SUMMARY: INVESTIGATION OF ENERGIZED OPTIONS FOR LEACHATE MANAGEMENT

Daniel E. Meeroff (PI), C. T. Tsai (Co-PI)

Because of widely varying practices in solid waste management across the State of Florida, an understanding of emerging issues and an inclusive solution to long-term management of landfill leachate is currently not available. Leachate is typically too strong to be discharged to classical wastewater treatment systems, and deep well injection systems are becoming increasingly more difficult to implement in certain portions of the State of Florida. 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 include the futuristic photochemical iron-mediated aeration (PIMA) and TiO_2-magnetite photocatalytic technologies.

This research will build upon the FCSHWM-funded project entitled, "*Investigation of options for management of leachate and wastewater*," directed by Dr. J.D. Englehardt and Dr. D.E. Meeroff, who were the first to successfully demonstrate the iron-mediated aeration (IMA) process for in-situ remediation of organic and metallic contaminants in soil and groundwater at former nuclear weapons facilities managed by the U.S. Department of Energy, in laboratory tests. The IMA process was shown to remove 99.996 percent of arsenic and 99 percent of organic contamination from a high strength organic wastewater, with costs projected at one order of magnitude lower than competing processes. Dr. Meeroff designed the first photochemically-assisted iron-mediated aeration (PIMA) reactor and performed the first experiments to demonstrate its effectiveness using ethylenediamine tetraacetic acid (EDTA) and cadmium metal as the model contaminants. Results showed that PIMA accelerated reaction kinetics by a factor of 6 compared to non-energized controls without pH adjustment or chemical addition, indicating the potential that PIMA can be more rapid, and perhaps more thorough, than natural biodegradation and some forms of passive treatment (e.g. non-energized iron mediated aeration). Regarding photocatalytic nanoparticles, Dr. C.T. Tsai is a pioneer in this field and has recently developed a TiO_2-magnetite nanopowder through a collaboration between Florida Atlantic University and Dr. Xudong Sun (visiting research professor at FAU from Northeastern University, China) using a novel microemulsion method to coat a magnetic substrate for military applications. However, these nanoparticles have characteristics suitable for water treatment applications and are an excellent candidate for long-term leachate management. Dr. Tsai (Department of Mechanical Engineering) and Dr. Meeroff (Director of the Laboratories for Engineered Environmental Solutions) have teamed up to establish the Florida Atlantic University Nanoparticle Applications Laboratory to investigate other engineering uses of nanocatalysts.

The objectives of the research are to:

1. To examine the literature on energized alternatives for detoxification and treatment of leachate; collect leachate quality data; identify issues/trends associated with long-term leachate management; and prepare a list of energized alternatives ranked according to environmental sustainability, efficiency, risk, and economic factors.
2. To design and test laboratory reactors for leachate treatment using energized options such as the photochemical iron-mediated aeration technology (PIMA) and TiO_2-magnetite photocatalytic processes.
3. To prepare preliminary cost analyses and risk assessments on selected technologies to provide a Florida-specific matrix of engineering alternatives that are innovative, economical, and environmentally sound to aid solid waste management personnel in decision-making.

Before the grant was awarded in 2005, Eli Brossell (undergraduate) and Courtney Skinner (graduate) completed construction of the PIMA process reactor. It is functional, and the aeration system has been calibrated. Courtney Skinner, Tammy Martin (Lanny Hickman Internship Program) and François Gasnier have begun work towards their masters thesis on this project. Ms. Skinner and Mr. Gasnier conducted validation testing and method development of the equipment required to evaluate the concentrations of the six target pollutants (Pb, conductivity, TDS, ammonia, COD and BOD_5) to be monitored during performance testing of the photochemical oxidation technologies. The aim is to determine the conditions necessary to allow for safe discharge of treated leachate to the sanitary sewer or reuse on site. Using existing data on currently available technologies in conjunction with performance data generated from laboratory tests to develop unit treatment costs for scale-up, a matrix of Florida-specific engineering alternatives that are innovative, economical, and environmentally sound will be developed to aid solid waste management personnel in decision-making. This tool will help to address current barriers to the use of futuristic technologies for reducing toxic loads in water, wastewater, and soils in addition to leachate.

PROGRESS REPORT

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Project Title: Investigation of energized options for leachate management
Principal Investigators: Daniel E. Meeroff, C. T. Tsai
Affiliation: FAU
Phone number: (561) 297-3099
Project website: http://slab.civil.fau.edu/~daniel/labees/html/leachate.html

Work accomplished:

- A literature review is ongoing concerning the photochemically-assisted iron-mediated aeration (PIMA) process and the TiO_2-magnetite photocatalysis process. Leachate composition data have been collected and composite characterization of typical leachate quality has been assembled. It appears that Florida leachate is slightly weaker than the worldwide average, likely due to higher local rainfall, which increases dilution. Table 1 summarizes these results.

Table 1: Average leachate composition

	Ammonia in mg/L as N		Conductivity in µS/cm		COD in mg/L as O2		Lead in mg/L	
	Average	Range	Average	Range	Average	Range	Average	Range
Global	844	0.1 - 8,752	13,467	5.2 - 95,000	10,573	0.4 - 152,000	0.11	BDL* - 5.0
Florida	488	BDL - 800	12,070	1,000 - 95,000	2,990	55 - 13,960	0.030	BDL - 0.1

	TDS in mg/L		TSS in mg/L		BOD5 in mg/L		pH	
	Average	Range	Average	Range	Average	Range	Average	Range
Global	11,404	0.0 - 88,000	843	10 - 45,000	4,092	BDL - 80,800	7.5	2.0 - 11.3
Florida	9,716	900 - 88,000	-	-	148	BDL - 445	7.5	2.0 - 11.3

- The second goal is to produce a matrix of different technologies, ranked according to process performance (removal efficiency of selected pollutant classes), economics, and risk. This work is underway and ongoing. Table 2 and Table 3 are presenting some preliminary results concerning this part of the literature review. They clearly demonstrate the benefices of using AOPs over traditional on-site techniques. Equally, the addition of UV energy improves the performances of the AOPs.

Table 2: Comparative statement of the AOPs and EPs on COD

Technology		% COD removal	Source
AOP	H_2O_2	16	Loizidou et al. (1993)
	Fenton	35	Loizidou et al. (1993)
	Ozone	35	Imai et al. (1998)
	H_2O_2	60	Shu et al. (2006)
	Fenton	61	Englehardt et al. (2005)
EP	UV / O_3	54	Ince (1998)
	UV / H_2O_2	59	Ince (1998)
	UV / H_2O_2	65	Shu et al. (2006)
	Photo-Fenton	70	Soo-M. Kim et al. (1997)
	UV / O_3 / H_2O_2	89	Ince (1998)
	IMA	56	Englehardt et al. (2005)
	PIMA	??	Present work

Table 3: Comparative statement of on-site treatment techniques on COD

Technology	% COD removal	Source
Coagulation and flocculation	23	Silva et al. (2003)
Coagulation and flocculation	60	Wu et al. (2004)
Reverse osmosis	68	Slater et al. (1983)
Acclimated sludge	93	Anagiotou et al. (1993)

- Design and construction of the PIMA pilot scale reactor (see Figure 1 below) is complete, and pilot scoping tests with simulated leachate and mixtures have been completed.
- Method development for monitoring the concentration of the six target pollutants (Pb, conductivity, TDS, ammonia, BOD_5 and COD) is complete. Standard operating procedures for these components have been developed and approved. Figure 2 shows François Gasnier analyzing an ammonia sample.
- The first experimental phase is finished: individual scoping tests on the six components have been completed. Figure 4 to Figure 9 below are graphs showing the results obtained during these scoping tests. Table 7 summarizes the maximum removal percentages obtained after 16 hours of treatment (unless stated otherwise in the remarks) and the initial values.
- The second experimental phase is also complete. Mixtures containing low, middle and high levels of the parameters of interest have been tested. Table 8 summarizes

the maximum removal percentages obtained after 16 hours of treatment. The analysis of these results is ongoing.

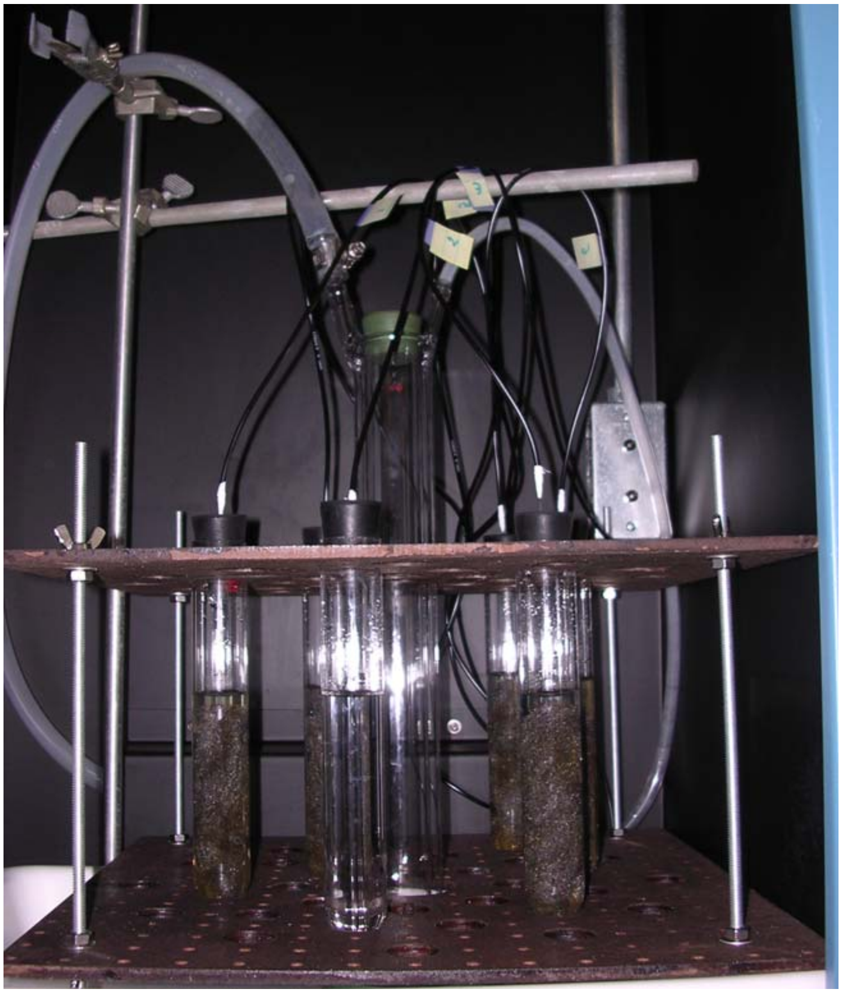

Figure 1: PIMA process reactor

Figure 2: Experiments to validate the ammonia meter.

Significant results:

- The PIMA reactor is operational and performance data is still being collected. The reactor is able to handle up to eight different samples simultaneously. Typically, one of the samples is an IMA process control, a second sample is a UV control without iron, and the six remaining samples are run using the PIMA process with 3 different UV intensities possible, given the configuration of the reactor. This setup allows for the research team to collect multiple replicates during the same experiment. The reactor design has been updated after the completion of the individual scoping tests as shown in Figure 3.

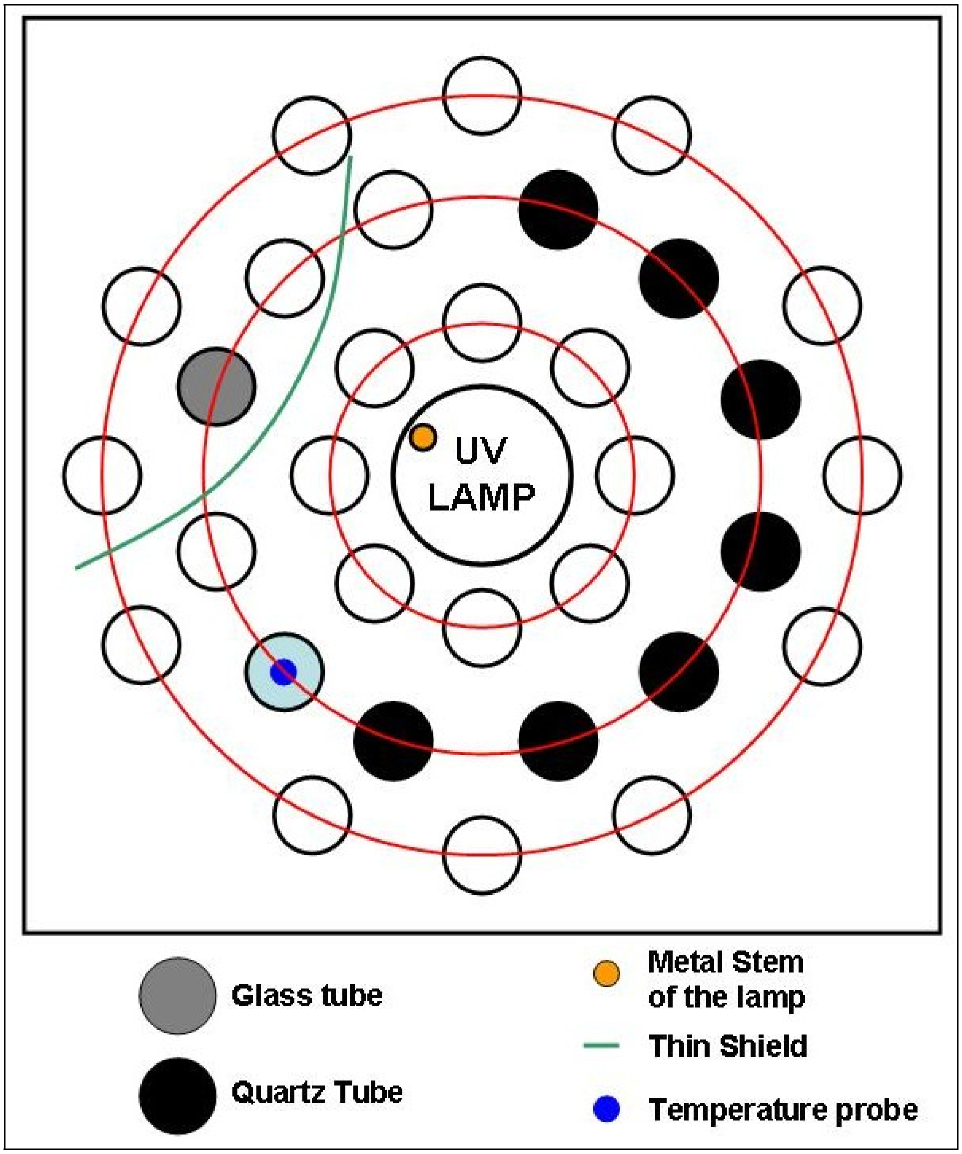

Figure 3: Reactor configuration with test tubes placement

- The aeration delivery system has been upgraded, and the air flow rate is checked with a digital flowmeter, prior to each experiment. Figure 10 is a picture of the system, and Table 4 summarizes the recorded air flow measurements.

Table 4: Air flow measurements

	Flow path	Date of measurement 05/03/06	05/04/06
Air flow in L/min	1	0.138	0.130
	2	0.101	0.110
	3	0.093	0.109
	4	0.054	0.067
	5	0.152	0.196
	6	0.202	0.338
	7	0.206	0.435
	8	0.080	0.089

- UV intensity has been measured. Table 5 below summarizes the results obtained. Measurements have been conducted a second time, after approximately 290 hours of utilization. The intensity declined by 27 percent.

Table 5: UV intensity measurements and calculations

Parameters	Distance: Close	Middle	Far
Distance from the lamp in cm	6.3	10.2	15.2
Irradiance in mW/cm^2	56.7	21.6	9.7
Intensity in mW	2251.5	2251.5	2251.5

- During every experiment, each of the following parameters is evaluated: temperature, pH, dose of iron, and residence time.
- In terms of PIMA process performance measured during the individual scoping tests, the following were found:
  - COD: After 24 hours, the highest removal efficiency recorded was 40 percent with an initial concentration of approximately 10,000 mg/L (high level). However, after 16 hours, the highest removal efficiency recorded was 50 percent with an initial concentration of approximately 3,000 mg/L (medium level).
  - Conductivity and TDS: After 2 hours, initial removal efficiency was low and concentrations started to increase due to the dissolution of iron and the reduction in volume due to evaporation.
  - Ammonia: No to low removal was observed. After additional research and experiments, the acidic pH of the simulated leachate is likely responsible for these results. Ionized aqueous ammonia exists in equilibrium with gaseous ammonia as shown in the following equation:

$$NH_4^+ \longleftrightarrow NH_{3(\uparrow)} + H^+$$

The pKa of the NH_4^+/NH_3 couple is 9.2. Since the unadjusted pH was recorded to be below 7.0 during each experiment, ammonia did not strip out of the simulated leachate. An additional experiment where the pH was adjusted to a higher value than this pKa verified this conclusion. An additional experiment is planned to establish the influence of reactor design in limiting mass transfer to the gaseous phase.

- BOD_5: After 16 hours of treatment, an average of 44 percent removal was observed on the high concentration level. The addition of UV greatly increased the action of IMA process for the decrease of BOD_5 modeled by glucose and glutamic acid. Indeed, in the same amount of time, the IMA process removed only 28 percent of the initial BOD_5.
- Lead: After 16 hours of treatment, a removal greater than 99.97 percent was achieved with the PIMA process. As noticed during the literature review, the IMA process also achieved a removal greater than 99.96 percent for metals such as arsenic. On the other hand, the UV control process, achieved only a removal of 54 percent.

- Because iron is a reactant or catalyst for the PIMA process, the iron concentration was measured after a 24-hour experiment. This was done using a colorimetric technique (Method 8214: TitraVer Titration Cartridge, from Hach). Results showed a concentration of 200 mg/L in the process effluent. Other samples were sent to a certified laboratory for analysis and showed disparate iron concentration in the effluent of multiple replicates. Results were repeated for verification. Table 6 below summarizes these results. Complementary measurements will be made with real leachate samples. No correlation of dissolved iron levels with treatment efficiency was found so far. This discovery deserves further investigation.

Table 6: Iron concentration in the effluent

	Experiment 14, Lead Medium		Experiment 15, mixture Medium	Experiment 16, Lead Medium	Experiment 15, mixture Medium
	Iron concentration in the effluent after 16 hrs in mg/L		**Iron concentration in the effluent after 16 hours in mg/L**	**Iron concentration in the effluent after 4 hours in mg/L**	**Iron concentration in the effluent after 16 hours in mg/L**
Process	Measurement 1	Measurement 2			
IMA, x = 10.2 cm	U	U	110.00	16.00	-
PIMA, x = 6.3 cm	U	U	20.00	-	-
PIMA, x = 6.3 cm	U	U	58.00	-	-
PIMA, x = 10.2 cm	4.40	3.70	52.00	67.00	4.50
PIMA, x = 10.2 cm	4.50	6.80	-	0.15	6.30
PIMA, x = 10.2 cm	-	-	-	-	6.90
PIMA, x = 10.2 cm	-	-	-	-	8.10
PIMA, x = 15.2 cm	7.50	6.30	-	-	-
PIMA, x = 15.2 cm	0.15	0.13	-	-	-

U The concentration was measured below the MDL of = 0.075 mg/L

- The iron was not measured for during this test

Next step:

- Pursue the literature review to complete the ranking of leachate treatment alternatives
- Complete the cost analysis of candidate alternatives
- A visiting scholar, Swapnil Jain, from the India Institute of Technology has been hired to assist the team with TiO_2-magnetite process testing.
- Dr. Chen has synthesized the first TiO_2-magnetite nanoparticles at FAU. He will begin the process of manufacturing sufficient particles to begin scoping tests with Mr. Jain.
- Testing of PIMA with actual leachate collected from the Solid Waste Authority of Palm Beach County is underway.

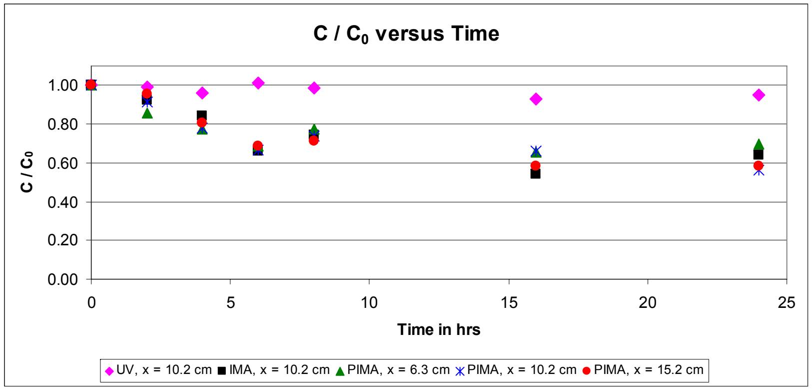

Figure 4: COD scoping tests results

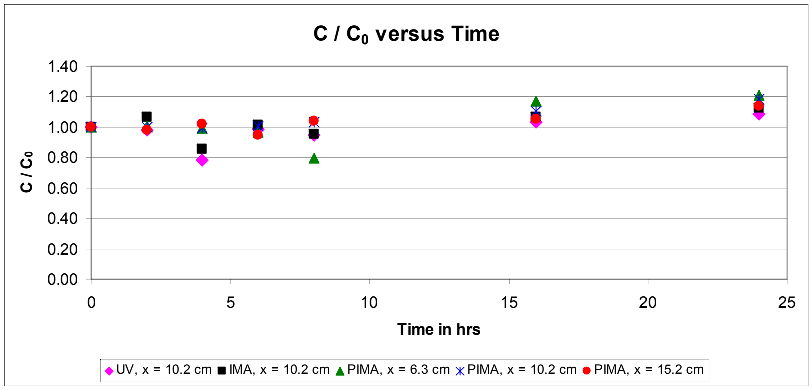

Figure 5: Conductivity scoping tests results

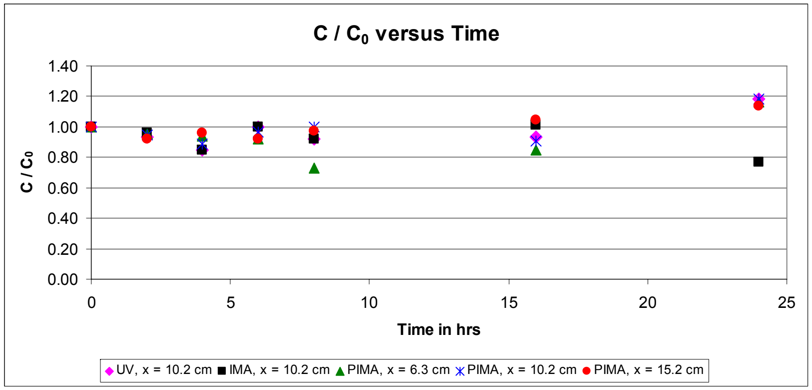

Figure 6: TDS scoping tests results

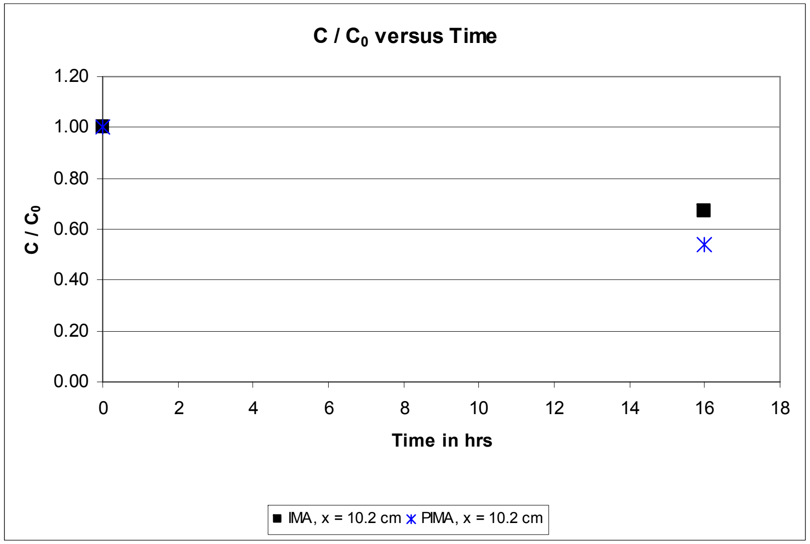

Figure 7: BOD_5 scoping tests results

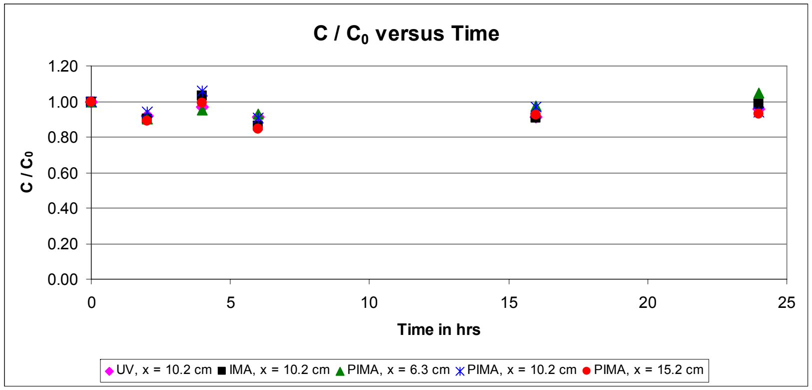

Figure 8: Ammonia scoping tests results

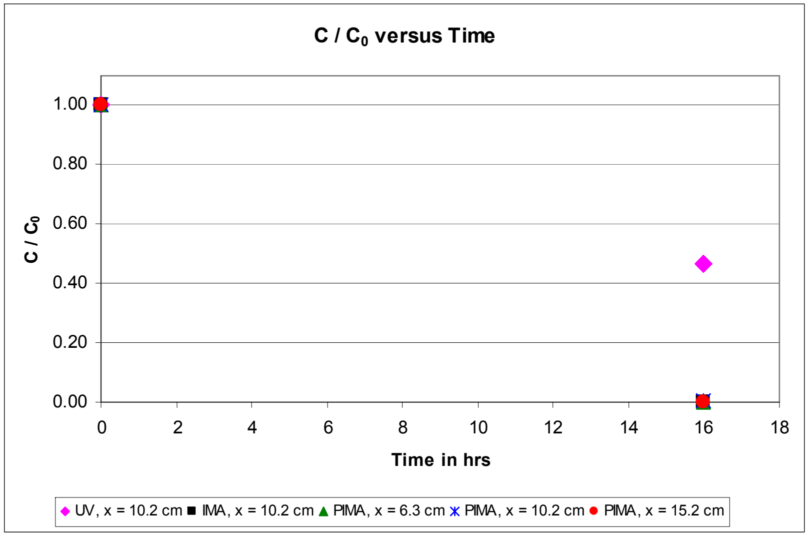

Figure 9: Lead scoping tests results

Table 7: Best removal percentage observed during individual scoping tests.

		COD			Conductivity			TDS		
		Low	Medium	High	Low	Medium	High	Low	Medium	High
Starting concentration or value		1.05	3.30	10.90	2,750	16,250	81,625	0.83	8.12	40.00
Process	IMA, x = 10.2 cm	21	53	39	-3	-14	-2	-	-3	0
	UV, x = 10.2 cm	-	11	3	3	-19	2	-	8	6
	PIMA, x = 6.3 cm	54	42	35	-26	-16	-9	-	38	-8
	PIMA, x = 10.2 cm	51	49	29	-12	-14	0	-	13	3
	PIMA, x = 15.2 cm	44	52	32	6	-12	-3	-	-8	-1
Remarks		concentrations in g/L as O_2 values after 24 hrs			values in µS/cm			concentrations in g/L Sensitivity issue		

		BOD_5			Ammonia			Lead
		Low	Medium	High	Low	Medium	High	Medium
Starting concentration or value		55	120	425	110	540	930	0.30
Process	IMA, x = 10.2 cm	38	-	28	-5	24	-8	99.96
	UV, x = 10.2 cm	-	100	-	-2	20	-12	53.33
	PIMA, x = 6.3 cm	-	-	-	-16	21	-4	99.97
	PIMA, x = 10.2 cm	39	55	44	-13	19	-3	99.97
	PIMA, x = 15.2 cm	-	-	-	-5	22	13	99.97
Remarks		concentrations in mg/L as O_2			concentrations in mg/L as NH_3-N values after 24 hrs			concentration in mg/L

Table 8: Best removal percentage observed during mixture scoping tests.

		COD			Conductivity			TDS		
		Low	Medium	High	Low	Medium	High	Low	Medium	High
Starting concentration or value		0.74	3.83	11.60	3,915	28,250	78,750	0.17	13.34	43.75
Process	IMA, x = 10.2 cm	28	36	20	2	2	14	0	0	23
	UV, x = 10.2 cm	40	3	14	2	2	19	0	0	20
	PIMA, x = 10.2 cm	38	28	33	5	0	10	0	-2	19
Remarks		concentrations in g/L as O_2			values in µS/cm			concentrations in g/L Sensitivity issue	Sensitivity issue	

		BOD_5			Ammonia			Lead		
		Low	Medium	High	Low	Medium	High	Low	Medium	High
Starting concentration or value		> 417	-	> 1,650	52.5	470	-	0.07	0.3	0.3
Process	IMA, x = 10.2 cm	> 37	-	-	-13	10	-	-	95	> 99.97
	UV, x = 10.2 cm	> 65	-	-	-25	12	-	-	3	79
	PIMA, x = 10.2 cm	> 48	-	*	-15	7	-	77	98	> 99.95
Remarks		concentrations in mg/L as O_2	No results		concentrations in mg/L as NH_3-N		No results	concentration in mg/L		

- No results obtained (experiment not completed)
* Can not conclude due to the inequality

Here are some more pictures of the student working on the project.

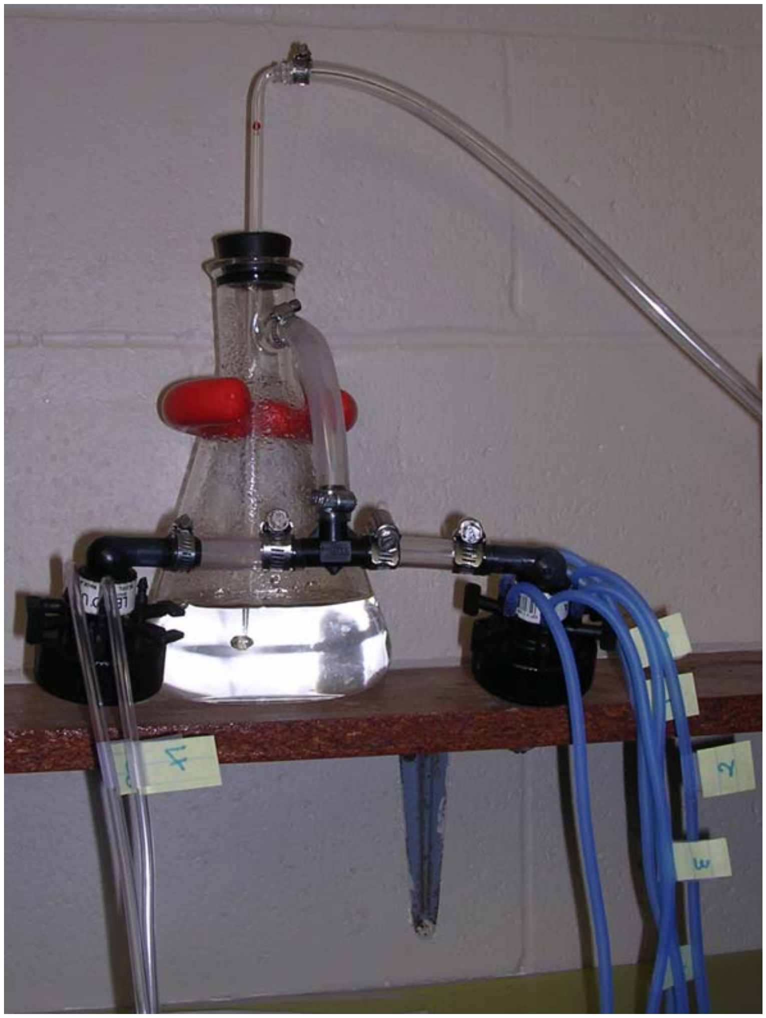

Figure 10: Upgraded aeration system.

Figure 11: Laboratory bench scale ammonia analyses.

Figure 12: Disposal of the hazardous waste collected during NH_3 testing.

Figure 13: Preparation of the COD tests.

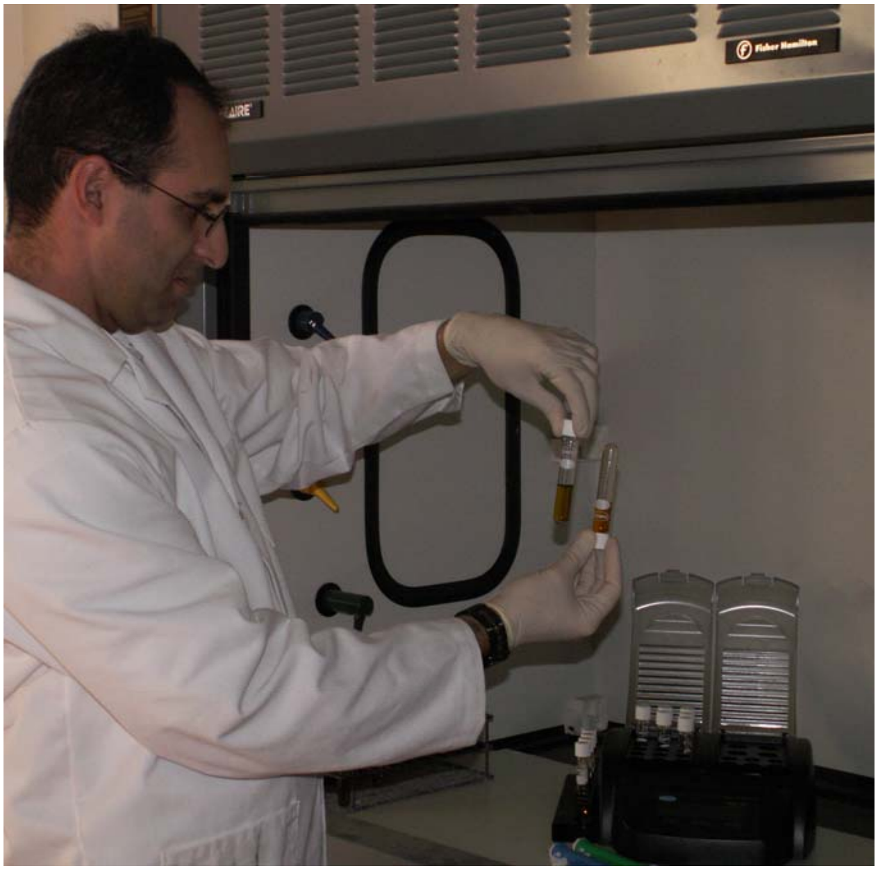

Figure 14: Dr. Meeroff performing chemical oxygen demand tests

Figure 15: Checking the light sensitivity of the new PIMA photoreactor.

Figure 16: Measurement of the air flow rate.