SUMMARY: ONSITE TREATMENT OF LEACHATE USING ENERGIZED PROCESSES

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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. Previous work has led to the development of reactor prototypes for pilot scale testing. This proposal describes the next logical step in this line of research, which is the field testing 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 the prototype photooxidative reactors 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 ultraviolet light, which is potentially free, 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).

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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 an innovative photochemical oxidation process currently being developed at FAU, which uses ultraviolet light to activate the surface of a semi-conductor to produce highly reactive substances derived from water called radicals. These 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 types of 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 the proposed energized technology for the removal of certain parameters of interest (such as COD/BOD, ammonia, heavy metals, color, pathogens, and others mutually agreed upon by FAU and the TAG) in order to develop preliminary cost estimates, process footprints, and pre-treatment requirements.

PROGRESS REPORT
(March 2012)

Project Title: Onsite Treatment of Leachate Using Energized Processes
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Progress to Date:

- **Task 1**. **Literature review**. Based on previous work started by D.E. Meeroff, Tammy Martin, Swapnil Jain, Hatsucko Hamguchi, Richard Reichenbach, Anthony Ruffini, and André McBarnette, a state-of-the-science literature review of landfill leachate treatment process efficiency with photocatalytic oxidation and other novel advanced oxidation processes was conducted. 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 wastewater treatment applications. In this review, specific questions are targeted, such as the following: 1) efficacy and reaction times for various pollutants (in particular those targeted for this study), 2) appropriate UV intensity range using the new UV fluence determination methods, 3) appropriate range of reactant or catalyst dose (in grams or m^2), and 4) any factors that can impact the efficiency of the process such as catalyst poisoning, pH/temperature effects, etc. Currently, we have hired an outstanding undergraduate student, Frank Youngman, who is enrolled in the 5-year Bachelor/Masters degree program in civil engineering, to conduct this work as part of his graduate thesis research. The research team is also in the process of preparing a review article for publication to disseminate these results.

- **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 September 2011 and is ongoing. We have characterized the leachate samples for pH, COD, alkalinity, TDS, TSS, HPC, BOD, conductivity, ammonia, copper, and arsenic. Mr. Youngman has conducted all of the baseline studies to develop familiarity with the testing protocols for chemical analysis of leachate. His results are found below.

Parameter	Units	CDSL 03/16/2010	CDSL step up station 09/30/2011
Alkalinity	mg/L as $CaCO_3$	4500	4625
pH	pH units	7.6	7.8
Color	PCU	500	1125
Ammonia	mg/L as NH_3-N	1748	1855
COD	mg/L as O_2	n/a	6250
BOD	mg/L as O_2	n/a	n/a

- **TASK 3. Preliminary testing.** Using the samples collected in Task 2, preliminary testing began with initial screening experiments. First, a hydraulic modification to the pilot testing unit was completed to allow for longer term experiments. In the previous study, we were limited to only 4 hours of testing before the temperatures became excessive (T>60°C). We purchased a recirculating chiller unit and filled it with Dynalene, which is a silicone-based bath fluid which has the capability of maximizing our heat transfer to provide the best thermal stability for our reactor, as possible given the technological limitations. The maximum temperature range for this fluid is -50 to 60°C. Next, we installed the cooling system using a compatible thin walled PTFE pipe wrapped around the reaction chamber (Figure 1). Finally, we installed a stainless steel three-way valve (Figure 2) that will allow us to stop the unit, drain the pump, and recirculate the catalyst so that it will not collect in the weir above the falling film reaction zone during long term kinetics experiments in which we start and stop the unit overnight for cooling.

Figure 1. Frank Youngman testing the temperature control system provided by the recirculating chiller unit (in the background). The PTFE pipe is seen wrapped around the reaction chamber of the pilot unit in the foreground.

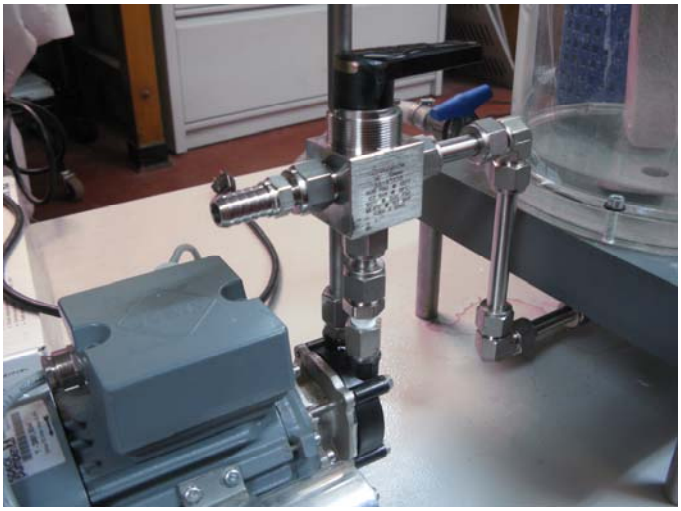

Figure 2. Three way valve modification for flushing and priming the recirculating pump.

After running the pilot unit for a total of 44 hours over an 11-day period, we were able to keep the reaction temperatures below 20-35°C, consistently, as shown in Figure 3. The goal is to determine the magnitude of residual generation, energy consumption, and preliminary removal kinetics as well as appropriate flow rate, reactor volume, and treatment targets.

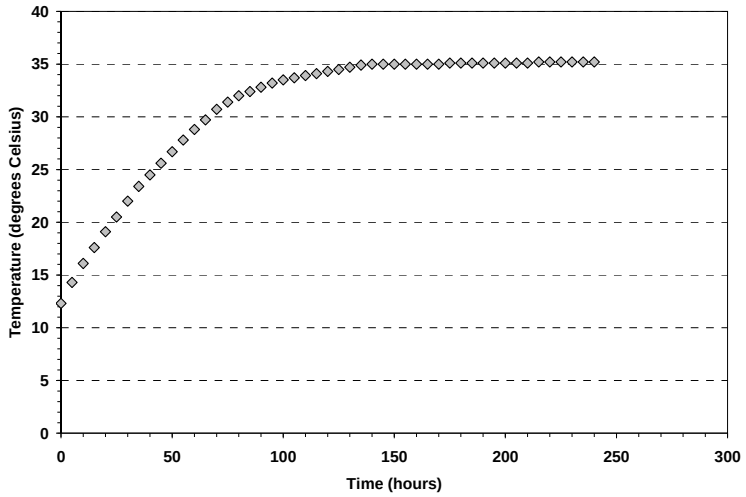

Figure 3. Typical temperature curve collected during one of the 4-hour pilot test runs (January 13, 2012).

- **TASK 4. Preliminary assessment of pilot performance.** During operation of the preliminary testing pilot unit, measurements of COD/BOD, ammonia, heavy metals, color, and/or pathogens will be taken to investigate system performance. Troubleshooting and fine-tuning for maximum performance will be investigated, as needed. The operators at the

facility will be invited for a demonstration of the unit and will be queried as to the desired performance characteristics and operation of the system, if scale-up is potentially achievable.

For the first long time trial, we used real leachate from CDSL step up station collected on September 30, 2011, with an initial COD concentration of 6250 mg/L and 4 g/L of TiO_2 photocatalyst. We ran the test at four hour intervals with removal of the leachate for cooling back to room temperature and flushing any suspended materials from the pump after each 4-hour period. Samples were collected at t=0 and t=4 hours for each daily run, and the unit was operated until most of the alkalinity was destroyed, which in this case took about 44 hours total. The COD removal after 44 hours was 37%. Kinetics data was plotted for zero order (Figure 4), first order (Figure 5) and second order (Figure 6) behavior.

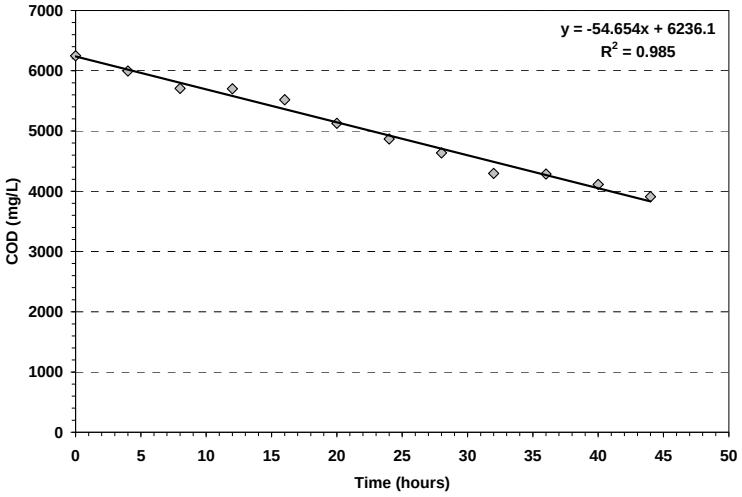

Figure 4. Zero order COD kinetics plot for 44 hour test conducted with 110923 sample from CDSL step up station.

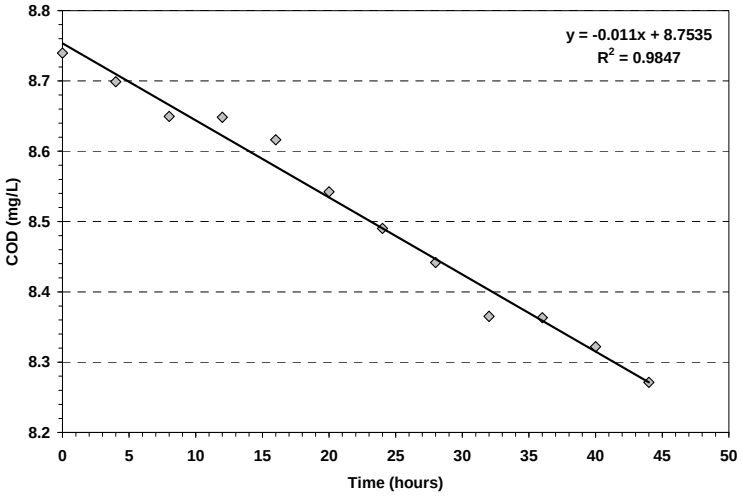

Figure 5. First order COD kinetics plot for 44 hour test conducted with 110923 sample from CDSL step up station.

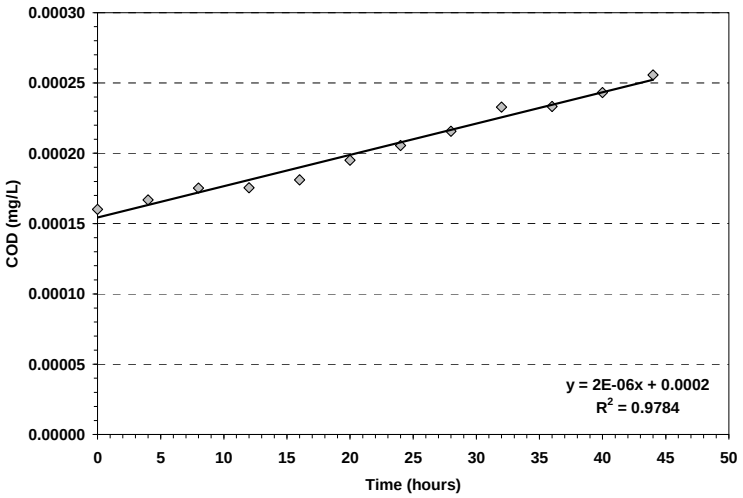

Figure 6. Second order COD kinetics plot for 44 hour test conducted with 110923 sample from CDSL step up station.

As shown in previous testing by our lab and in the literature, the kinetics could follow either zero or first order, since both have the same fit (r^2 = 0.985). The alkalinity was rapidly removed (first order) to 89% of the initial concentration of 4625 mg/L as $CaCO_3$. The ammonia was also rapidly removed (first order) to 90% of the initial concentration of 1710 mg/L as NH_3-N. Color removal was 53% and the pH remained within 8.35 – 9.23 during testing.

Using this data we estimate that it would take approximately 99 hours to achieve the 800 mg/L COD target for sewer disposal using the zero order kinetics model and 190 hours using the first order kinetics model. For the other parameters, we used the first order model to estimate 36 hours for 90% removal of ammonia and alkalinity, and 140 hours from 90% color removal.

At this point, we recommend increasing the TiO_2 dosage incrementally to attempt to improve efficiency. We started with the 4 g/L dose that gave 100% removal in 4 hours at the bench scale, but the pilot plant has a lower UV fluence and much lower contact time in the reaction zone, so we hypothesize that increasing the TiO_2 dose to 16 g/L, will improve the process efficiency. Previous pilot tests with 28 g/L conducted by our laboratory did not show promising results with respect to COD removal.

We made a decision to stop further testing beyond the 44 hours of the first run because we know from the bench scale that when all of the alkalinity is destroyed in the sample, we will not see any removal of COD. After 44 hours, the alkalinity concentration was below 500 mg/L as $CaCO_3$. So additional planned experiments will attempt to optimize the catalyst dosage, understand more about the alkalinity dependence, and learn more about the reaction order kinetics, if feasible.

- **TASK 5. Develop final recommendations and preliminary cost analysis.** Using the data developed in Task 3 and 4, an appropriate level of reactant/catalyst and UV fluence needed to meet the water quality guidelines for general sewer discharge will be determined. The carbon

footprint of the process will be calculated and preliminary operating costs will be monitored in terms of electricity consumption, pre-treatment, chemicals, and residuals disposal requirements, as time allows. An assessment will be conducted to evaluate the associated costs per gallon treated, and the environmental consequences of the proposed full scale unit will be evaluated in context with leachate hauling to offsite wastewater treatment plants. To date, no work in this task has been initiated.

- **TASK 6. Prepare publication materials**. Interim and final reports will be developed and submitted. A plan will be developed for follow-up work based on comments from reviews of same. Furthermore, a scholarly publication will be developed, including but not limited to, a poster and a conference paper. The website for the project and the first progress report have been created and submitted. TAB meeting was held in February, and a presentation was made by Frank Youngman and Dr. Meeroff. Questions that arose at the TAG meeting included: 1) Are there other contaminants of concern that we are not testing? 2) What are the treatment targets for those? 3) How much does your leachate management cost? 4) Will this proposed process be cost competitive? 5) How much leachate is produced at your landfills? 6) Do you want us to test your leachate?

  Sam Levin from the TAG added that the costs for leachate management statewide can be estimated at about 7-15 cents per gallon or around $3-$15 per thousand gallons. The CDSL landfill is currently on the order of $3.65-$8.33 per thousand gallons. He also provided a rule of thumb about leachate production from active landfills that generate about 40,000 gallons per acre per month. He also mentioned that closed landfills produce a lot less. In terms of additional parameters to investigate, the following were proposed: chlorides, sodium, ammonia (which is already being analyzed), and arsenic. Sam Levin mentioned that the removal of ammonia alone in a recirculating bioreactor landfill could enhance the biodegradation rate of other pollutants inside the landfill in a self-treatment approach, which would be another interesting application for this process.\.