SUMMARY: ENERGIZED PROCESSES FOR ONSITE TREATMENT OF LEACHATE

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FAU has pioneered the advancement of landfill leachate treatment systems using the photochemical iron-mediated aeration process and the TiO_2 photocatalytic process at lab scale in previous research funded by the Hinkley Center. This proposal describes the development of the next logical step, which is the development of pilot scale onsite treatment systems capable of detoxifying leachate with the power of ultraviolet light and advanced oxidation. The objective of the proposed research is to test photooxidative processes at pilot scale for the removal of COD/BOD, ammonia, heavy metals, color, and pathogens.

Leachate management options include on-site treatment, municipal sewer discharge, natural attenuation (including deep well injection), hauling offsite, or a combination approach. Typically, some form of aerobic treatment is employed to reduce leachate strength prior to discharge. However, biological systems are not well-suited for removal of bio-toxics from water and are inefficient in dealing with wastes of varying quality, such as leachate. Thus post-treatment, using constructed wetlands, combined physical/chemical/biological treatment, or evaporative systems, is generally required. Unfortunately, activated carbon and certain advanced treatment processes, such as ozone or ultraviolet light, do not adequately address inorganics, and membrane systems or air stripping merely transfer organics to another phase. Furthermore, multiple barrier systems are complicated to operate, costly, and generally inefficient. Unfortunately, most current processes cannot adequately address inorganics and organics simultaneously. From our previous work funded by the HCSHWM, our research team evaluated 23 different engineering alternatives for long-term leachate management. The results indicated that the most effective and sustainable strategies for the future would involve technologies that can destroy different classes of harmful contaminants all at once, without producing adverse byproducts and residuals. **So the question is: “Can we develop systems to treat landfill leachate at the source, cost effectively?”**

If energized processes work as well in the field (at pilot scale) as they do in the laboratory, then the answer is **“yes,”** because energized processes are: 1) designed to use the power of sunlight, which is free and requires no additional energy input, 2) easy to operate because they just require sufficient contact time and do not rely on complex precipitation reactions or biochemical processes, 3) not subject to biological upsets because they are physico-chemical processes that create broad spectrum oxidants to remove aqueous contaminants, and 4) designed to avoid merely transferring the pollutant to another medium (i.e. air or sludge).

This research will address a major technological need for sustainable, economical options for routine leachate treatment and safe discharge to the environment by investigating energized processes, such as photochemical oxidation (which includes photochemical iron-mediated aeration, TiO_2, and UV/peroxide). Two of these emerging technologies are currently being developed at FAU. These include: photochemical iron-mediated aeration (PIMA) and magnetic-photocatalytic oxidation. These new and innovative processes work by using ultraviolet light

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(energy from sunlight) to activate the surface of a semi-conductor (i.e. titanium dioxide or metallic iron) to produce highly reactive substances derived from water. These reactive radicals rapidly destroy man-made organic chemicals, breaking them down into carbon dioxide, water, and innocuous salts. In addition, it has been discovered recently by a UM-FAU partnership (funded by HCSHWM) that these processes can also remove heavy metals and reduce nitrogen-containing constituents. Thus it may now be possible to eliminate impurities in water all at once using a single process.

The objective of the proposed research is to pilot test up to three energized treatment options for the removal of parameters of interest (such as COD/BOD, ammonia, heavy metals, color, pathogens, and others mutually agreed upon by FAU and the TAG) using non-biological methods that landfill operators with little training can routinely and reliably employ without spending too much time on the task.

PROGRESS REPORT
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Project Title: Energized Processes for Onsite Treatment of Leachate
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Progress to Date:

- **Task 1**. Literature review. Richard Reichenbach, Anthony Ruffini, and André McBarnette have completed the literature review of landfill leachate treatment process efficiency with photocatalytic oxidation and other novel advanced oxidation processes. The main focus of the literature review topics has been to identify precedents using energized processes such as UV/peroxide, PIMA, photo-Fenton, aerated corrosive cell Fenton, and TiO_2 for water treatment applications. In these studies, specific questions were targeted, such as the following: 1) efficacy for various pollutants (in particular those targeted for this study), 2) appropriate UV intensity range using the new UV fluence determination methods, 3) appropriate testing conditions, 4) appropriate range of reactant or catalyst dose (in grams or m^2), 5) appropriate hydraulic retention times or reaction/exposure times for certain pollutants, 6) appropriate mixing regimes, 7) appropriate pilot reactor design and scale-up. In addition, any factors that can impact the efficiency of the process such as catalyst poisoning, pH/temperature effects, etc. were identified.

- **Task 2. Conduct baseline leachate quality characterization.** Approval and permission for sampling raw leachate has been obtained from Jeff Roccapriore, District Manager, Broward County Central Disposal, Waste Management Inc. of Florida for the landfill facility located on Sample Road and Florida's Turnpike. Sample collection began in early January 2010 and is ongoing. We have characterized the leachate samples for pH, COD, alkalinity, TDS, TSS, HPC, and conductivity, but not yet for BOD, ammonia, and lead.

- **Task 3. Concept testing for reactor configuration/design.** Using a prototype photocatalytic reactor module for aquarium-scale testing, we have completed preparations for mock scale up experiments with simulated and real leachates. Also, bench scale tests with simulated leachates have been performed to determine optimum dosing requirements as a starting point for scale-up testing.

  The total volume of the bench scale reactor is 375 mL. The first set of experiments were conducted using a TIO_2 catalyst dosage of 1.0 g/L of and 7.3 g/L of $NaHCO_3$ (as a photosensitizer for simulated leachate testing). Under these conditions, a maximum removal of COD of 36% was achieved in 4 hours with an initial COD concentration of 1110 mg/L. During this experiment there was a maximum temperature of 75 degrees Celsius in the reaction chamber due to the heating of the lamp and the relatively small volume of the reactor. This temperature change would not be expected to occur in pilot flow-through reactors with larger volumes. The UV dose was measured as 58 $\mu W/cm^2$, and the pH rose from 7.85 to 9.14 after 4 hours. In the next set of experiments, the catalyst dose was increased to 1.3 g/L, and the maximum removal after 4 hours increased to 43% with an initial COD concentration of 1060 mg/L. The maximum temperature decreased to 48 degrees Celsius, even though the maximum UV dosage was recorded as 70 $\mu W/cm^2$.

In the next set of experiments, the catalyst dose was further increased to 2.6 g/L with an initial concentration of 1130 mg/L COD. After 4 hours, a maximum removal efficiency of 54% was recorded. During the 4 hour detention time, the pH rose from 7.84 to 9.13 and the maximum temperature was 60 degrees Celsius, even though the maximum UV dosage was recorded as 65 $\mu W/cm^2$. In the next set of experiments, the catalyst dose was further increased to 3.2 g/L with an initial concentration of 1115 mg/L COD. After 4 hours, a maximum removal efficiency of 62% was recorded. During the 4 hour detention time, the pH rose from 7.2 to 9.2 and the maximum UV dosage was recorded as 60 $\mu W/cm^2$. As we continued to test the reactor to develop the optimum catalyst dosage, we tested 3.4 g/L (78% removal) and then we tested 4.0 g/L, which achieved >98% removal from an initial COD concentration of 1035 mg/L. In this last experiment, the values for pH were in the same range as seen in prior runs (increasing from 7.5 to 9.2, as the sensitizer is converted), and the UV dosage remained roughly around 60 $\mu W/cm^2$ with a maximum recorded reactor temperature of 55 degrees Celsius. Next we backed down from the 4.0 g/L dose to minimize catalyst requirements and tested 3.7 g/L, which achieved >99% removal. To make sure that the dose optimization was behaving as expected, a slightly higher dose was used (4.6 g/L), and indeed the removal efficiency was reduced to 94%, since more catalyst particles overcrowded the reactor and started reducing the efficiency of the reaction by blocking UV radiation from illuminating reaction sites. To confirm this effect, we increased the dosage to 5.3 g/L and observed a reduction in removal efficiency to 74%. The final bench scale dose optimization curve is shown in Figure 1.

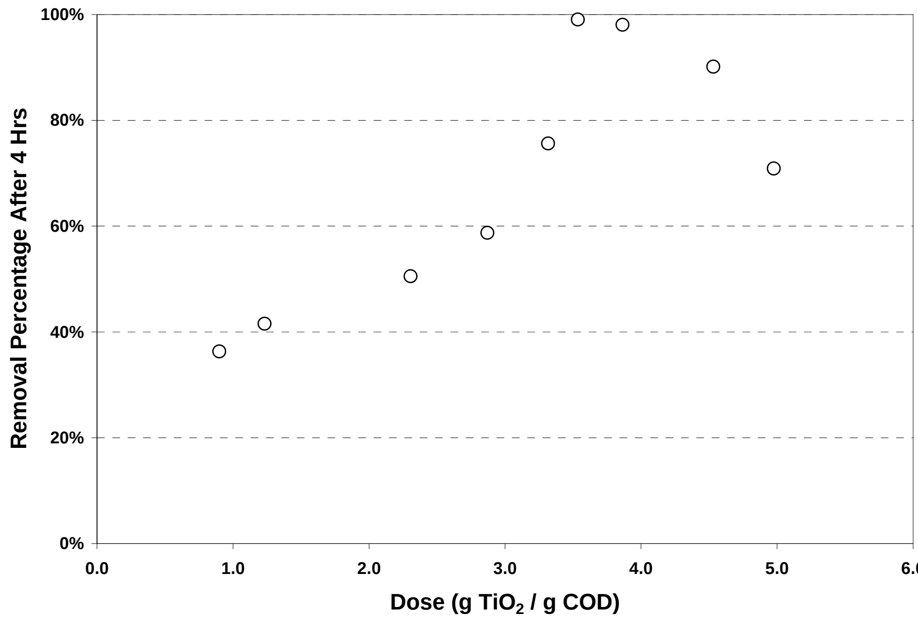

Figure 1. Catalyst dose optimization for bench-scale experiments involving TiO_2 photocatalysis.

The next stage involved optimizing the dosage of photosensitizer (bicarbonate). For the catalyst optimization experiments, the bicarbonate concentrations ranged from 6.5 to 7.2 g $NaHCO_3$ per g COD. So we varied the bicarbonate dose from 4.9 to 8.4 g $NaHCO_3$ per g COD and monitored the maximum removal rate as shown in Figure 2.

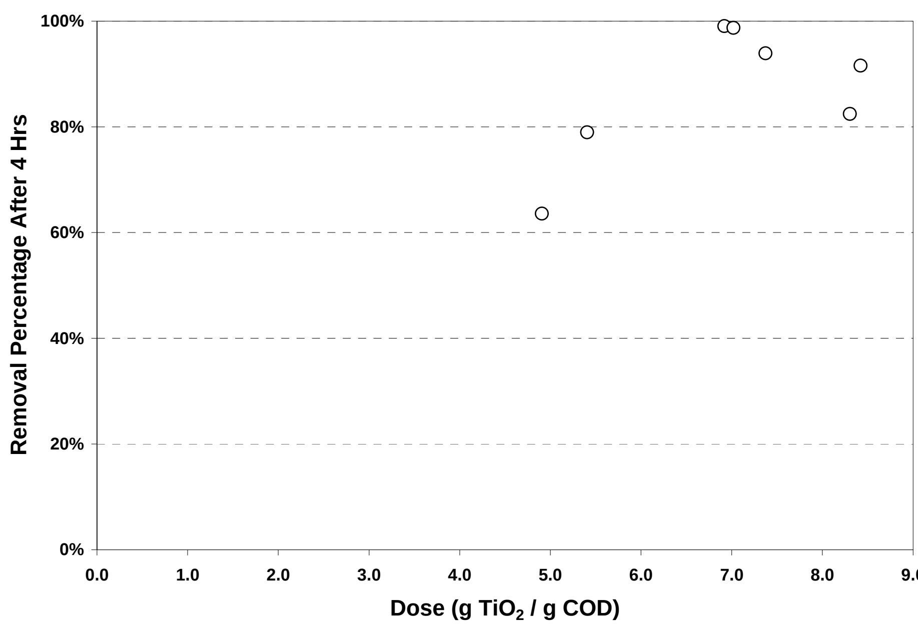

Figure 2. Photosensitizer dose optimization for bench-scale experiments involving TiO_2 photocatalysis.

Therefore, testing of photocatalysis with artificial leachates to replicate the conditions of successful previous lab scale experiments in preparation for scale-up is basically wrapping up, and testing of photocatalysis with actual leachates is underway. Composite leachate samples from the Sample Road landfill facility were collected in January and analyzed for COD and alkalinity, resulting in values of 4600 ± 26 mg/L COD and 4400 ± 170 mg/L as $CaCO_3$, respectively. Using the data from the previous optimization studies, the theoretical starting point for the catalyst dose would be 6.7 grams, and for the alkalinity, this would be 1625 mg/L as $CaCO_3$, but we have more than the amount needed to sensitize the reaction, so we may need to either consume some of the alkalinity by adding strong acid or run the reaction longer to achieve the desired results. These tests are underway.

Aquarium-scale testing of the flow-through reactor concept is scheduled to begin in March with simulated leachates, in preparation for Task 4. Establish pilot testing requirements, which will provide important information for the development of the experimental conditions for the pilot-scale flow through tests at the Sample Road facility.

- **TAG Meeting.** A TAG meeting was conducted on January 22, 2010. The members have been consulted and brought up to date on the progress of the research. The minutes of the TAG meeting are found on the project website. Notable items were that the Southeast District DEP office volunteered to take our graduate student, two undergraduate students, and principle investigator on guided tours of all landfill facilities in the district. CDM offered to assist the research team in expanding its research effort to other facilities, sharing data sets, and touring facilities outside of the Southeast District.

Research planned for the upcoming months:

- Conceptual design of scale-up for pilot testing is ongoing
- Reach out to Geosyntec Consultants and Heyward Inc. for assistance in prototype development
- Take advantage of Southeast District and CDM offers of additional assistance on the project.
- Ramp up aquarium-scale testing
- Start actual leachate tests with aquarium-scale unit
- Prepare for pilot tests and design experiments