

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 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).

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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

(October 2012)

Project Title: Onsite Treatment of Leachate Using Energized Processes

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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 continuing to update the existing review with more recent advances from 2009 to present. A draft of the literature review has been provided to the PI for feedback and comments.
- **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
Alkalinity	mg/L as CaCO ₃	4500	4625	3560	4125
pH	pH units	7.6	7.8	7.4	7.7
Color	PCU	500	1125	950	760
Ammonia	mg/L as NH ₃ -N	1748	1855	1310	1635
COD	mg/L as O ₂	Not recorded	6250	5270	6560

- **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. Previous pilot tests with 28 g/L conducted by our laboratory did not show promising results with respect to COD removal. 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 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 CaCO₃. 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.

To date, five experiments have been completed in an attempt to determine the optimum dosage of TiO₂. The two additional catalyst dosages, used in experiments 4 and 5, were 40 g/L and 30 g/L, respectively. The removal efficiency comparisons are displayed in Figure 1. The degradation of alkalinity remained at its greatest using a catalyst dosage of 4 g/L. The two additional tests (40 g/L and 30 g/L) provided degradation at levels higher than the 2nd and 3rd experiments (16 g/L and 25 g/L).

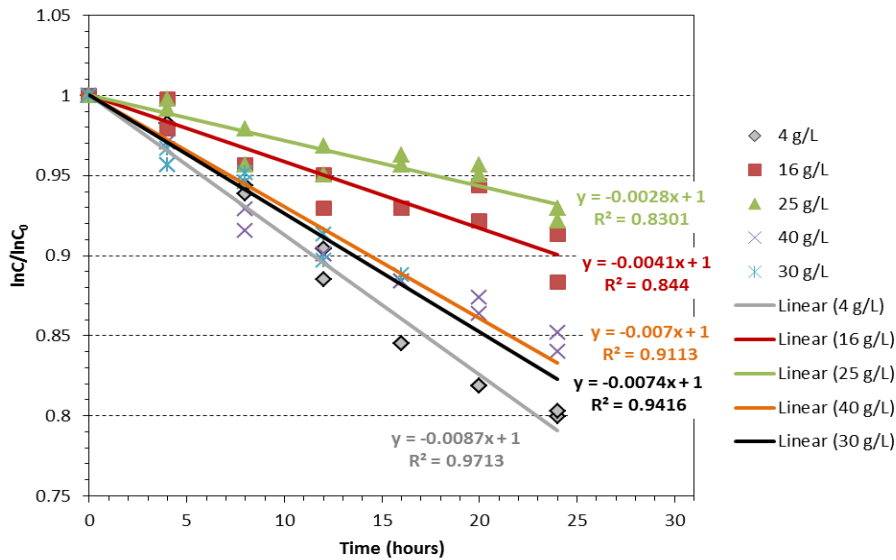


Figure 1. Comparison plot of first order alkalinity removal after 24 hours for the catalyst dosages from five experiments.

With respect to ammonia removal, the 1st experiment (4 g/L) exhibited the greatest ammonia degradation. The most recent tests (30 g/L and 40 g/L) actually provided the lowest amount of ammonia decay (see Figure 2). From a cost perspective, this is good news because this points to lower catalyst amounts having a positive result on both the alkalinity and ammonia.

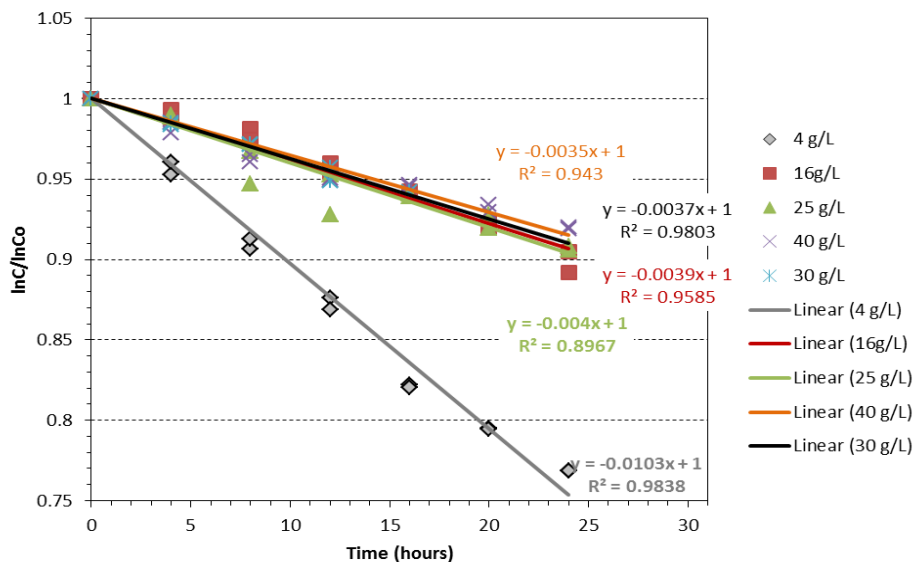


Figure 2. Comparison plot of first order Ammonia removal after 24 hours for the catalyst dosages from five experiments.

With respect to COD removal, Figure 2 shows that 25g TiO_2 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 fifth experiment (30 g/L) surprisingly showed a much lower removal than the 3rd and 4th trials.

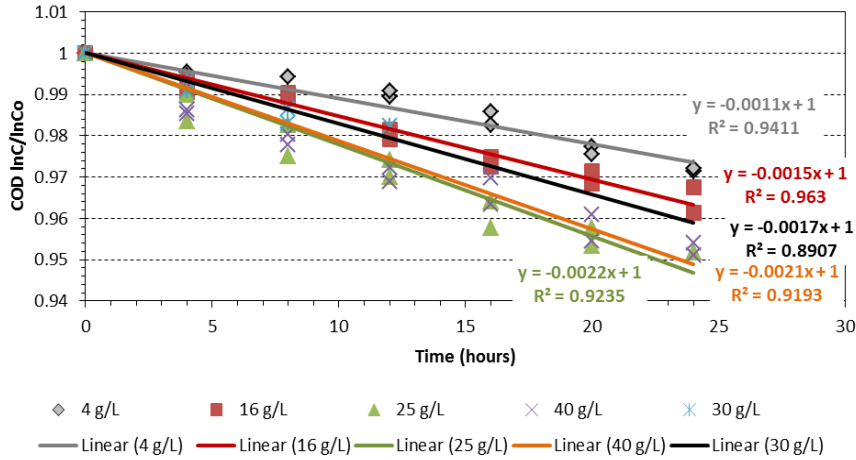


Figure 3. Comparison plot of first order COD removal after 24 hours for catalyst dosages from five experiments.

Taking the five experiments and estimating the percent COD removal at 24 hours based on first order kinetics, we made a catalyst optimization plot as shown in Figure 4. The efficiency was increasing with the dosage of TiO₂ 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 expectation of a peak value existing 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 this chart appears to be asymptotic. So we are going to test 10 g/L to see if it peaks or falls on the curve that we have developed.

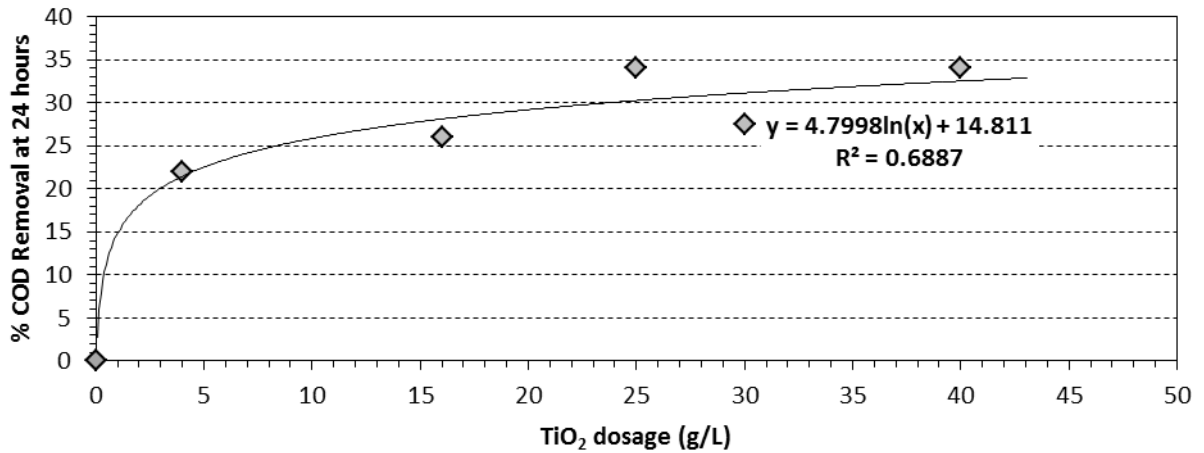


Figure 4. Catalyst optimization curve

Once the optimum catalyst dosage is found, the next step is to design 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. The method for attaching the bag to the system is still in the design process. Once the design is complete, the appropriate bags will be selected and 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. 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 four 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 November 9, 2012. The announcement will be made available shortly.