

SUMMARY: ONSITE TREATMENT OF LEACHATE USING ENERGIZED PROCESSES

Daniel E. Meeroff (PI)¹

FAU has pioneered the advancement of landfill leachate treatment systems using the photochemical iron-mediated aeration process and the TiO₂ 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 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 photo-oxidative 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 and ultraviolet light, do not adequately address inorganics, while membrane systems and air stripping merely transfer organics to another phase. Furthermore, multiple barrier systems are complicated to operate, costly, and generally inefficient. As a result, most current treatment 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).

¹ Associate Prof., Dept. of Civil, Environmental & Geomatics Engineering, Florida Atlantic University, 777 Glades Road, 36/222, Boca Raton, FL 33431-0091, Phone: (561) 297-3099, FAX: (561) 297-0493, E-Mail: dmeeroff@fau.edu

¹ Associate Professor, Dept. of Civil Engineering, Florida Atlantic University, 777 Glades Road, 36/222, Boca Raton, FL 33431-0091, Phone: (561) 297-3099, FAX: (561) 297-0493, E-Mail: dmeeroff@fau.edu

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

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Project Title: Onsite Treatment of Leachate Using Energized Processes

Principal Investigators: Daniel E. Meeroff, Ph.D.

Affiliation: FAU

Phone number: (561) 297-2658

Project website: <http://labees.civil.fau.edu/leachate.html>

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, a graduate student, Frank Youngman, who is enrolled in the 5-year Bachelor/Masters degree program in civil engineering, is finishing 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, and has recently published an article of our results in the Journal of Hazardous Waste. Mr. Youngman is completing his update to the existing review with more recent advances from 2009 to present. The draft of the literature review has been provided to the PI for feedback and comments, and is now in the revision stage for inclusion into the final report.
- **Task 2. Conduct baseline leachate quality characterization.** Approval and permission to obtain samples of raw leachate from the landfill facility located on Sample Road and Florida's Turnpike (Monarch Hill) has been obtained from Jeff Roccapriore, District Manager, Broward County Central Disposal, Waste Management Inc. of Florida. We have characterized the leachate samples for pH, COD, alkalinity, color, and ammonia. Mr. Youngman has conducted all of the baseline studies to develop familiarity with the testing protocols for chemical analysis of leachate. Additional samples were collected on July 18, 2012. Results are as follows:

Parameter	Units	CDSL composite sample 03/16/2010	CDSL step up station 09/30/2011	CDSL step up station 03/09/2012	CDSL step up station 07/18/2012	CDSL step up station 11/26/2012
Alkalinity	mg/L as CaCO ₃	4500	4625	3560	4125	4690
pH	pH units	7.6	7.8	7.4	7.7	7.7
Color	PCU	500	1125	950	760	750
Ammonia	mg/L as NH ₃ -N	1748	1855	1310	1635	1700
COD	mg/L as O ₂	n/a	6250	5270	6560	6180

- **TASK 3. Preliminary testing.** This task is completed, and we are proceeding with laboratory tests associated with Task 4.
- **TASK 4. Preliminary assessment of pilot performance.** During operation of the preliminary testing pilot unit, measurements of COD, ammonia, color, alkalinity, and pH are taken to investigate system performance. For the first long time trial, we used real leachate from the CDSL step up station collected on September 30, 2011, with an initial COD concentration of 6250 mg/L and 4 g/L of TiO₂ photocatalyst. We ran the test at four-hour intervals at which time the leachate was removed from the unit to cool it back down to room temperature and flush any suspended materials from the pump housing. This was repeated 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. As shown in previous testing by our lab and in the literature, the kinetics could follow either zero or first order, but the first order fit seems to work better for long term testing. From inspection of the data collected in this research, the highest collective correlation lies with the first order kinetics. We recommend modeling the removal of all parameters as a first order reaction.

After the first 44 hour test, we investigated increasing the TiO₂ dosage incrementally to attempt to improve efficiency. The starting point was 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 TiO₂ dose to 16 g/L will improve the process efficiency. To date, we have run 4, 16, 25, 30, and 40 g/L doses. We made a decision to stop further testing beyond the 44 hours of the first run because we learned 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 CaCO₃. To date, six experiments have been completed in an attempt to determine the optimum dosage of TiO₂. The latest catalyst dosage used in the 6th experiment was 10 g/L. The removal efficiency comparisons for alkalinity for all the catalyst dosages are displayed in Figure 1. The degradation of alkalinity was greatest at the last catalyst dosage of 10 g/L (first order $k = 0.0090 \text{ hr}^{-1}$), followed by the first experimental dosage of 4 g/L (first order $k = 0.0087 \text{ hr}^{-1}$).

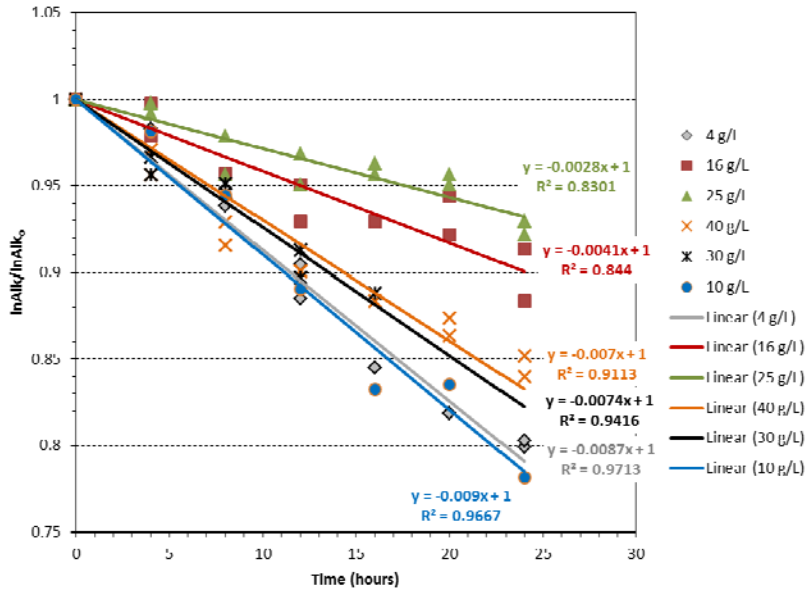


Figure 1. Comparison plot of first order alkalinity removal after 24 hours for the catalyst dosages from six experiments.

With respect to ammonia removal, the first experiment (4 g/L) exhibited the greatest ammonia degradation (first order $k = 0.0103 \text{ hr}^{-1}$). The most recent test (10 g/L) provided the second highest amount of ammonia decay (first order $k = 0.0082 \text{ hr}^{-1}$, see Figure 2). From a cost perspective, this points to potentially lower amounts of catalyst having a positive result on both the alkalinity and ammonia.

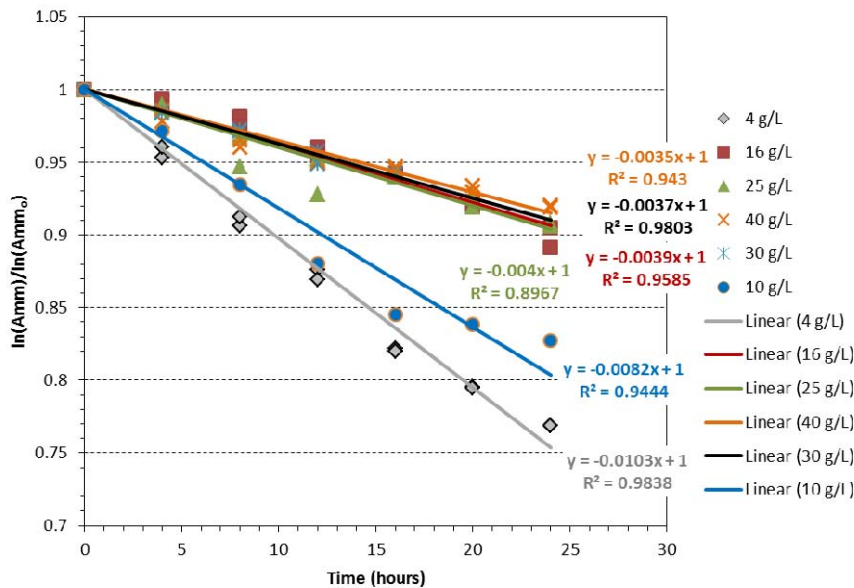


Figure 2. Comparison plot of first order ammonia removal after 24 hours for the catalyst dosages from six experiments.

With respect to COD removal, Figure 3 shows that 25g TiO₂ per L of leachate exhibits the

largest kinetics. The dosage in experiment 4 (40 g/L) had a similar removal efficiency, but with much more catalyst. The sixth experiment (10 g/L) displayed the third largest degradation of COD (first order $k = 0.0018 \text{ hr}^{-1}$).

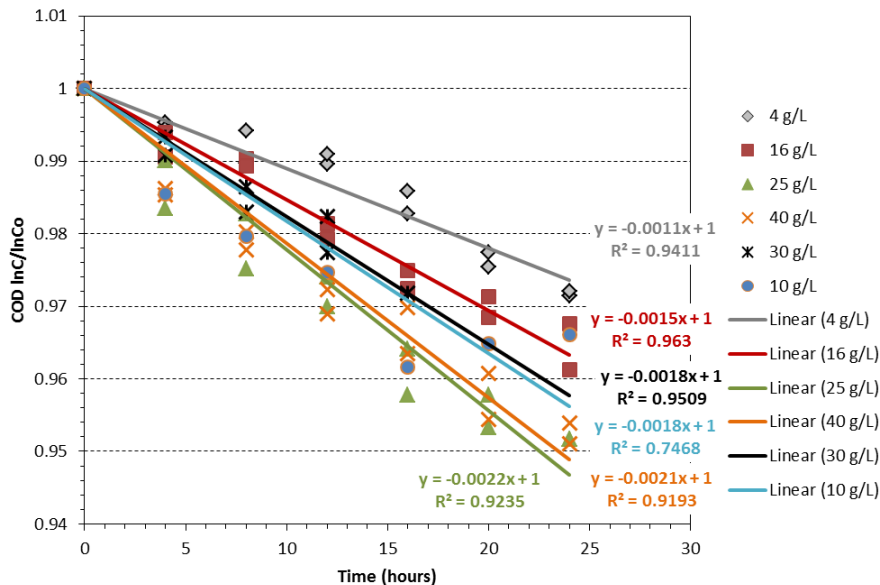


Figure 3. Comparison plot of first order COD removal after 24 hours for catalyst dosages from six experiments.

Taking the six experiments and estimating the percent COD removal at 24 hours based on first order kinetics, a catalyst optimization plot was created (Figure 4). The efficiency increased with the dosage of TiO_2 until the 25 g/L dose. Following that experiment, 40 g/L was chosen, and that dosage exhibited a similar percent removal to 25 g/L, not the increase which was expected. This led to the hypothesis that a peak value may exist in between 25 g/L and 40 g/L, so the 5th experiment utilized 30 g/L of catalyst. This trial delivered an unexpected result, displaying a percent removal less than both of the previous values. Based on our optimization plots at bench scale in previous testing, we expected to see a peak, but the optimization appears to be asymptotic. So we tested 10 g/L to see if it fell on the curve, and it did in fact, the removal matched up with the expected trend, as shown in Figure 4 by the red square.

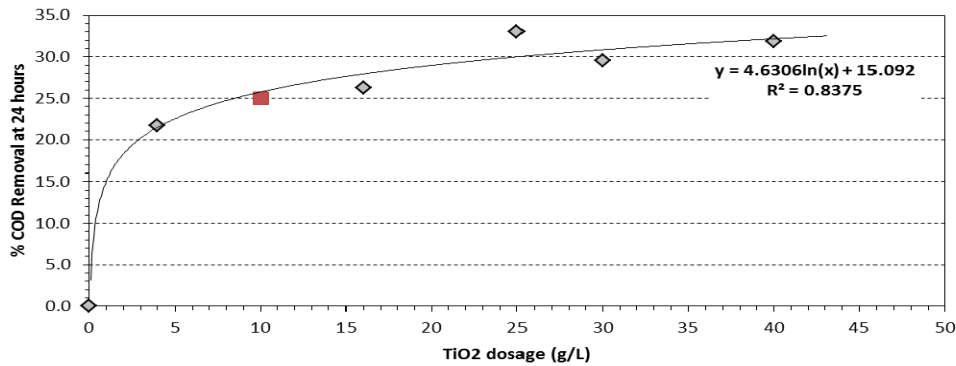


Figure 4. Catalyst optimization curve denoting the removal data from the 6th experiment (10 g/L)

Since the curve is following an asymptotic trend, the preliminary optimum dosage is now determined to be between 5-10 g/L.

The next step is to test a filtration system to add on to the advanced oxidation treatment unit in an effort to recover the TiO₂ photocatalytic particles after each treatment run. A number of filtration bags have been obtained for this purpose. Several nylon mesh bags of different nominal pore opening sizes have been selected and will be tested for their catalyst recovery efficiency.

- **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. 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. This task is being completed for development of the draft final report.
- **TASK 6. Prepare publication materials.** The draft final report is being 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 all required progress reports have been created and submitted.

Work is continuing on preparation of the draft final report and a draft scholarly review article. A TAG meeting is planned for March 2013. The announcement will be made available shortly.

Research planned for the upcoming months:

- Complete the TiO₂ particle capture filtration experiments.
- Refine cost estimates.
- Complete the draft final report.