C_0}$).

**Solenoid Frequency Optimization**

The sinusoidal signal frequency fed to the solenoid affected the rate at which the magnetic field gradient, and thus force on the catalyst, alternated direction [72]. This oscillating force caused the catalyst to move within the reactor thus increasing the mass transfer of phenol and photodegradation byproducts to the TiO$_2$ on the surface of the composite catalyst. For this experiment, each data point represents a variation in frequency where the current was fixed at 1.25 A, and 100 mg of catalyst was irradiated for 2 hours with three 365 nm UV lamps. The data demonstrate that nDOC is eliminated most effectively between 20 and 80 Hz where the variation in removal over the frequency range is less than the sample RSD from the methods section (Figure 5-4). The elimination of oxidation byproducts, which is indicated by nDOC decreases as frequency increases beyond 80 Hz. This effect may be due to a decrease in the ability of the catalyst to effectively respond to changes in the magnetic field at higher frequencies. As the catalyst motion response is diminished, there will be a corresponding decrease in mass transfer and thus photocatalytic degradation. In contrast to the nDOC result, phenol removal showed a less dramatic decrease at higher frequencies. This discrepancy in oxidation byproduct removal and phenol removal may be due to a higher mass transfer dependence of byproduct oxidation over phenol oxidation. This would mean that the first few steps of phenol oxidation to hydroxylated compounds [79] occur at the same rate for higher frequencies and lower mass transfer, but subsequent reaction steps such as loss of aromaticity and mineralization occur at a slower rate because they may be more dependent upon mass transfer. Since the catalyst is heat treated to 500 °C during synthesis, an increase in hydrophobicity is likely to occur due to
dehydroxylation of the silanol groups [80], thus decreasing adsorption of polar compounds (compounds with more hydroxyl groups such as the oxidation byproducts). Finally, at 0 Hz (a control with the alternating magnetic field absent and permanent magnet present), the least photocatalysis was observed confirming that the presence of an alternating magnetic field enhanced photocatalysis.

Figure 5-4. Solenoid signal frequency effect on phenol photocatalysis in the MAPR (Normalized Concentration Decrease = \( \frac{C_0 - C}{C_0} \)).

**Solenoid Current Optimization**

The magnetic flux of the alternating magnetic field generated by the solenoid is directly proportional to current according to the Biot-Savart law [72]. As such, the increase in magnetic flux is expected to correlate with an increase in catalyst motion and thus mass transfer of phenol to catalyst. The experimental data agreed with this expected increase from 0 to 1 A; there was a corresponding increase in both reduction of nDOC and phenol concentration (Figure 5-5). As seen in previous experiments, the normalized concentration decrease for phenol was higher than nDOC for all conditions except 0 A. This is believed to be the result of organic oxidation byproducts. As the current increased above 1 A, the photocatalytic degradation remained
constant. This change in the trend indicates that the system performs optimally with 1 A current as further increases in current increase energy requirements and heat generation without increasing the extent of photocatalytic oxidation.

Figure 5-5. Solenoid signal current effect on photocatalysis (Normalized Concentration Decrease $= \frac{C_0 - C}{C_0}$).
For long-term space missions, the MAPR provided a technique for reducing non-purgeable dissolved organic carbon in the air evaporation system effluent. In addition, magnetic photocatalyst characterization provided information about morphology, primary particle size, and the influence of a magnetic field on the formation of assembled structures.

**Photocatalyst Characterization**

It is readily apparent from visual observation of the MAPR when the magnetic field was present that assembled structures continually formed and broke apart. It was not, however, known what these structures looked like on a micron scale. The assembled structures of the catalyst determined how much of the total available surface area could be exposed to UV, and how much was readily accessible for contaminant adsorption. The structures formed were due to forces applied by both the static and oscillating components of the magnetic field in addition to the interparticle force due to the remanent magnetization. According to observation, the static field tended to induce very ordered needle-like structures. Similarly, observation indicated that the oscillating magnetic field caused the assembled needle-like structures to break and re-form. The rate of this breaking and re-formation was apparently determined by the oscillating frequency, with higher frequencies resulting in higher rates of formation and subsequent break up. By observing the structures with SEM before and after exposure to the magnetic field, it was possible to see the development of structures on a micron scale that are not apparent with visual observation. In the SEM images before exposure to the magnetic field (Figure 6-1), the catalyst appeared relatively planar and randomly distributed. In contrast, in the image taken after the magnetic field exposure the catalyst appeared to form a hollow assembled structure about 20 µm in diameter that comes out of the plane (Figure 6-2). Since this structure appeared to be only a
few catalyst particles in thickness, it would most likely not interfere with absorption of UV light or adsorption of contaminants with respect to much larger structures. Also, its hollow nature would provide additional available surface area for adsorption, which could subsequently be oxidized as the structures break and re-form.

XRD of the TiO₂ powder allowed an assessment of both the crystallinity and particle size. For the highest photoactivity, it is important that the TiO₂ be crystalline and primarily anatase phase because it has a higher photoactivity than rutile or other crystalline phases. Previous authors have found that TiO₂ coatings using organic precursors without adding acid to catalyze the particle formation produce primarily amorphous structures [25]. Since the method used for the TiO₂ synthesis in this work was the result of an organic precursor (titanium n-butoxide) and did not utilize acid, it was expected that the resulting coating would be primarily amorphous. From Figure 6-3 A, the XRD shows very broad low peaks that are not much higher than the noise. This type of XRD output is associated with materials that do not have significant crystallinity, providing evidence for confirmation of the contention that the coating would initially be amorphous. To improve photoactivity, the double coating was heat-treated with a 5°C ramp to 500°C where it was held for 1 hour. As can be see in Figure 6-3b, the XRD for the heat-treated material has much higher and narrower peaks, which indicates an increase in crystallinity. Since the most intense anatase peak was at 25.4° 2θ, it was used to estimate the crystalline size using the Scherrer equation (eq. 6-1)

\[
t = \frac{k\lambda}{B \times \cos \theta}
\]

Using a shape factor (k) of 0.9, λ of 0.1541 nm, B of 0.0140 radian 2θ of 25.4°, the particle size was estimated to be 10.1 nm.
Figure 6-1. Scanning electron microscope image of magnetic photocatalyst (not exposed to magnetic field).

The XRD analysis indicated that the double coating method and variation lowering the water to alkoxide ratio (130:1 to 110:1) from previous work increased the particle size from 5.9 nm [42]. Since the nanoparticles from the previous coating may have acted as nucleation sites during the double coating procedure, it was important to assess any changes in crystallinity or particle size. This increase in particle size likely decreased the specific surface area of the photocatalyst, yet may have avoided quantum confinement effects observed in smaller TiO$_2$ nanoparticles that can lead to a decrease in photoactivity due to bandgap widening [9].
Figure 6-2. Scanning electron microscope image of magnetic photocatalyst (exposed to magnetic field).

Figure 6-3. X-ray diffraction pattern of synthesized titanium dioxide before (A) and after (B) heat treatment.
Magnetic Field and Catalyst Mass Impact on Extent of Photocatalytic Oxidation of AES Ersatz

The magnetic field was used to control the photocatalyst motion and distribution in the reactor. By modifying the characteristics of the magnetic field, it was possible to assess their impact on the extent of photocatalysis. The frequency of the oscillating magnetic field was controlled by modifying the frequency output of the function generator while maintaining a consistent alternating current (1 A) to the solenoid array (Figure 6-4). Since the oscillating magnetic field is applying a force on the particles, it is hypothesized that the rate of change or frequency of the oscillation would determine both the distance traveled and the velocity of the photocatalyst particles in solution. The data indicate that there was an increase in performance as estimated by normalized concentration decrease between 0 and 40 Hz where the highest peak occurred. The decrease above 40 Hz was not observed in a previous study using phenol [19] but similar frequency-related performance behavior occurred in work focused on dry particle coating by Ramlakhan [21]. This work used oscillating magnetic fields to agitate magnetic particles, which induced dry impaction coating. Above 80 Hz, there was a slow decrease in performance, yet it was not as dramatic as the previous study with phenol. There are several possibilities for explaining this change in performance with respect to the phenol work. First, the nDOC in AES ersatz is comprised primarily (74%) of dextran, a polymer, but also has inorganic compounds that were not present in the previous work. Also, the light source in this work was 254 nm as opposed to the 365 nm source used previously. The decrease in wavelength corresponds to an increase in the energy per photon, which can induce photolysis of certain compounds and also production of ozone that were shown to either not be present or to not have an impact with the 365 nm light sources.
Figure 6-4. Normalized concentration decrease vs. oscillating magnetic field frequency.

The photocatalyst mass determined the number of potential photoactive reaction sites available and the light distribution within the reactor. Since the core material was barium ferrite, which absorbs UV light, an increase in catalyst mass corresponded to an increase in the light absorption by the magnetic core, which would have a detrimental effect on the extent of photocatalysis. In contrast, the increase in reaction sites would have a potentially beneficial effect on photocatalytic degradation, given that these sites were actually irradiated with UV. By incorporating both of these trends, it is clear that for most photocatalytic reactors there should be an optimal catalyst mass whereby the number of reaction sites is maximized while the light absorbing effect is controlled. In the experiments performed to assess this effect, evidence to support these hypotheses was found (Figure 6-5). The normalized concentration decrease for 50 mg and 100 mg catalyst mass loadings were found to be within the relative standard deviation (RSD) of replicate analysis of samples. The reason for this equality may be due to an increase in photolytic and ozone effects at 50 mg because of the lower light absorption by the photocatalyst.
cores and an increase in photoactive sites to compensate for the greater light absorbing effect at 100 mg. The steady increase in the extent of photocatalysis continued with increase in catalyst mass continued until 400 mg where it reached a peak. As the mass increased further, the extent of photocatalysis decreased, which was consistent with the initial hypothesis.

![Graph](image)

Figure 6-5. Normalized concentration decrease vs. catalyst mass.

The current fed to the solenoid provided an oscillating force on the particles and was critical to improving mass transfer of pollutants to the photocatalyst with respect to stationary particles. The Biot-Savart law suggested that the force exerted on the particles is proportional to the current in the solenoid. For long-term space missions, the implication of increasing current to an advanced life support system is disadvantageous because it will likely be at the expense of other support systems or possibly research activities. It is critical that the power used by these systems is adequate to provide satisfactory performance, but not greater than necessary to conserve power. In other work [19], it was found that there was an optimal operating current of 1 A and further increases in current did not lead to corresponding increases in photocatalytic
performance. A similar trend was found with an increase in the extent of photocatalysis between 0 and 1 A, while further increases in current did not have an impact greater the sample analysis RSD (Figure 6-6).

Figure 6-6. Normalized concentration decrease vs. oscillating magnetic field current.
CHAPTER 7
PHOTOCAT EXPERIMENTS USING GRAYWATER FORMULA

While previous chapters involved a MAPR, the work in this chapter explored the use of a Photocat® or slurry-based photocatalytic reactor with slurry separation device for oxidation of organic contaminants. Instead of using the air evaporation system effluent, the Photocat® was assessed for its ability to act as a post-processor after a biological water processor. The influence of bicarbonates on kinetic photocatalytic degradation rates was explored.

Biological Water Processor Effluent

The biological water processor effluent had an initial nDOC of approximately 51 ± 5.1 mg/L C. The treatment objective is to meet or exceed NASA specification of 500 μg/L C nDOC for potable water. Ammonium bicarbonate had a concentration of 724 mg/L in the BWP. The Photo-Cat® was operated with and without ammonium bicarbonate to determine the impact of high alkalinity on photocatalysis.

The Photo-Cat® ran in batch mode with all contaminants and TiO₂ circulating through the system at time zero when the UV lamps were turned on. The data are plotted as nDOC vs. kWh/m³ or cumulative energy per unit volume treated. The kWh/m³ value for each data point was calculated by dividing the product of total UV lamp power (the sum of all 75 watt bulbs used) and cumulative time by the total volume of contaminated water in the system. This power is necessary for testing with UV bulbs however; the flight hardware will use solar UV significantly reducing the power requirements and ultimately the ESM. The system was tested with and without ammonium bicarbonate to determine its effect on the rate of nDOC disappearance. With ammonium bicarbonate included in the BWP formula the endpoint nDOC was 0.390 mg/L C. Without ammonium bicarbonate, the endpoint is 0.360 mg/L C (Figure 7-1).
If the same data are plotted with a logarithmic scale on the nDOC axis, the change in pseudo-first order rate constant becomes more clear (Figure 7-2). The reaction rate for nDOC disappearance in the biological effluent without ammonium bicarbonate is approximately 40% greater than when it is present, or 0.0014 min\(^{-1}\) and 0.0010 min\(^{-1}\) respectively (Figure 7-3).

Figure 7-1. Biological water processor effluent nDOC vs. kWh/m\(^3\).

Figure 7-2. Biological water processor effluent nDOC vs. kWh/m\(^3\) (natural log scale).
Figure 7-3. Biological water processor effluent nDOC vs. kWh/m³ to 3500 min (natural log scale).

Figure 7-4. Low-flow nDOC data for simulated graywater without bicarbonate.

Figure 7-5. Low-flow nDOC data for simulated graywater with bicarbonate.
Figure 7-6. Low-flow nDOC data for biological water processor effluent with bicarbonate.

**Graywater Testing**

Although batch testing provides greater reaction kinetics than single pass testing, a single-pass, low flow mode was used for testing graywater. The purpose of treating the graywater in a low flow mode is to destroy the surfactant property of the shampoo so that it does not build up in the system. This is in contrast to the batch mode testing where the surfactant concentration is at a maximum at time 0. In this type of experiment, an equilibrium effluent nDOC is obtained once the system is at steady-state. This value varied by input water type and presence of ammonium bicarbonate. For the simulated graywater without ammonium bicarbonate, at a flow rate of 4.4 mL/min (initial TOC of 447 mg/L) the nDOC from the Photo-Cat discharge increased from 0 to 16 mg/L C in approximately 2500 minutes at which time it was at steady state. (Figure 7-4). In contrast, when ammonium bicarbonate is present in the graywater the nDOC increased at a slightly faster rate until it reached a final concentration of 34 mg/L C (Figure 7-5) due to the hydroxyl radical scavenging by the bicarbonate ion [81]. As a comparison, the BWP with ammonium bicarbonate had a similar linear increase in nDOC, but its final value is only 2.5 mg/L C (Figure 7-6) due to the lower feed concentration of 50ppm nDOC.

More testing is required to further quantify single-pass destruction of organic contaminants in graywater. Additional treatment is required to reduce the TOC of the graywater below
0.5ppm. It is also recommended that other types of soaps/shampoo materials be investigated for photocatalytic efficiency including NASA Whole Body Shower Soap (Geropon TC-42). Choosing a soap that mineralizes readily in the system is desirable.

**Size Requirement Estimation**

Given the UV output of the Photocat® system used for this paper and an estimate of the UV flux on the moon it is possible to estimate the size of a solar collector of similar flux. According to the manufacturer, each lamp provides approximately 25 W UV radiation to the slurry or 200 W total. In addition, if we assume that the solar UV radiation on the moon is primarily below 380 nm as is necessary for photocatalytic oxidation using titanium dioxide there would be a flux of 101 W/m² [82]. Using both of these values and assuming the quantum efficiency of the lunar photocatalytic reactor is equivalent to its terrestrial counterpart, the lunar solar collector would need to be approximately 1.98 m².
CHAPTER 8
PHOTOCATALYST COMPARISON USING THE PHOTOCAT REACTOR

In the previous chapter Degussa P25 was used as a photocatalyst. Degussa P25 is a benchmark material that is frequently used in literature to establish improvements due to variations in photocatalyst composition due to incorporation of a support material or doping with carbon, nitrogen, or metals. This chapter focused on the performance of a silica-titania composite with respect to Degussa P25.

Composite Characterization

The silica-titania composite was synthesized by impregnating a mesoporous silica gel with Degussa P25 and its morphological properties were elucidated by examining secondary electron SEM images. In Figure 8-1 it is clear that the photocatalyst that had been ground and sieved was composed of larger 45-90 µm particles whose surface is clearly covered by much smaller particles. The smaller particles provide an incomplete and sporadic coverage of the surface, which may be the result of van der Waals forces between the smaller particles and the larger plate-like structures formed during the grinding and sieving process.

SEM secondary electron images do not provide any direct information about composition; however, if one examines the backscatter electrons it is possible to see average atomic mass contrast. Hence, if a material is composed of two elements of sufficiently different atomic number and sufficiently large enough domain size, it is possible to distinguish between regions of each element. While secondary electrons are liberated from the specimen, backscatter electrons are the original beam electrons that are deflected back to the polepiece where a solid-state detector is located. The amount of energy which the electrons possess is a function of atomic mass and can be measured by the solid-state detector.
Figure 8-2 is the result of imaging the 45-90 µm composite photocatalyst using secondary electrons (top) and backscatter electrons (bottom). The secondary electron image shows some charging behavior at both edge sites and in particular sites on the surface of a few of the particles. This behavior was expected due to the non-conductive nature of the silica in the photocatalyst. The same type of partial coverage of the larger plate-like structures by the smaller particles seen on the higher magnification image in Figure 8-1 is evident. The backscatter image clearly showed regions of varying intensity electron energy indicating regions composed of different average atomic mass elements. Since the higher atomic number elements absorb less of the beam electron energy, the portions of the image that are brighter indicate a higher average atomic mass region. Based on the composite photocatalyst synthesis method, it is clear that the elements present should include titanium, silicon, and oxygen with atomic masses of 47.87, 28.09, and 16.00 g/mol respectively. From the atomic mass data, it was clear that if the contrast is sufficient, regions rich in titanium dioxide should appear brightest. An examination of the backscatter image indicates that there are several bright spots on the surface of the particle that
are approximately 1 µm in diameter. To further verify whether the spots were indeed an
indication of titanium dioxide an EDS spectra was obtained for both one of the bright spots and a
darker region nearby. Figure 8-3 shows the spectra of the region indicated by the circle in Figure
8-2, which is a relatively dark spot whereas the spectra in Figure 8-4 are indicated by the square,
which is a relatively bright spot. A comparison of the two spectra showed that the peak for the
alpha energy level for titanium is less than 500 for the dark region; it is greater than 1000 for the
bright region. This increase in titanium indicated by EDS is further evidence that the regions
indicated are titanium dioxide. Silica is likely present in both spectra because the interaction
volume includes a portion of the silica matrix for both regions.

It is important to understand how the titanium dioxide is distributed within the composite
photocatalyst for optimization purposes. If the titanium dioxide forms prohibitively large
agglomerates, it is possible that the reactive sites near the center of these agglomerates will be
physically inaccessible to either UV light or contaminants. Previous work with titanium dioxide
slurries has shown that they also form agglomerates in water such that the approximately 30 nm
primary particles of Degussa P25 will form agglomerates of about 1.34 µm [81]. The backscatter
electron images provide evidence supporting the formation of agglomerates, but quantitative data
concerning particle size is not easily determined due to the qualitative nature of the backscatter
technique and the inability to determine precise size measurements using SEM.
Figure 8-2: Secondary electron image and backscatter complement of 45-90 µm silica-titania composite photocatalyst surface.

Figure 8-3. Energy dispersive x-ray spectroscopy of 45-90 µm silica-titania composite photocatalyst surface (circle region).

Figure 8-4. Energy dispersive x-ray spectroscopy of 45-90 µm silica-titania composite photocatalyst surface (square region).
**Biological Water Processor Effluent**

The biological water processor effluent was a simulated formula that is intended to replicate the probable contaminants leaving a biological water processor. The formula contains polymers, volatile organic carbon compounds, and inorganic salts. Of the constituents, dextran, a high molecular weight polymer (15k-20k g/mol) contributes almost 63% of the organic carbon content of the ersatz water. The primary treatment objective is to meet or exceed NASA specification of 0.5 mg/L nDOC for potable water.

![Normalized nDOC vs. time](image)

Figure 8-5. Biological water processor effluent normalized nDOC vs. time (equal total mass basis).

As a primary comparison, 10 grams of composite photocatalyst and Degussa P25 respectively were added to the Photocat after preparation of the BWP ersatz. It is readily apparent from Figure 8-5 that the decrease in nDOC happens at a faster rate and reaches a lower endpoint using the Degussa P25 with respect to the composite photocatalyst. Additionally, the samples from the experiment using the composite photocatalyst contained small opaque particles.
Figure 8-6. Biological water processor effluent pseudo-first order rate models. (equal total mass basis).

The reaction rate is important because it will affect the reactor volume necessary to provide a particular conversion. If the reactor is designed based on a plug flow model, which is reasonable given the proposed reactor design of a tubular reactor that is exposed to solar UV, then the reactor volume is inversely proportional to the reaction rate [83]. To quantify the difference in reaction rates, a pseudo-first order initial rate constant was determined for both experiments as seen in Figure 8-6. The slope of the line indicates the reaction rate determined by the model. In this case, the Degussa P25 has a reaction rate that is over three times that of the composite photocatalyst. It is important to note that the composite photocatalyst was composed of approximately 70% silica and 30% titanium dioxide by mass. This means that the Degussa P25 had over three times the mass of TiO₂ for the experiment shown in Figure 8-6. The increased mass also corresponded to an increase in potential reactive sites for oxidation of organic material and may have contributed to the discrepancy in pseudo-first order initial rate constant.

One method for estimating changes in aromatic carbon content is to measure the spectrophotometric absorbance of a solution at 254 nm. For the BWP ersatz, dextran, which is the primary contributor to nDOC is composed of aromatic monomer units that will absorb light at 254 nm. As dextran was removed from the effluent by adsorption or oxidation, the absorbance
should also decrease given that no reactions are taking place which might produce UV absorbing species. The UV-254 data for the equal total mass basis comparison shown in Figure 8-7 illustrates a more similar trend for both photocatalyst types than that in Figure 8-5. A plausible explanation is that the dextran is not being oxidized as readily by the composite as Degussa P25, but rather is being adsorbed and possibly interfering with the subsequent photocatalytic oxidation of organic material.

![Figure 8-7. Biological water processor effluent UV-254 vs. time (equal total mass basis).](image)

As a method to determine the efficacy of the hypothesis that the deficiency in reaction sites was a cause for the diminished reaction rate for the composite, an experiment was performed using an equal mass basis of TiO₂ (Figure 8-8). In contrast to the earlier experiment with equal total mass basis, the reaction rates were quite similar for the composite and Degussa P25. In fact, the estimated pseudo-first order reaction rate for the composite is 24% greater than for the Degussa P25 (Figure 8-9), which provides evidence to support the contention that providing an equal number of potential reaction sites would improve the reaction rate. A trend similar to that of the equal total mass comparison for the UV-254 absorbance can be seen in Figure 8-10. Since the UV-254 and the nDOC trends were similar for both photocatalysts, it is likely that the proposed oxidation interference effect observed in the previous experiment is not taking place. It
is possible that the increased ratio of reaction sites to dextran concentration for the equal mass TiO$_2$ basis is sufficient to prevent any significant interference effects.

Figure 8-8. Biological water processor effluent normalized nDOC vs. time (equal mass TiO$_2$ basis).

Figure 8-9. Biological water processor effluent pseudo-first order rate models (equal mass TiO$_2$ basis).

Figure 8-10. Biological water processor effluent UV-254 vs. time (equal mass TiO$_2$ basis).
While the BWP ersatz has an nDOC of 51 mg/L, the AES ersatz is only 9.5 mg/L. However, it also contains inorganic contaminants including ammonium carbonate, which may have a similar detrimental effect on photocatalysis as demonstrated in previous work [14]. The primary contribution to nDOC in AES is dextran (74%) as it was in the BWP, yet the total dextran concentration was 15 mg/L whereas it was 98 mg/L for BWP. This decreased concentration was expected to have an influence on the reaction rate comparison if the interference effect was occurring. Figure 8-11 shows the result of the equal mass TiO₂ basis experiment, which indicates that there is a significant improvement in the extent of photocatalysis over the experimental time period shown. Additionally, Figure 8-12 shows the result of pseudo-first order initial rate regression modeling. The modeling suggested that the reaction rate is almost twice as high for the composite as for the Degussa P25. This increase in reaction rate was expected due to the synergistic effect of the high specific surface area adsorbent combined with TiO₂ that may have been obfuscated by the interference effect due to the dextran adsorption.

![Graph](image)

Figure 8-11. Air evaporation system normalized nDOC vs. time (equal mass TiO₂ basis).
Figure 8-12. Air evaporation system pseudo-first order rate models (equal mass TiO$_2$ basis).
In contrast to previous work, this chapter focused on how the synthesis technique of a co-precipitated composite material impacted performance for oxidation of a textile dye. It explored the influence of elemental composition and heat treatment including calcination and hydrothermal techniques. Specifically, the influence of particle size, zeta potential and bandgap energy estimates were explored for their influence on photocatalytic oxidation and adsorption.

**Impact of Composition**

For hydrothermally prepared samples, the trend for the extent of photocatalytic oxidation shows that the highest activity occurs in the samples that are near 100% ZnO or TiO$_2$ (Figures 9-1 and 9-2). Two parameters were chosen to assess the progress of photocatalytic oxidation: dye absorbance and non-purgeable dissolved organic carbon (nDOC). Absorbance was measured at 538 nm, which is an indication of color. Since oxidative attack of the azo bond is preferential, it is important to also follow the oxidation byproducts with non-purgeable dissolved organic carbon as these byproducts may be toxic even if the solution appears to be clear. Since it was demonstrated earlier that photolytic oxidation of the dye was negligible, it is thought that the primary mechanism for mineralization is photocatalytic oxidation. Bleaching of the dye as measured by absorbance changes was complete in the 5, 95 and 100% TiO$_2$ samples of both heat treatments, and the 90% TiO$_2$ hydrothermal treatment. The highest extent of photocatalytic oxidation (PCO) was for the calcined sample with 100% TiO$_2$, which still contained 30% of the original organic carbon, presumably as oxidation byproducts. For these samples with 100% absorbance decrease, kinetic information could not be inferred, yet information about the extent of mineralization as determined by non-purgeable dissolved organic carbon was used for
comparison. Additionally, the photocatalytic activity was negligible for samples between 10 and 70% TiO₂.

**Impact of Adsorption**

The relationship between adsorption capacity and photocatalysis is complex and there is not always a clear correlation between the two phenomena for materials with photocatalytic activity. For instance, previous work with activated carbon demonstrated an increase in adsorption of methylene blue dye on activated carbon that is thought to be due to a change in electron distribution in the dye molecule, which increases adsorption to the aromatic activated carbon basal planes [74]. The photocatalyst prepared using a calcination technique demonstrated a trend of low adsorption and low photocatalytic oxidation between 20 and 90% TiO₂ (Figure 9-3). It was also interesting to note that the adsorption for the calcined sample roughly followed the zeta potential trend (Figure 9-4) and was highest at 95% TiO₂ whereas for hydrothermally prepared it was relatively constant between 5 and 95%. These trends demonstrate that the higher adsorption capacity of the hydrothermally prepared materials did not translate to higher PCO.

**Influence of Zeta Potential**

Since the Procion Red is an anionic dye and its adsorption and photocatalytic activity have been proven to be related to the pH of solution for TiO₂, [84, 85] it was expected that a similar trend might be seen for the mixed oxide materials observed in this work. Electrostatic repulsion by the negatively charged photocatalyst at a given pH has a tendency to prevent close approach of dye molecules to the reaction sites on the particle surface. Since the PCO reactions occur at or near the surface of the photocatalyst because of the high reactivity of hydroxyl radicals and hence short diffusion distance, it is believed that phenomena which prevent this close approach such as a boundary layer diffusion resistance[19] or electrostatic repulsion [86] have a tendency to reduce PCO. Figure 9-4 shows the trend for zeta potential for the various mixed oxide
photocatalysts. Both photocatalysts demonstrate high negative zeta potentials for compositions between 20 and 70% TiO₂.

Figure 9-1. Comparison of photocatalytic oxidation for calcined and hydrothermally prepared ZnO-TiO₂ photocatalyst of varying composition.

Figure 9-2. Comparison of color changes for calcined and hydrothermally prepared ZnO-TiO₂ photocatalyst of varying composition.
This region also corresponded to relatively low adsorption and PCO for calcined photocatalysts as was expected due to electrostatic repulsion. Additionally, the higher performing photocatalysts had near neutral zeta potential, which corresponds to approximately equal quantities of positively and negatively charged sites on the surface. For calcined samples, the zeta potential was near neutral for the 0% TiO₂ samples, but was slightly negative for the hydrothermal sample, which may explain the higher PCO for the calcined sample. For the 95 and 100% TiO₂ samples, zeta potential was similar for both preparation methods and approximately neutral, which provided a more ideal environment for PCO.

Figure 9-3. Comparison of procion red MX-5B adsorption on ZnO-TiO₂ photocatalyst prepared by calcination and hydrothermal heat treatment (normalized concentration decrease $\frac{C_0 - C}{C_0}$).
Specific Surface Area

Specific surface area is often a useful tool for assessing the photocatalytic activity of a material since the reactions likely take place at or near the surface. Higher specific surface areas correspond to more reaction sites available given a constant surface density and quality of reaction sites. This trend is important, but since other variables such as zeta potential, quantum effects, and surface defects can also be a function of particle size for nanometer sized particles, surface area is not often an ultimate determinant of PCO. From the data that are shown in Figure 9-5, it is apparent that the highest specific surface area materials are the hydrothermally prepared photocatalyst with 70% TiO₂. Interestingly, this does not correspond to the highest photocatalytic activities or adsorption, which may be due in part to the highly negative zeta potential. Also, those photocatalysts with the highest photocatalytic activity for hydrothermal and calcined have
specific surface areas of 30.2 and 37.6 m²/g respectively, which was in the middle range of all specific surface areas.

Figure 9-5. Comparison of BET specific surface area for of ZnO-TiO₂ photocatalyst prepared by hydrothermal and calcination technique with varying composition.

Figure 9-6. Comparison of XRD patterns of ZnO-TiO₂ photocatalysts prepared using a calcination technique with varying composition.
X-ray Diffraction

X-ray diffraction can provide information about the crystalline structure, composition, and particle size of materials. For photocatalysis, this is important because the crystalline structure and particle size have been proven to have a strong influence on photocatalytic activity [9]. Researchers have demonstrated that calcination of TiO₂ produced using alkoxide precursors can generate anatase or at higher temperatures rutile crystalline phase [9]. The anatase phase has a higher photocatalytic activity and sintering of TiO₂ produces larger particle size rutile, which has a lower photocatalytic activity than anatase. This is in contrast to Degussa P25 where there is apparently a synergy between the anatase and smaller rutile phase crystals produced by flame synthesis [87]. Figures 9-6 and 9-7 show the XRD patterns for several ZnO-TiO₂ samples. The Figures show a similar pattern for both 5% TiO₂ samples, with no strong indication of typical anatase or rutile TiO₂ peaks. The pure TiO₂ samples both have anatase 101 plane peaks at about 25.4° 2θ, yet no rutile 100 plane peaks indicating that only the anatase crystalline phase is present. Using the Scherrer equation (eq. 9-1), particle size (t) can be estimated based on peak width (B). Given a shape factor (k) of 0.9, λ (wavelength of the CuKα₁ x-ray source) of 0.1541 nm, B (full peak width at half maximum corrected for instrumental broadening) of 0.0065 and 0.0090 radian for pure TiO₂ calcined and hydrothermally prepared samples respectively, and 2θ (anatase 101 peak) of 25.4°,

\[ t = \frac{k \lambda}{B \times \cos \theta} \]  

(9-1)

The Scherrer equation indicates that particle sizes for the calcined and hydrothermally treated TiO₂ were 21.1 and 16.0 nm respectively. The larger particle size indicates that sintering has taken place for the calcined TiO₂, which may explain its more intense 101 peak. Either this increase in particle size or an increase in crystallinity is believed to provide a reason for the
higher PCO for the calcined photocatalyst. The 5H and 5C samples show characteristic peaks of ZnO at 31.5, 34.3, 36.1, 47.3, 56.0, 62.7, and 67.6 corresponding to (100), (002), (101), (102), (110), (103), and (112) planes respectively. Even though these samples had 5% TiO₂, they showed no evidence of the characteristic peaks of either anatase or rutile crystalline phases.

Figure 9-7. Comparison of XRD patterns of ZnO-TiO₂ photocatalysts prepared using a hydrothermal technique with varying composition.

Figure 9-8. Modified Kubelka-Munk spectra for calcined ZnO-TiO₂ photocatalyst.
Figure 9-9. Modified Kubelka-Munk spectra for hydrothermal ZnO-TiO$_2$ photocatalyst.

**Diffuse Reflectance**

Optical properties of photocatalyst materials can have a strong influence on performance. For TiO$_2$, the relationship between particle size, bandgap energy and performance is well documented [88]. Particle size increases lead to decreases in specific surface area and decrease in bandgap energy. For the ZnO-TiO$_2$ composites explored in this work, bandgap energy was estimated with the Kubelka-Munk method using diffuse reflectance spectra. The modified Kubelka-Munk function was determined using the equation 9-2

$$\frac{(1-R)^2}{2R} \times h\nu \left(1 - \frac{\nu}{\nu_0} \right)^{\frac{3}{2}}$$

(9-2)

where $R$ is the proportion reflected, $h$ is Planck’s constant, and $\nu$ is the frequency of light. Plots of this parameter were used to determine bandgap energy by determining a linear model for the linear portion of the absorption transition using least squares regression and extrapolating to zero at the corresponding photon energy [32]. The modified Kubelka-Munk spectra can be seen in Figures 9-8 and 9-9 and the corresponding bandgap energies can be seen in Figure 9-10. The
increase in bandgap energy for the hydrothermally prepared samples between 10 and 70% may
be due to an increase in atomic dispersion and decrease in primary particle size as indicated by
specific surface area. Additionally, the bandgap decrease for the calcined photocatalyst between
20 and 70% TiO₂ is thought to be the result of sintering-related particle size increases and
increased interaction between ZnO and TiO₂ induced by calcination.

Figure 9-10. Estimated bandgap for calcined and hydrothermally prepared ZnO-TiO₂
photocatalyst materials.
Prior chapters exploring magnetic photocatalysts used a modified conventional procedure to produce a magnetic photocatalyst with a specific surface area of nearly 30 m²/g. The work reported in this chapter was unique by incorporating a high surface area silica support for silica coated barium ferrite and titanium dioxide powder providing specific surface areas greater than 500 m²/g. Several parameters including synthesis technique and catalyst loading were shown to have an impact on photocatalytic oxidation.

**Characterization**

SEM images provide information about particle shape and distribution of material. For the HSAMP, it was critical to understand how changes in the synthesis method affected these textural properties. The silica coated barium ferrite demonstrates an irregular platelet like structure very similar to previous work [19] (Figure 10-1). Alternatively, the HSAMP morphology resembles broken pieces of glass that are approximately 45-90 μm in diameter that is likely a function of the material preparation including grinding and sieving. On a smaller scale, differences between the HSAMPS can be distinguished. HSAMP1, which was synthesized with a greater concentration of hydrofluoric acid, has a greater degree of porosity than the other HSAMP materials. For the purposes of this work, hydrofluoric acid was used to modify the pore structure. Hydrofluoric acid increased the rate of gelation and increased the solubility of silica. It is believed that this increased porosity is due to the combination of these two effects in presence of higher concentrations of HF. However, the resolution of the SEM images is not adequate to see small mesoporous structures.
To assess the distribution of smaller mesopores, which are thought to have an impact on the transport of contaminants for photocatalytic oxidation, nitrogen adsorption isotherms were used. First, BET specific surface area was estimated using 12 points for each material in the linear range between relative pressures of 0.05 and 0.30. The resulting specific surface areas were 374, 543, and 550 m$^2$/g for HSAMP1, 4, and 8 respectively. The higher surface area for the low hydrofluoric acid concentration was apparently due to small mesopores not evident in SEM imaging. To further identify this difference, pore size distributions were estimated using the BJH (Barret-Joyner-Halenda) methodology. The resulting pore size distribution can be seen in Figure 10-2. The median pore diameter appears to decrease with a decrease in hydrofluoric acid concentration. In addition, the total pore volume, which is indicated by the area under the curve,
decreases with a decrease in HF. These changes will have the functional impact of changing the adsorption and transport characteristics of the support material.

The magnetic properties of HSAMP are a critical and distinguishing characteristic of this work with respect to past work on supported photocatalysts. The raw magnetic material chosen for this work was barium ferrite due to its strong remanent magnetization and ferromagnetic properties. In the future, it is believed that these properties will allow the HSAMP to be used for an agitation/confinement reactor much like the MAPR. However, for this work, the magnetic properties were necessary for separation using a magnetic field. As explored in the introduction, magnetic materials are subject to oxidation during processing and use, which can diminish or eliminate their beneficial properties. Vibrating sample magnetometry (VSM) was used to compare the different HSAMP compositions. The process involves magnetizing and demagnetizing the material by varying the externally applied magnetic field and determining the impact of these fluctuations on the magnetic moment of the material. The barium ferrite’s high remanent magnetization can be seen in Figure 10-3 when its moment is close to 0.6 mAm^2 in the absence of an externally applied magnetic field. After processing, the remanent magnetization is diminished, which is primarily due to the decreased mass loading of barium ferrite in the composite. However, the wide hysteresis loop of the HSAMPs in Figure 10-4 indicates that the material maintained its ferromagnetic properties despite being exposed to the highly corrosive environment during the acid catalyzed sol-gel process.
Figure 10-2. Estimated pore size distribution estimate for HSAMP1, 4, and 8.

XRD provides evidence of changes in crystalline structure during synthesis, which is important for both the magnetic and photocatalytic properties of HSAMP (Figure 10-5). The particle size of titanium dioxide has a well established link to photocatalytic activity. Sintering during heat treatment and dissolution in the corrosive synthesis environment could potentially increase or decrease the particle size. Using the Scherrer equation (eq. 10-1), particle size ($t$) was estimated based on peak width ($B$). Given a shape factor ($k$) of 0.9, wavelength of the CuK$_{\alpha1}$ x-ray source ($\lambda$) of 0.1541 nm, $B$ (full peak width at half maximum corrected for instrumental broadening) of 0.004790, 0.004888, 0.005298, and 0.005444 radian obtained from data for Degussa P25, HSAMP8, HSAMP4, and HSAMP1 in Figure 10-4, and 2$\theta$ (anatase 101 peak) of 25.4º, particle sizes for each of the three samples were calculated.

$$ t = \frac{k\lambda}{B \times \cos \theta} \quad (10-1) $$
Using the analysis described, the Scherrer equation indicates that particle sizes for the Degussa P25 anatase crystalline phase decreases slightly from 30.0 for Degussa P25 to 29.4, 27.1, and 26.4 nm in the HSAMP8, 4, and 1 respectively. The smaller particle size in the composite material may be due to an increase in solubility of Ti during the synthesis process due to the presence of hydrofluoric and nitric acid. Since the decrease in particle size estimate is small this is not believed to have a significant adverse impact on photocatalytic oxidation, yet it could pose a problem if the acid concentration is increased beyond that used by these synthesis methods.

![Figure 10-3. Vibrating sample magnetometry hysteresis loop of barium ferrite.](image)
The catalyst mass loading is an important operational parameter for reactor design. The sensitivity to changes in photocatalyst concentration was previously explored for the MAPR [19]. In that work, the increase in photocatalyst mass corresponded to an increase in the extent of photocatalysis until an optima was reached and further increases resulted in declining reactor performance. A similar trend can be seen in Figure 10-6. As the photocatalyst mass was
increased from 30 to 120 mg, there was a dramatic increase in both the change in phenol and nDOC concentrations. However, above 240 mg, there was a steady decrease in both performance metrics. This decrease is believed to be associated with an unfavorable light distribution within the reactor. Understanding this phenomena is critical for effective scale-up and a fundamental understanding of photocatalytic reactor performance.

![Figure 10-6. X-ray diffraction patterns for HSAMP, Degussa P25 and barium ferrite.](image)

**Effect of Preparation Technique on Phenol and Non-Purgeable Organic Carbon Removal**

HSAMP synthesis allowed for a customizable pore size distribution by changing the concentration of HF. It was important to understand what impact these changes have on elimination of phenol and its oxidation byproducts measured as nDOC. For these experiments, the reaction was followed over time to determine the impact of material type on kinetics and the extent of photocatalysis. Complete oxidation, as evidenced by elimination of the nDOC, is most desirable since the oxidation byproducts are known to also have associated toxicity. As can be seen in Figure 10-7, the concentration of phenol decreases most rapidly for the Degussa P25 and was less rapid for HSAMP4 and HSAMP8 compositions. HSAMP1, with the lowest specific surface area, had the slowest removal of phenol and demonstrated almost linear or zero-order
kinetics. When looking at the change in normalized concentration of nDOC, the trend was somewhat similar initially to phenol removal (Figure 10-8). However, at longer times the extent of photocatalysis over 7 hours was more complete for HSAMPs than Degussa P25 alone. This results in fewer potentially toxic oxidation byproducts given the proposed photocatalytic oxidation mechanism (Figure 10-9).

Figure 10-7. Normalized phenol concentration as a function of time for HSAMP1,4, and 8.

Figure 10-8. Normalized nDOC concentration as a function of time for HSAMP1,4, and 8.
**Effect of Repeated Use**

In addition to the recoverability of the magnetic photocatalyst, it is also desirable for the material to be reused with its high photoactivity maintained. For the series of experiments seen in Figure 10-10, the magnetic photocatalyst was recovered using a permanent magnet, and immediately re-used after experimentation without rinsing, drying or cleaning the surface. Separate experiments determined the mass recovery is nearly 99% using the permanent magnet recovery technique. For the higher specific surface area materials, HSAMP4 and HSAMP8, there was nearly complete removal of nDOC during all 6 repeated UV exposure periods (Figure 10-10). However, for the lower surface area material, there was an increase in performance with repeated use. This may be related to adsorption of organic fragments during photocatalytic oxidation. The consistent performance shown for the HSAMPs would be advantageous for long-term use in a continuous flow reactor using an agitation confinement magnetic field in addition to recovery using a static magnetic field in a batch reactor.

![Diagram of proposed reaction mechanism](image)

Figure 10-9. Proposed reaction mechanism for photocatalytic oxidation of phenol.
Figure 10-10. Effect of repeated use on the extent of photocatalysis for HSAMP1,4 and 8.
CHAPTER 11
CONCLUSIONS

Contributions to Science

- Demonstrated the feasibility of reducing total organic carbon below the NASA specified limit of 0.5 ppm with a commercial photocatalytic reactor for water recovery during long-term space missions using ersatz water using both Degussa P25 and a silica-titania composite material

- Increased understanding of the influence of bicarbonates on reducing reaction rates during photocatalytic oxidation using a simulated graywater

- Developed a higher performance magnetic photocatalyst by modifying the coating technique

- Improved the magnetic field of the magnetically agitated photocatalytic reactor such that the reaction rate for disappearance of non-purgeable dissolved organic carbon was at least 2.5 times greater.

- Elucidated the influence of operational parameters on magnetically agitated photocatalytic reactor performance

- Increased understanding of ZnO-TiO₂ composite material composition and heat treatment influence on dye photocatalytic oxidation performance

- Developed a new high surface area magnetic photocatalyst that outperforms Degussa P25 for extent of reduction in non-purgeable dissolved organic carbon

Future Work

Future work should include

- Development of a modular MAPR reactor that can be easily scaled to a particular application

- Exploration of the distinction between magnetic and mechanical agitation and their influence on photocatalytic oxidation

- Further develop understanding of the superior performance of HSAMP

- Specifically exploring the influence of lamp conditions on MAPR and photocatalytic reactors in general including lamp temperature, age, and thermal history using spectral distribution

- Increasing understanding of competitive oxidation in photocatalytic reactors and whether specific conditions including pore size distribution of support or agitation conditions can
positively influence total mineralization or specific mineralization of highly toxic compounds

- Develop a MAPR for air-phase photocatalytic oxidation
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

William L. “Beau” Kostedt, IV was born in 1980 in St. Louis, Missouri. He lived in the central west end and attended New City School until 1990 when he moved to Clayton. He attended Clayton schools and graduated high school in 1998. He then began attending Trinity University in San Antonio where he studied chemical engineering and earned his bachelors degree in 2002. After graduation, he taught at Affton High School in St. Louis for two years before beginning graduate school at the University of Florida. At the University of Florida, he was advised by Dr. David Mazyck in the Department of Environmental Engineering Sciences where he performed research on photocatalysts and photocatalytic reactors.