

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 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
(June 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 TiO₂ 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 m²), 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 conducting 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. Mr. Youngman has begun updating the existing review with more recent advances from 2009 to present.
- **Task 2. Conduct baseline leachate quality characterization.** Approval and permission for sampling raw leachate has been obtained from Jeff Roccapiore, District Manager, Broward County Central Disposal, Waste Management Inc. of Florida for the landfill facility located on Sample Road and Florida's Turnpike. 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. His results are found below.

Parameter	Units	CDSL composite 03/16/2010	CDSL step up station 09/23/2011	CDSL step up station 03/09/2012
Sample ID		100316	110923	120309
Alkalinity	mg/L as CaCO ₃	4500	4625	3560
pH	pH units	7.6	7.8	7.4
Color	PCU	500	1125	950
Ammonia	mg/L as NH ₃ -N	1748	1855	1310
COD	mg/L as O ₂	n/a	6250	5270

- **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 ($T > 60^{\circ}\text{C}$). 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.

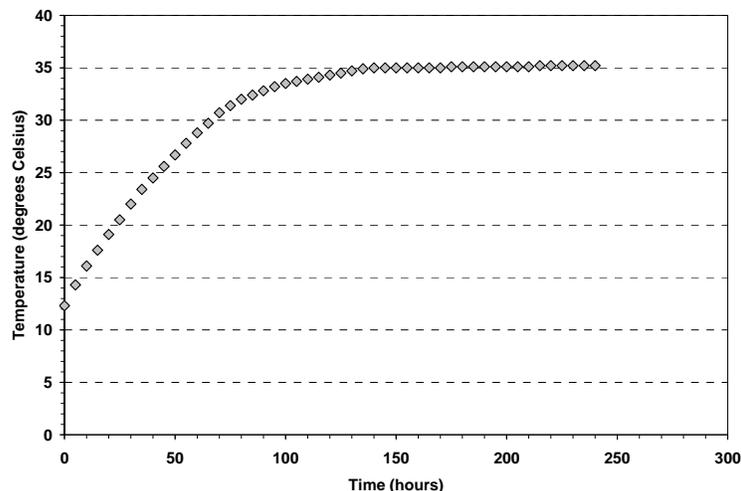


Figure 3. Typical temperature curve collected during one of the 4-hour pilot test runs (January 13, 2012).

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, 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.

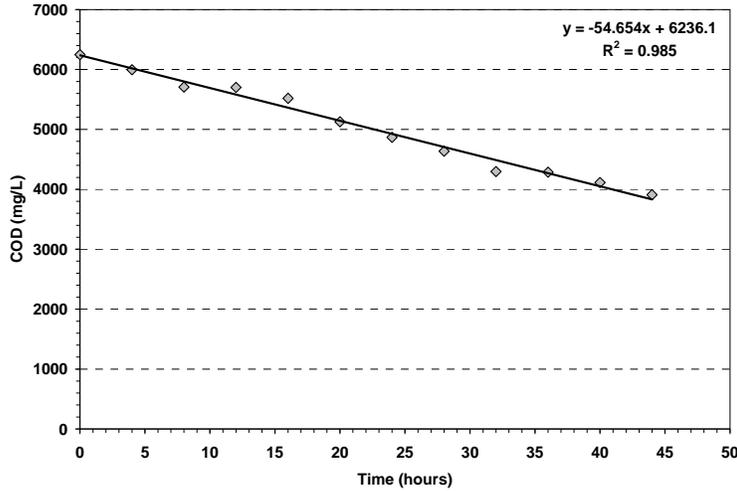


Figure 4. Zero order COD kinetics plot for 44 hour test conducted with 110923 sample from CDSL step up station.

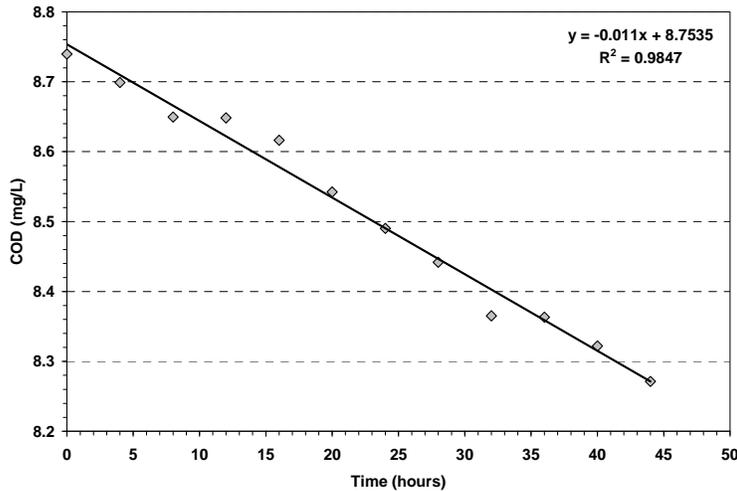


Figure 5. First order COD kinetics plot for 44 hour test conducted with 110923 sample from CDSL step up station.

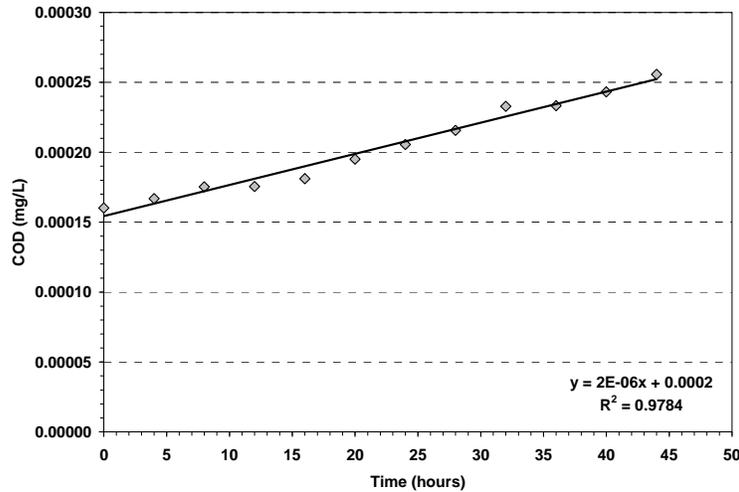


Figure 6. Second order COD kinetics plot for 44 hour test conducted with 110923 sample from CDSL step up station.

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 $\text{NH}_3\text{-N}$. 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 to achieve 90% color removal.

After the first 44 hour test, we investigated increasing the TiO_2 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 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.

For the second long time experiment, we used real leachate from CDSL South East step-up station collected on March 9, 2012, with an initial COD concentration of 5270 mg/L and 16 g/L of TiO_2 photocatalyst. Samples were collected at $t=0$ and $t=4$ hours for each daily run for a total of 40 hours. The COD removal after 40 hours was 39%. Kinetics data was plotted for zero order (Figure 7), first order (Figure 8) and second order (Figure 9) behavior.

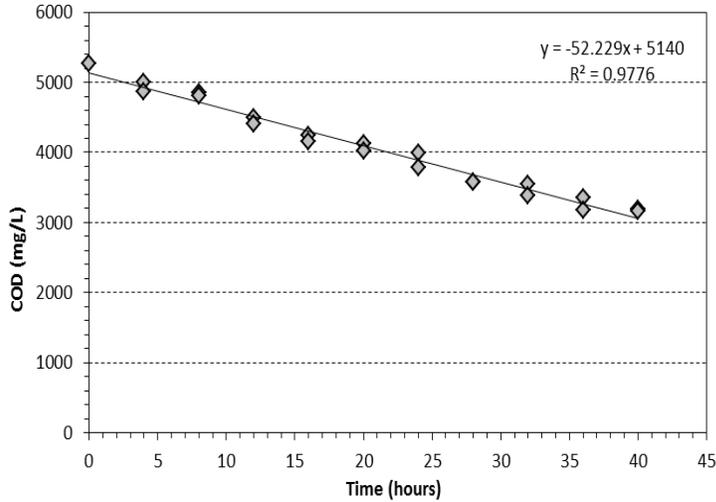


Figure 7. Zero order COD kinetics plot for 40 hour test conducted with 120309 sample from CDSL south east step up station.

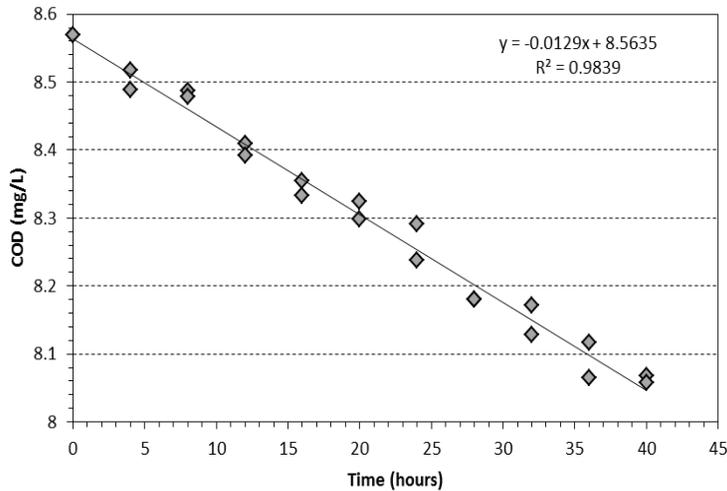


Figure 8. First order COD kinetics plot for 40 hour test conducted with 120309 sample from CDSL south east step up station.

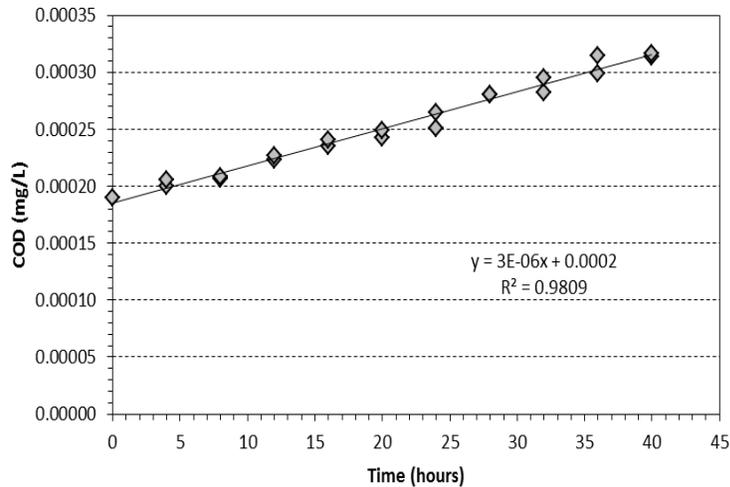


Figure 9. Second order COD kinetics plot for 40 hour test conducted with 120309 sample from CDSL south east step up station.

The kinetics in this experiment seem to follow first order, since it represents the highest linear fit ($r^2 = 0.984$), although zero and second order cannot be discounted. The alkalinity was rapidly removed (first order) to 72% of the initial concentration of 3560 mg/L as CaCO_3 . The ammonia was also rapidly removed (first order) to 69% of the initial concentration of 1310 mg/L as $\text{NH}_3\text{-N}$. Color removal was 48%, and the pH remained within 8.56 – 9.18 during testing.

Using this data, it is estimated that it would take 83 hours to achieve the 800 mg/L COD target for sewer disposal using the zero order kinetics model and 188 hours using the first order kinetics model. For the other parameters, we used the first order model to estimate 38 hours for 90% removal of ammonia, 45 hours for 90% removal of alkalinity, and 151 hours from 90% color removal.

A juxtaposition of COD removal at 40 hours to show the effect of catalyst dosage was plotted (Figure 10).

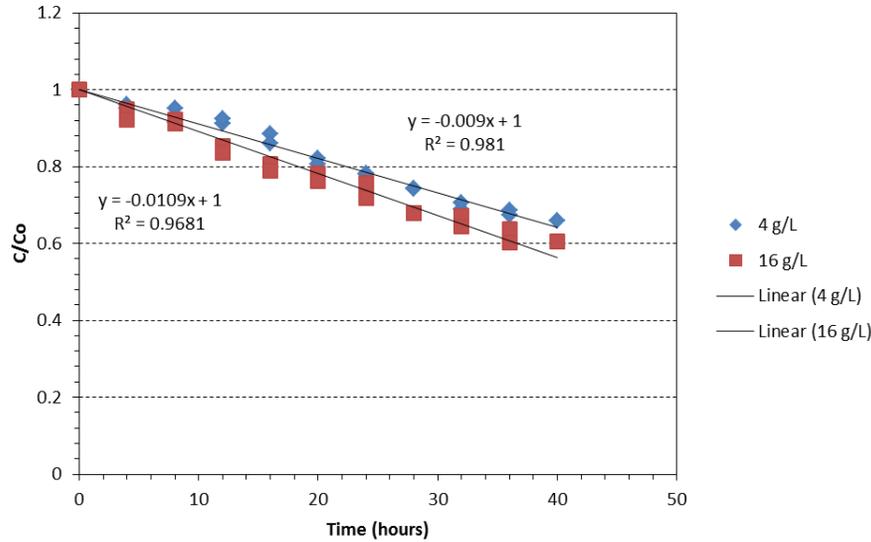


Figure 10. Comparison plot of COD removal for catalyst dosages from first two long time experiments.

The plot above shows that the higher dosage of catalyst (16g/L) exhibited a greater percentage removal of COD. This was the basis for the selection of the dosage in the third experiment. The third long time experiment, currently ongoing, is using the real leachate from CDSL South East step-up station collected on March 9, 2012, with an initial COD concentration of 5270 mg/L and 25 g/L of TiO₂ photocatalyst. The experiment is currently 24 hours in. The COD removal after 24 hours was 39%. Kinetics data was plotted for zero order (Figure 11), first order (Figure 12) and second order (Figure 13) behavior.

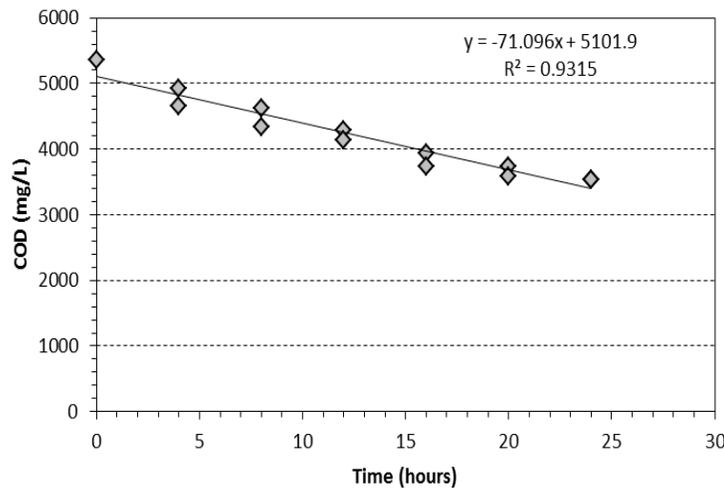


Figure 11. Zero order COD kinetics plot for 24 hour test conducted with 120309 sample from CDSL south east step up station using 25g/L TiO₂.

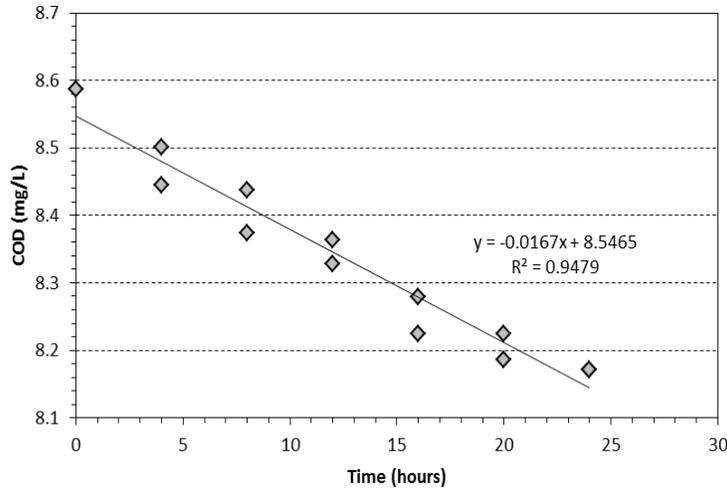


Figure 12. First order COD kinetics plot for 24 hour test conducted with 120309 sample from CDSL south east step up station using 25 g/L TiO₂.

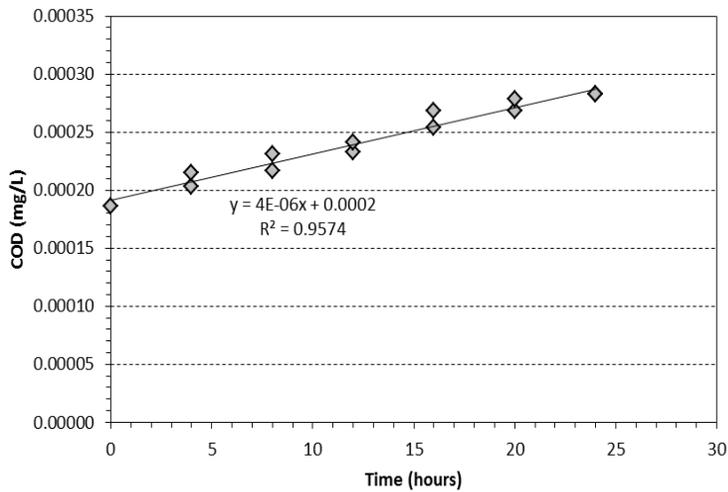


Figure 13. Second order COD kinetics plot for 24 hour test conducted with 120309 sample from CDSL south east step up station using 25 g/L TiO₂.

From inspection of the above plots, the kinetics in this experiment could follow first order or second order. Due to the previous experiments and literature review, the highest collective correlation lies in the first order kinetics. We recommend modeling this removal as a first order reaction.

A juxtaposition of COD removal at 24 hours to show the effect of catalyst dosage was plotted (Figure 14).

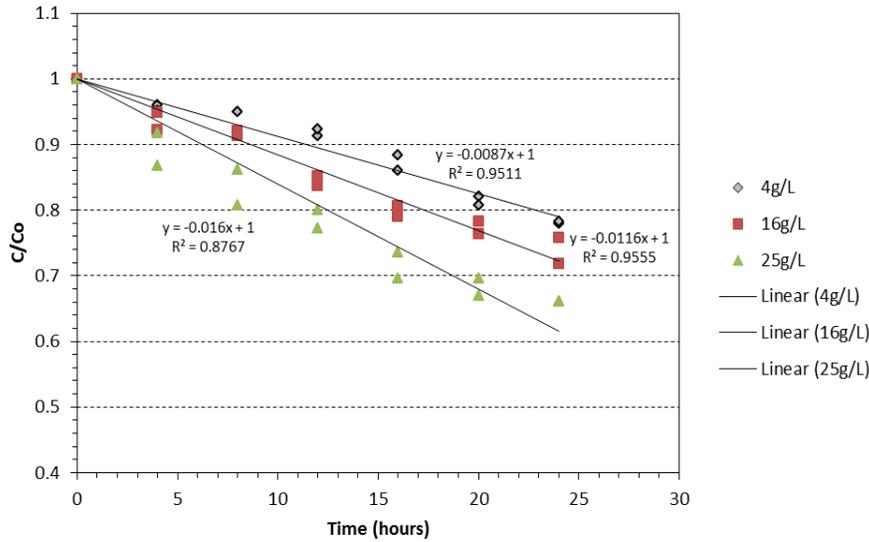


Figure 14. Comparison plot of COD removal after 24 hours for catalyst dosages from first three long time experiments.

The plot above shows that the higher dosage of catalyst (25g/L) exhibited a greater percentage removal of COD at 24 hours. The experiment will still be run to 40 hours to get a full comparison between experiments.

The other parameters will also be monitored and compared for the full 40 hours to better determine the relationship between parameter removal and catalyst dosage. A plot comparing the removal of ammonia and alkalinity for the three experiments at 24 hours can be seen in Figure 15 and Figure 16 respectively.

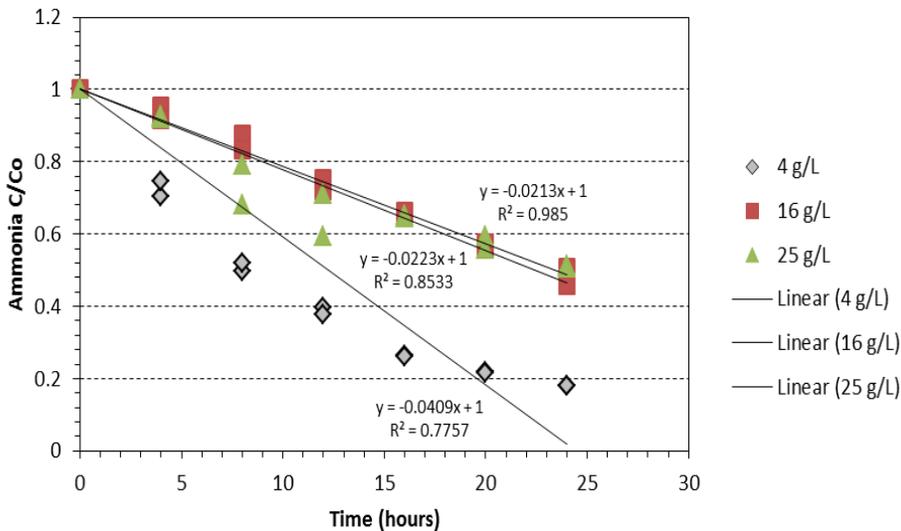


Figure 15. Comparison plot of Ammonia removal after 24 hours for catalyst dosages from first three long time experiments.

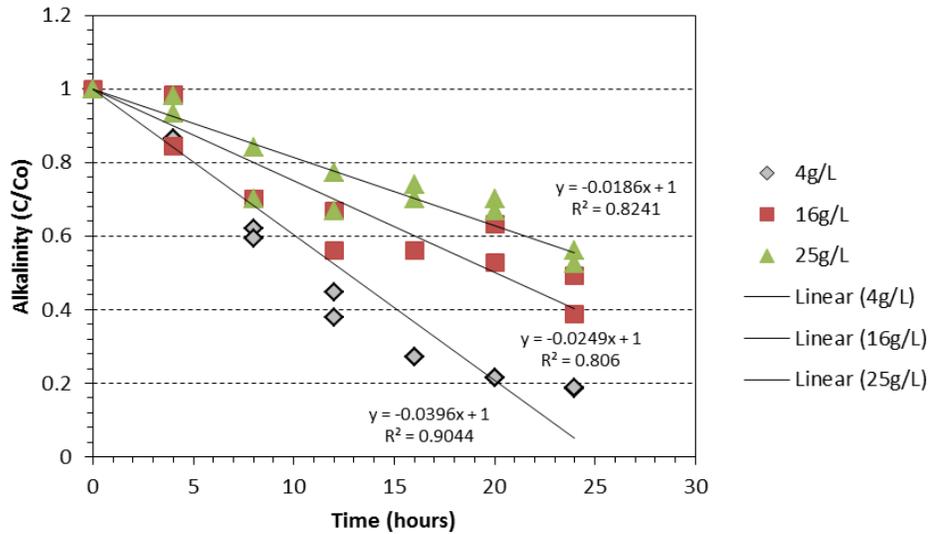


Figure 16. Comparison plot of Alkalinity removal after 24 hours for catalyst dosages from first three long time experiments.

The two graphs above indicate that the highest percentage removal of both alkalinity and ammonia after 24 hours occurs at the lowest dosage of TiO_2 photocatalyst (4g/L). One point to be made is that the lower dosages of catalyst showed highest removal of alkalinity and ammonia but exhibited less effective removal of COD, comparatively.

One issue that has arisen in these experiments is that of leachate dilution resulting from daily rinse water trapped in the advanced oxidation unit. The machine is rinsed daily with tap water after every four-hour run, and a small amount of the water does not drain out of the system. It collects and remains in the weir and various locations throughout the plumbing of the unit. After the current (third) experiment is completed, the unit will be taken apart to determine exactly where and how much water remains in the system during these cleanings. Depending on the amount of dilution, this could result in a percentage correction for all tested data.

- 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 three progress reports have been created and submitted. A TAG 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.

Work is continuing on preparation of the draft final report and a draft scholarly review article.