Evaluation of a Photocatalytic Water Treatment Process

William L. Kostedt IV and David W. Mazyck

William L. Kostedt IV is a Ph.D. candidate in environmental engineering sciences at the University of Florida. David W. Mazyck is an associate professor of environmental engineering sciences at the University of Florida.

Drinking water supplies are becoming increasingly polluted with biological and chemical compounds by anthropogenic activity, including inadequate or improperly designed water and wastewater treatment facilities, industrial waste, and efforts to mediate other environmental problems. For example, in Milwaukee, a cryptosporidium outbreak affecting 403,000 people was implicated in the deaths of many immunocompromised residents [1].

Domestic industry is regulated by the Environmental Protection Agency (EPA) to prevent human and environmental exposure to known hazards when they are discharged into the water supply. 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 were discharged before regulations were established.

Endocrine disrupting compounds represent a class of chemicals that are difficult to eliminate using traditional biological or thermal oxidation, although their risk has been proven [2]. Another source of water pollution is created when methyl tert-butyl ether (MTBE) is added to gasoline to reduce air pollution. The addition of this compound to gasoline in areas with high population densities 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 robustness, or a technology's 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 is a pollution hazard itself [6].

Another option is thermal oxidation, which is very robust but energy intensive. Finally, biological treatment provides a low-energy approach to treat a variety of challenging pollutants [7].

The disadvantage is that the microbial community may be difficult to maintain and may not be effective in treating a water stream with large transient fluctuations in nutrients or pollutants. Furthermore, biological treatment may not be effective for certain compounds. [8]

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 the 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 its design for inclusion in municipal wastewater treatment, as well as industrial treatment of MTBE and cyanide. Calgon Carbon Corporation has licensed its UV systems to inactivate cryptosporidium, giardia, and other pathogenic microorganisms in three municipal water treatment plants. This successful commercial activity is indicative of an advanced oxidation industry that is able to provide unique solutions to challenging problems.

Another approach for advanced oxidation is to irradiate a wide bandgap semiconductor such as titanium dioxide (TiO^2) with UV light. The TiO^2 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 TiO^2 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 (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 TiO^2 that consists of 30 nm primary particles [13].

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. developed and patented a slurry separation device that solves this problem and applied the technology to military and industrial markets [14].

Immobilization of the TiO^2 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 TiO^2 on a high specific surface area substrate such as amorphous silica prepared using an acid catalyzed sol-gel procedure [15].

To combine the advantages of the slurry-based and immobilized photocatalytic systems, a magnetic photocatalyst has been used in the past [16-17]. The magnetic photocatalyst is synthesized by coating small magnetic particles (nm or µm) first with silica (SiO^2) and then with TiO^2.

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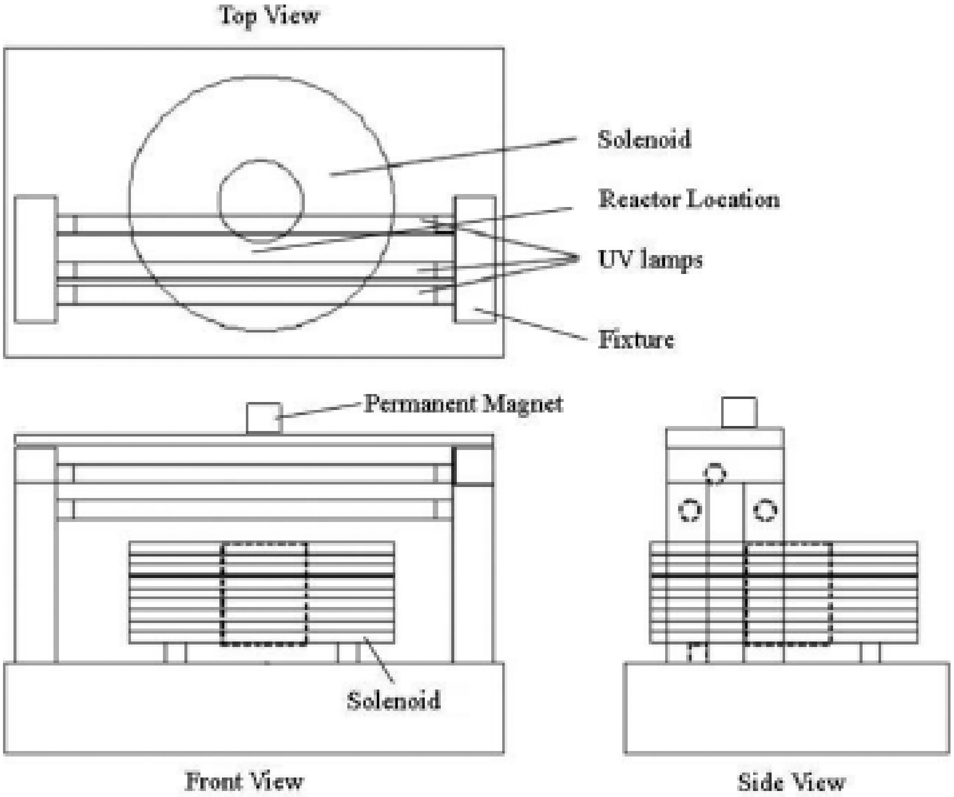

Figure 1: Drawing of MAPR Test Stand

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The silica layer acts as an insulator to prevent photodissolution or separation of the TiO^2 and the magnetic particle when irradiated by UV light [16]. 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.

Materials and Methods

Photocatalyst Synthesis

The photocatalyst used for this study consisted of a barium ferrite core coated first twice with silica and then twice with titanium dioxide, described in more detail in a previous publication [18]. The approximately 1-2 µm diameter barium ferrite core material was obtained from Alfa Aesar. The silica coating was accomplished by stirring the barium ferrite particles vigorously in a sol-gel suspension that resulted from a base-catalyzed reaction with tetraethyl orthosilicate (TEOS).

The resulting silica-coated particles were dried at room temperature and coated with amorphous titanium dioxide nanoparticles using an alkoxide hydrolysis and precipitation technique with a titanium n-butoxide precursor. It was important to heat treat the catalyst to transform the amorphous TiO^2 to the highly photoactive anatase polymorph. This was done by heating to 500°C with a 5°C/min ramp where the temperature was held for 60 minutes before cooling to room temperature.

Test Stand Configuration

The test stand for the magnetically agitated photocatalytic reactor (MAPR) consisted of components to generate the desired magnetic field, a curved quartz reactor, and fixtures for three UV bulbs (**Figure 1**). The dynamic component of the magnetic field was generated in the solenoid, which was located below the reactor.

The magnetic field gradient alternated in direction over time because it was powered with an alternating current (AC) signal. This AC signal originated from a function generator and was subsequently amplified by an audio amplifier before being fed a series of two solenoids. The second solenoid was not utilized for magnetic field generation, but rather to provide additional impedance to prevent damage to the amplifier.

The U-shaped quartz reactor was constructed of three quartz tubes oriented at right angles with the middle portion curved to follow the polar symmetry of the magnetic field. Also, a permanent magnet was placed above the reactor to provide a magnetic field gradient and hence force in the opposite direction of gravity to more evenly distribute the catalyst within the reactor.

The UV light was provided by three 365-nm peak output lamps surrounding the reactor. To prevent confounding radiation and for safety purposes, a black box was placed over the reactor during all experiments.

Assessment of Photocatalytic Oxidation

Phenol was used as a model contaminant because it represents a challenge to photocatalytic systems, is straightforward to analyze, and does not provide adsorption confounded results as other organic compounds like organic dyes may [19]. For all experiments the reactor was filled with 10 mL of an 11 mg/L stock solution.

The reactor effluent was tested for phenol concentration using a gas chromatograph with mass spectrometer, as has been done in the past [20]. The effluent was tested for nonpurgeable dissolved organic carbon (nDOC) to assess the extent of photocatalytic oxidation. Since the proposed photocatalytic oxidation reaction mechanism involves formation of a series of organic compounds including hydroxylated aromatics [21], nDOC analysis will measure the progress of oxidation to carbon dioxide and water.

Results and Discussion

Catalyst Synthesis

The composite photocatalyst was characterized using a scanning electron microscope (SEM). It is evident from the first micrograph (**Figure 2**) that the raw material has a consistent flat hexagonal shape and tends to form columns of particles. These formations may be due to the alignment of magnetic field dipoles.

The second micrograph (**Figure 3**) indicates that the composite photocatalyst particles consist of agglomerates of the smaller barium ferrite particles with an increasing curvature of the edges. The agglomeration is likely due to silica necking between particles, and the increased curvature due to the smooth, amorphous shape of the silica.

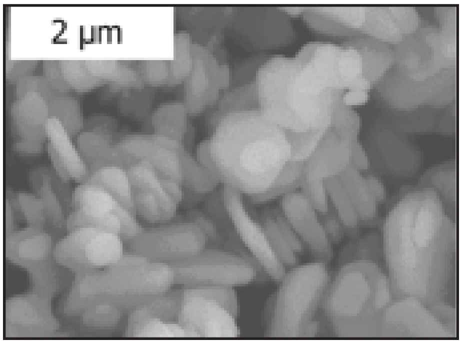

Figure 2:
SEM image of barium ferrite core.

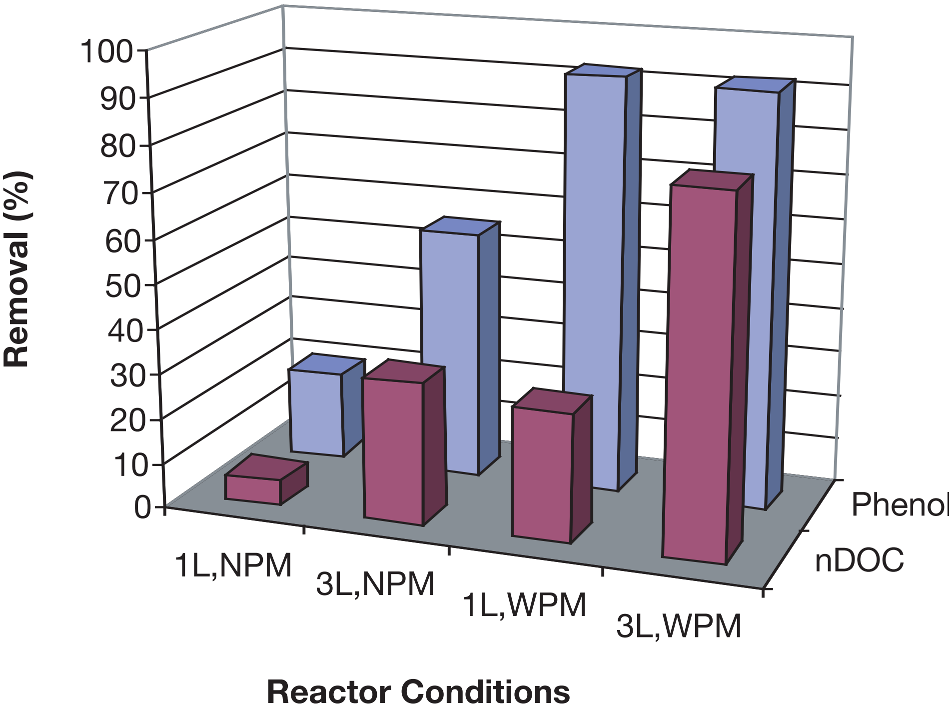

Figure 4: Comparison of number of lamps and presence of permanent magnet for photocatalytic oxidation of phenol in the MAPR (WPM = with permanent magnet, NPM = no permanent magnet, 1L = 1-365 nm lamp, 3L = 3-365 nm lamps).

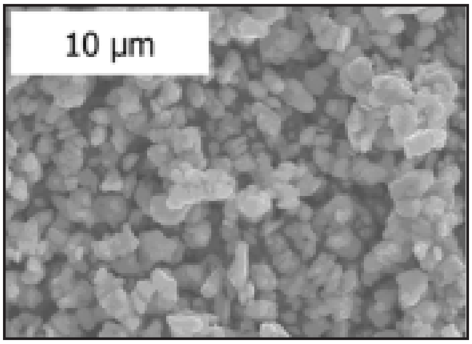

Figure 3
SEM image of magnetic composite catalyst.

Photocatalytic Oxidation

Recent work has demonstrated that a dynamic magnetic field can be used to agitate and confine the catalyst within a MAPR, such that its exposure to UV light and thus photocatalytic oxidation is optimized [18]. 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 [18] and [20].

Results for photocatalytic oxidation of phenol after three hours under various reactor conditions can be seen in Figure 4. The plot shows phenol removal measured as a result of GC analysis, which analyzes only the effluent solution for phenol.

The comparison of reactor conditions shows that the percent phenol disappearance increases when three UV lamps were used, as opposed to one without the permanent magnet; however, the data also indicates that if the permanent magnet is present, the disappearance of phenol is the same (within statistical variability of replicate sample analysis), whether one or three lamps were used.

Figure 4 also shows the result of nDOC analysis, which, as explained previously, includes oxidation byproducts as well as the original phenol molecules. For nDOC, all percentage removal quantities are lower than for GC analysis, which indicates that oxidation byproducts were present under all reactor conditions. Also, it is apparent that although the phenol removal was identical for one-lamp and three-lamp conditions with the permanent magnet, nDOC data indicates that more oxidation (of byproducts) is taking place when the additional lamps are present.

This data demonstrated several key pieces of information that are applicable to photocatalytic treatment of water. First, improvements in system configuration, including addition of a permanent magnet, can increase the photocatalytic oxidation effectiveness without increasing the power requirement. Second, it is important to consider the presence and toxicity of oxidation byproducts.

Although photocatalytic reactors have the potential to oxidize compounds to carbon dioxide and water, the reactor design must provide sufficient conditions (residence time, mass transfer and UV flux) to ensure that complete oxidation takes place. The future of this technology will depend on demand due to current and emerging pollution issues and innovative reactor designs that maximize the effectiveness of photocatalysis so it can compete economically with established technologies like activated carbon adsorption and biological treatment.

References

[1] Vakil, N. B.; Schwartz, S. M.; Buggy, B. P.; Brummitt, C. F.; Kherellah, M.; Letzer, D. M.; Gilson, I. H.; Jones, P. G. Biliary cryptosporidiosis in HIV-infected people after the waterborne outbreak of cryptosporidiosis in Milwaukee. *New England Journal of Medicine* 1996, 334(1), 19-23.

[2] Horikoshi, S.; Hidaka, H. Non-degradable triazine substrates of atrazine and cyanuric acid hydrothermally and in supercritical water under the UV-illuminated photocatalytic cooperation. *Chemosphere* 2003, 51(2), 139-142.

[3] Brocard, J. C.; Baronnet, F.; O'Neal, H. E. Chemical kinetics of the oxidation of methyl tert-butyl ether (MTBE). *Combustion and Flame* 1983, 52, 25-35.

[4] Williams, P. R. D.; Scott, P. K.; Sheehan, P. J.; Paustenbach, D. J. A Probabilistic Assessment of Household Exposures to MTBE from Drinking Water. *Human and Ecological Risk Assessment* 2000, 6(5), 827-849.

[5] Nowack, K. O.; Cannon, F. S.; Mazyck, D. W. Enhancing Activated Carbon Adsorption of 2-Methylisoborneol: Methane and Steam Treatments. *Environmental Science & Technology* 2004, 38(1), 276-284.

[6] Bayer, P.; Heuer, E.; Karl, U.; Finkel, M. Economical and ecological comparison of granular activated carbon (GAC) adsorber refill strategies. *Water Research* 2005, 39(9), 1719-1728.

[7] Ang, E. L.; Zhao, H.; Obbard, J. P. Recent advances in the bioremediation of persistent

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organic pollutants via biomolecular engineering. *Enzyme and Microbial Technology* 2005 Volume 37(5), 487-496.

[8] Parra, S.; Sarria, V.; Malato, S.; Péringer, P.; Pulgarin, C. Photochemical versus coupled photochemical–biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon. *Applied Catalysis B: Environmental* 2000 27(3), 153-168.

[9] Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews* 1995 95(1), 69-96.

[10] Rosenfeldt, E. J.; Linden, K. G. Degradation of Endocrine Disrupting Chemicals Bisphenol A, Ethinyl Estradiol, and Estradiol during UV Photolysis and Advanced Oxidation Processes. *Environmental Science & Technology* 2004, 38(20), 5476-5483.

[11] Neamtu, M.; Siminiceanu, I,; Yediler, A.; Kettrup, A. Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H2O2 oxidation. *Dyes and Pigments* 2002 53(2), 93-99.

[12] Doerffler, W.; Hauffe, K. Heterogeneous photocatalysis I. The influence of oxidizing and reducing gases on the electrical conductivity of dark and illuminated zinc oxide surfaces. *Journal of Catalysis* 1964 3(2) April 1964, Pages 156-170.

[13] Lee, W.; Gao, Y.-M.; Dwight, K.; Wold, A. Preparation and characterization of Titanium(IV) oxide photocatalysts. *Materials Research Bulletin* 1992, 27(6), 685-692.

[14] Kostedt, W. L., IV.; Witwer, Mickal A.; Mazyck, D. W.; Powell, Tony; Butters, Brian. A slurry-based photocatalytic reactor with slurry separation for water recovery. In Proceedings of the 35th International Conference on Environmental Systems, Society of Automotive Engineers (SAE): Rome, Italy, July 11-14, 2005. 2005-01-2994.

[15] Holmes, F. R.; Chadik, P. A.; Mazyck, D. W.; Wu, C-Y; Garton, M. J.; Powers, K. W.; Londeree, D. J. Photocatalytic oxidation of selected organic contaminants in a continuous flow reactor packed with titania-doped silica. In Proceedings of the 35th International Conference on Environmental Systems, Society of Automotive Engineers (SAE): Colorado Springs, CO, 19-22 July 2004. 2004-01-2403.

[16] Beydoun, D.; Amal, R.; Low, G; McEvoy, S. Occurrence and prevention of photodissolution at the phase junction of magnetite and titanium dioxide. *Journal of Molecular Catalysis A: Chemical* 2002, 180(1-2), 193-200.

[17] Watson, S.; Beydoun, D.; Amal, R. Synthesis of a novel magnetic photocatalyst by direct deposition of nanosized TiO^2 crystals onto a magnetic core. *Journal of Photochemistry and Photobiology A: Chemistry* 2002, 148(1-3), 303-313.

[18] Kostedt, W. L., IV.; Drwiega, J; Mazyck, D. W.; Lee, S.-W.; Sigmund, W.; Wu, C.-Y.; Chadik, P. Magnetically agitated photocatalytic reactor for photocatalytic oxidation of aqueous phase organic pollutants. *Environmental Science and Technology*, in press.

[19] Khan, A. Y.; Mazyck, D. W. The effect of UV irradiation on adsorption by activated carbon/ TiO^2 composites. *Carbon*, in press.

[20] Kostedt, W. L., IV.; Mazyck, D. W.; Wu, C.-Y.; Chadik, P. Optimization of a magnetically agitated photocatalytic reactor for water recovery. In Proceedings of the 35th International Conference on Environmental Systems, Society of Automotive Engineers (SAE): Rome, Italy, July 11-14, 2005. 2005-01-2995.

[21] Sivalingam, G.; Priya M. H.; Madras, G. Kinetics of the photodegradation of substituted phenols by solution combustion synthesized TiO^2. *Applied Catalysis B: Environmental* 2004, 51(1), 67-76.