Liquid and Solid for Fenton Oxidation of Leachate

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February 10, 2012

Outline

- Problem Statement
- Liquid Hydrogen Peroxide
- Solid Calcium Peroxide
- Theoretical Foundations
- Experiments
- Scheduled Activities
- References

Statement of Problem

Landfill Leachate

- BL is promising technology to generate methane as renewable energy.
- Leachate is difficult to be biodegraded if the landfill ages.
- Leachate biodegradability decrease significantly with landfill age

Conventional Pollutants in Typical Leachate

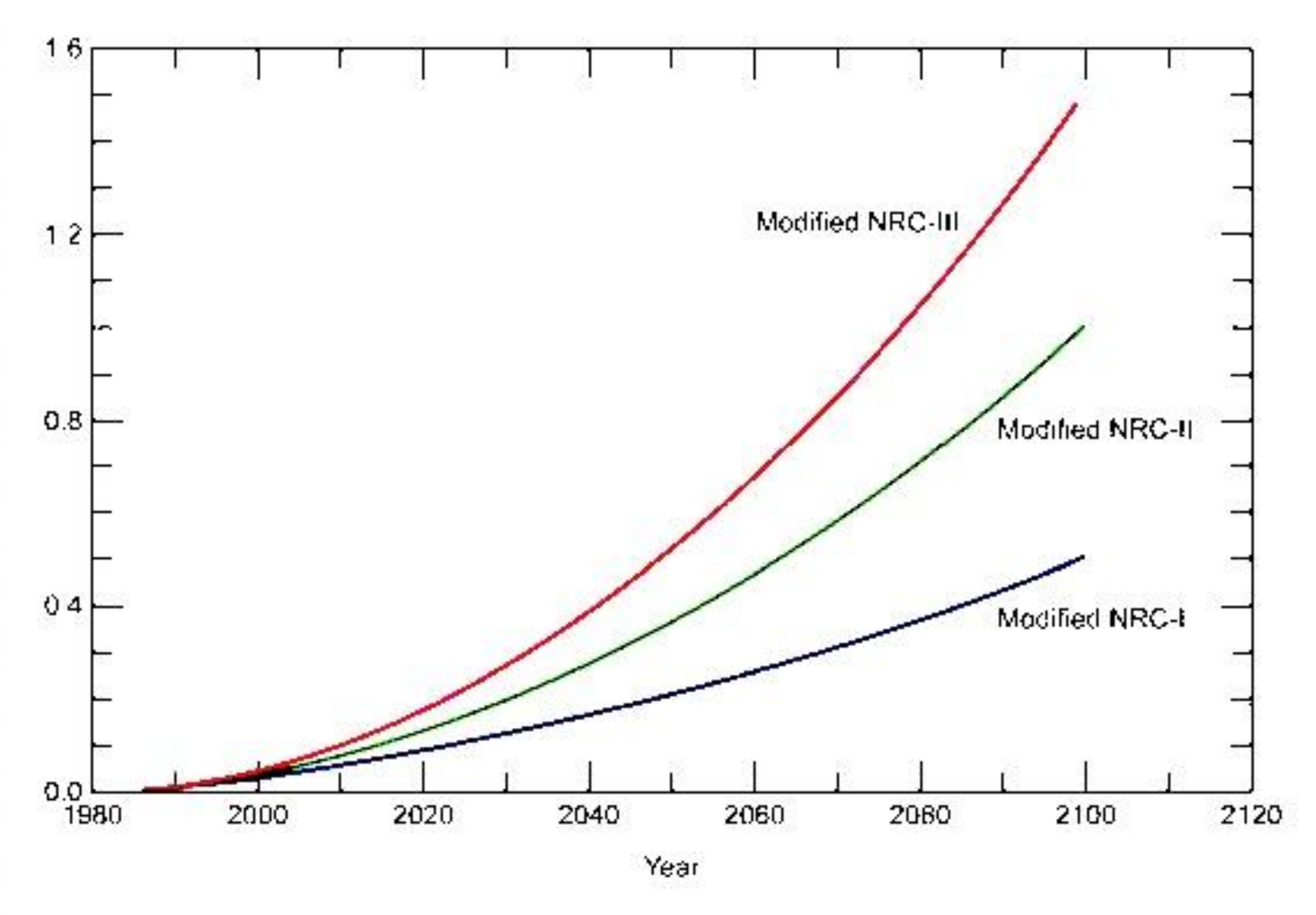
mg/L (except pH)

Constituent	New Landfill (< 2yrs) Range	Typical	Mature Landfill (> 10 yrs)
BOD_5	2,000-30,000	10,000	100-200
TOC	1,500-20,000	6,000	80-160
COD	3,000-60,000	18,000	100-500
Total suspended solids	200-2,000	500	100-400
Organic nitrogen	10-800	200	80-120
Ammonia nitrogen	10-800	200	20-40
Nitrate	5-40	25	5-10
Total phosphorus	5-100	30	5-10
Ortho phosphorus	4-80	20	4-8
Alkalinity as $CaCO_3$	1,000-10,000	3,000	200-1,000
pH	4.5-7.5	6	6.6-7.5
Total hardness as $CaCO_3$	300-10,000	3,500	200-500
Calcium	200-3,000	1,000	100-400
Magnesium	50-1,500	250	50-200
Potassium	200-1,000	300	50-400
Sodium	200-2,500	500	100-200
Chloride	200-3,000	500	100-400
Sulfate	50-1,000	300	20-50
Total iron	50-1,200	60	20-200

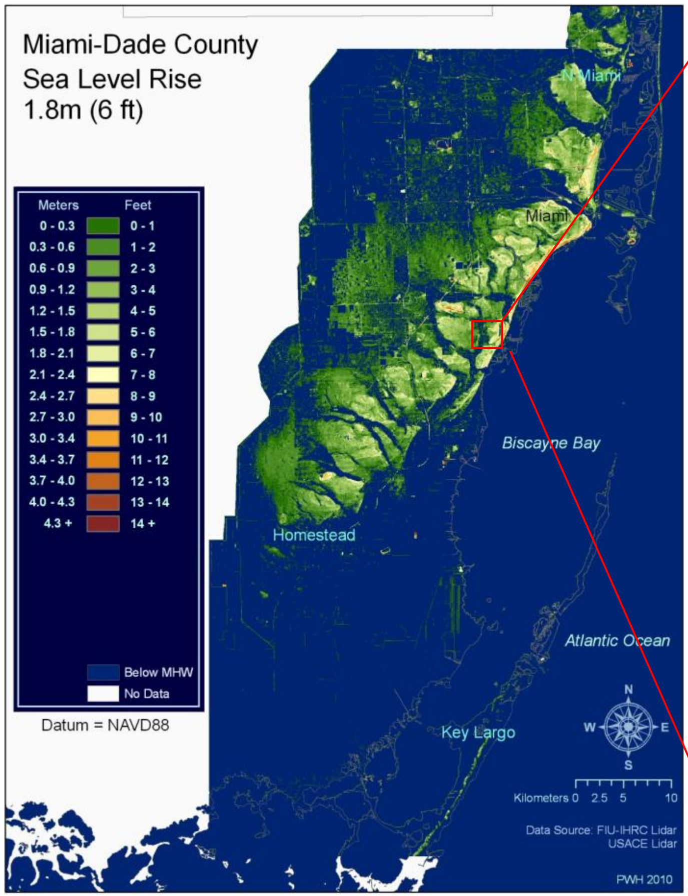
Relative Biodegradability of Leachate

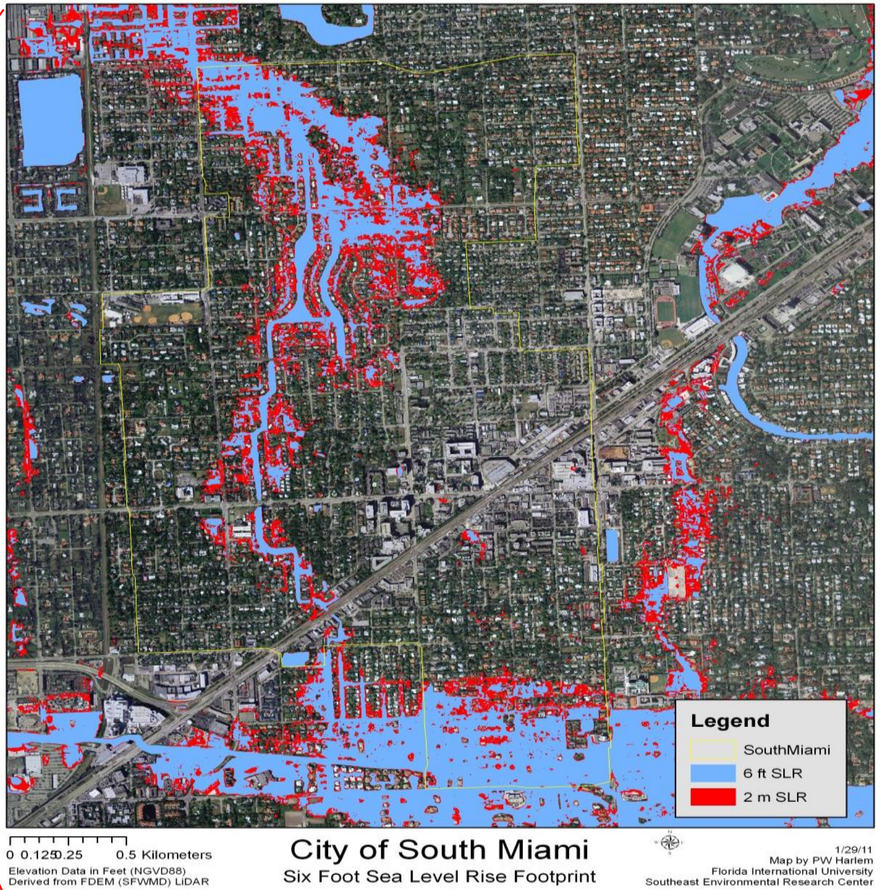
Bio-degradability	BOD/COD	COD/TOC
Low	< 0.5	< 2
Medium	0.5 – 0.75	2 – 3
High	> 0.75	> 3

Projected Sea Rise in Meters Used by the US Army Corps



Miami-Dade County at SLR of 1.8 m





South Dade Landfill

- Address: 23707 SW 97 Ave, Miami, FL 33190
- Soid Wastes:
  - Garbage
  - Trash
  - Yard Trash
  - Off road tires (48" in diameter or larger)
  - Automobile
  - Construction and demolition debris
  - Dead Animals

Combining Landfill Gas and Wastewater Plants

- Landfill gas, produced at the Solid Waste Department's South Dade Landfill, will be collected and piped to the treatment plant, where it will be mixed with digester gases to create electricity.
- Combining landfill and digester gases will let the county increase the amount of self-generated electricity it produces, reducing Miami-Dade's consumption of electricity from fossil fuel.
- The project has potential to produce 63,800 kilowatts each day and could generate 40 jobs

Increasing Biodegradability Using FR for Bioreactor Landfill Is the Answer?

- Increase potential for waste to energy conversion,
- Store and treat leachate,
- Recover air space,
- Ensure sustainability.

Status

- 1993 - less than 20 landfills recirculating leachate
- 1997 - ~ 130 landfills recirculating leachate
- Dr. Reinhart estimated 5-10% of landfills recirculating leachate in 2003.

Leachate On-Site Storage

Leachate Color

Leachate Off-Site Treatment

Treated Leachate Effluent

Objectives

- Compare and develop the most sustainable technology for landfill management that is adaptive to water pollution control, storm water management, and water supplies by using liquid or solid peroxides.

- Quantify infrastructure vulnerability of technologies based on sustainable index of landfill management considering the following factors:

Solid vs. Liquid Peroxides for Sustainable Management of Leachate

- Leachate collection
- Leachate treatment options: solid vs. liquid peroxides
- Cost effectiveness
- Sustainability
- Design criteria
- Geotechnical stability
- Evaluate benefits of increasing biodegradability of leachate using Fenton processes
- Technical challenges
- Design criteria using solid vs. liquid peroxides

- In conventional “dry tomb” landfills, waste biodegradation is very slow because of the lack of adequate moisture. These landfills require long-term monitoring for any potential environmental problems (regarding the water and air pollution).
- The leachate re-injection or addition of selected liquids to landfill waste (bioreactor) has potential to accelerate waste decomposition and settlement, but will affect the waste properties and slope stability.
- Urgent need exists to accelerate degradation of leachate using Fenton process either using solid vs. liquid peroxides.

Theoretical Foundation

Fenton Reaction Mechanism

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\cdot$ $\quad k=55\ (M^{-1}s^{-1})$

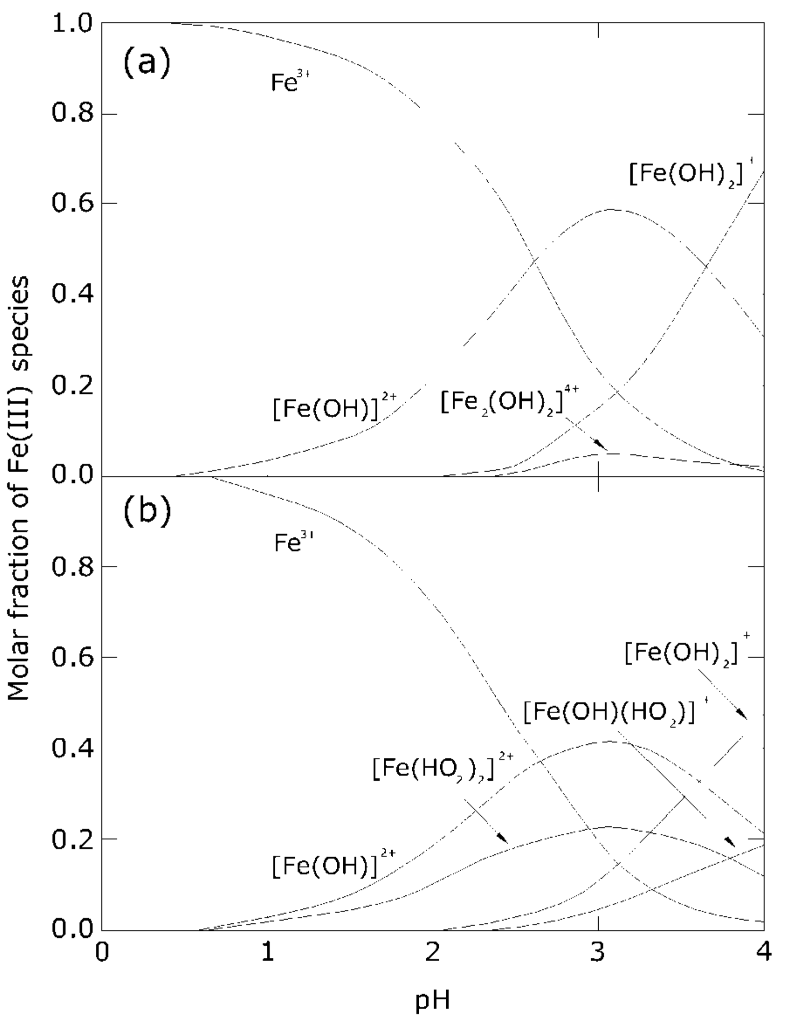
$HO^\cdot + H_2O_2 \rightarrow HO_2^\cdot + H_2O$ $\quad k_{H2O2}=3.3*10^7\ (M^{-1}s^{-1})$

$HO^\cdot + Fe^{2+} \rightarrow Fe^{3+} + OH^-$ $\quad k_{Fe2+}=3.2*10^8\ (M^{-1}s^{-1})$

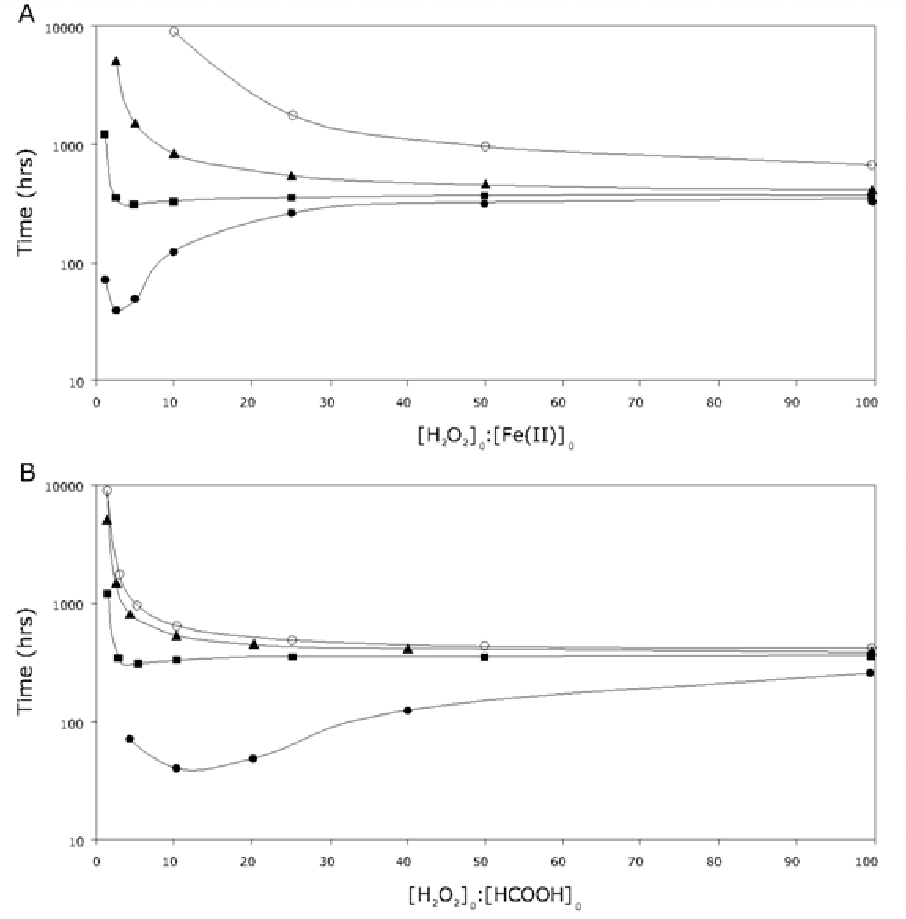
$H_2O_2/Fe^{2+}_{Opt.} = k_{OH,\ Fe2+}/k_{OH,\ H2O2} = 3*10^8/2.7*10^7=11$

(Tang 2004)

Speciation of soluble Fe(III) species in aqueous medium with 0.1 M $NaClO_4$ at 25 ºC: (a) in the presence of 0.5 M H_2O_2 and 0.5 mM Fe^{3+} (Laat 2006).

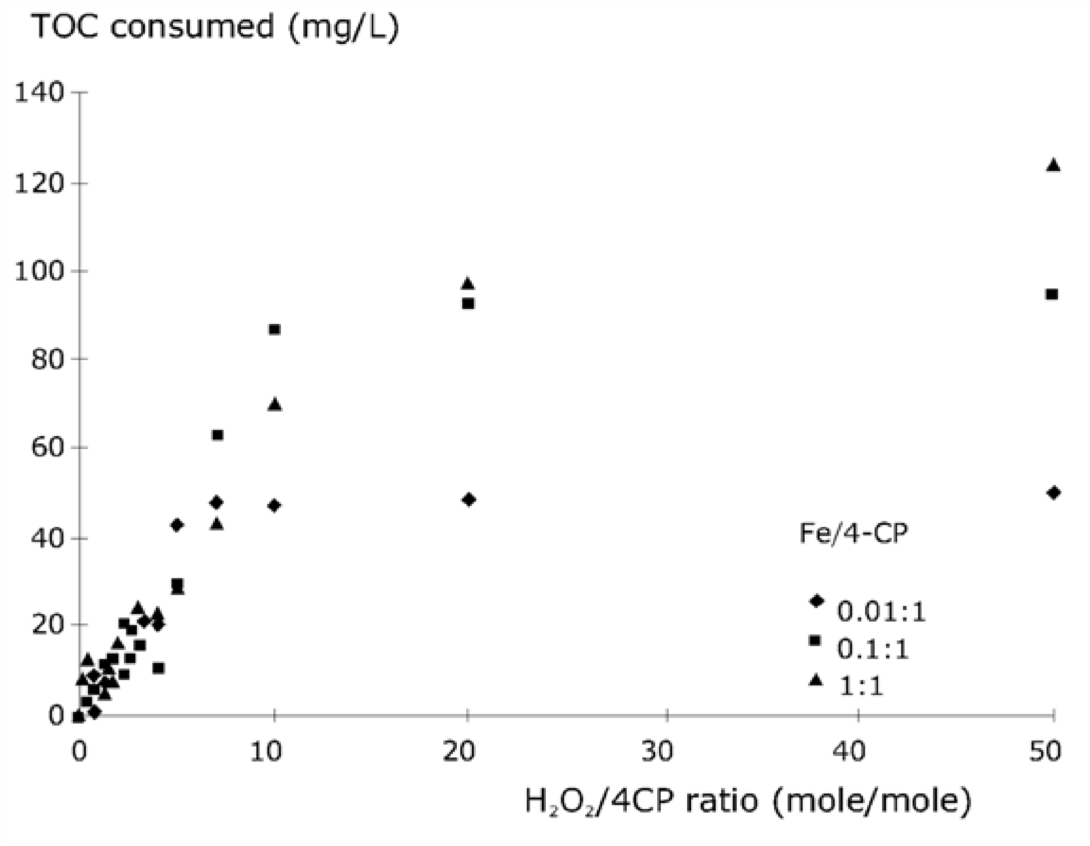


Hydrogen Peroxide to Fe(II) Ratio = 11



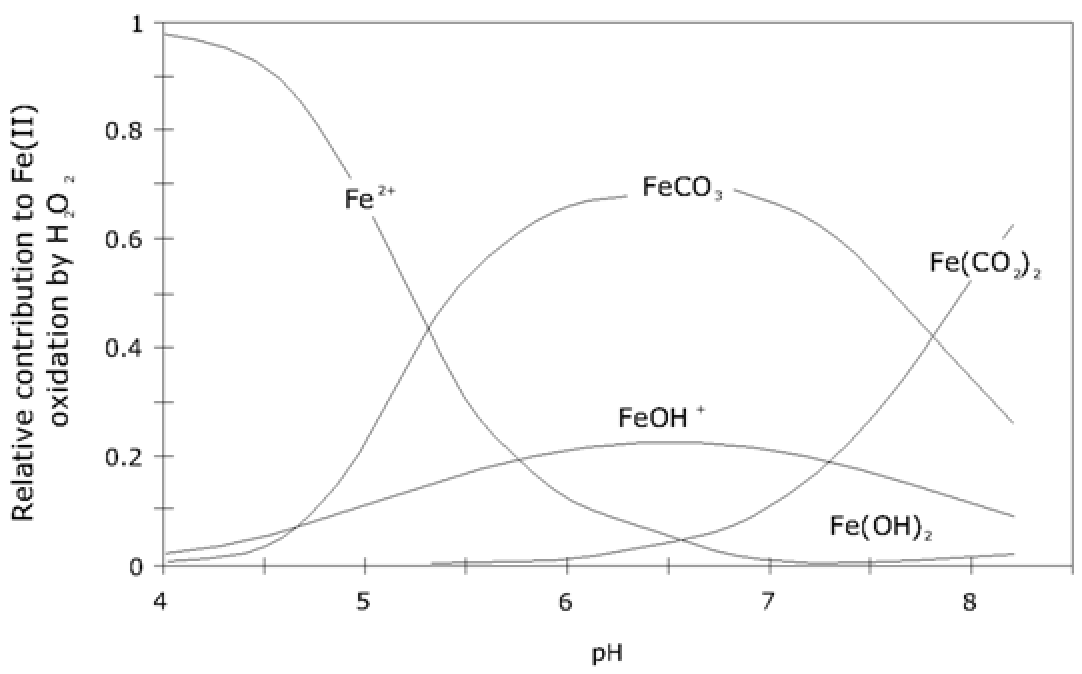
Results of kinetic simulations showing the time required to reach 90% oxidation of HCOOH at pH 3 and in the presence of oxygen. Initial conditions: $(Fe(II))_0$=400nM; $(HCOOH)_0$=100 nM, 400 nM, 1µM, and 4 µM. (Duesterberg and Waite, ES&T, 2006)

Hydrogen Peroxide and Fe (II) Ratio



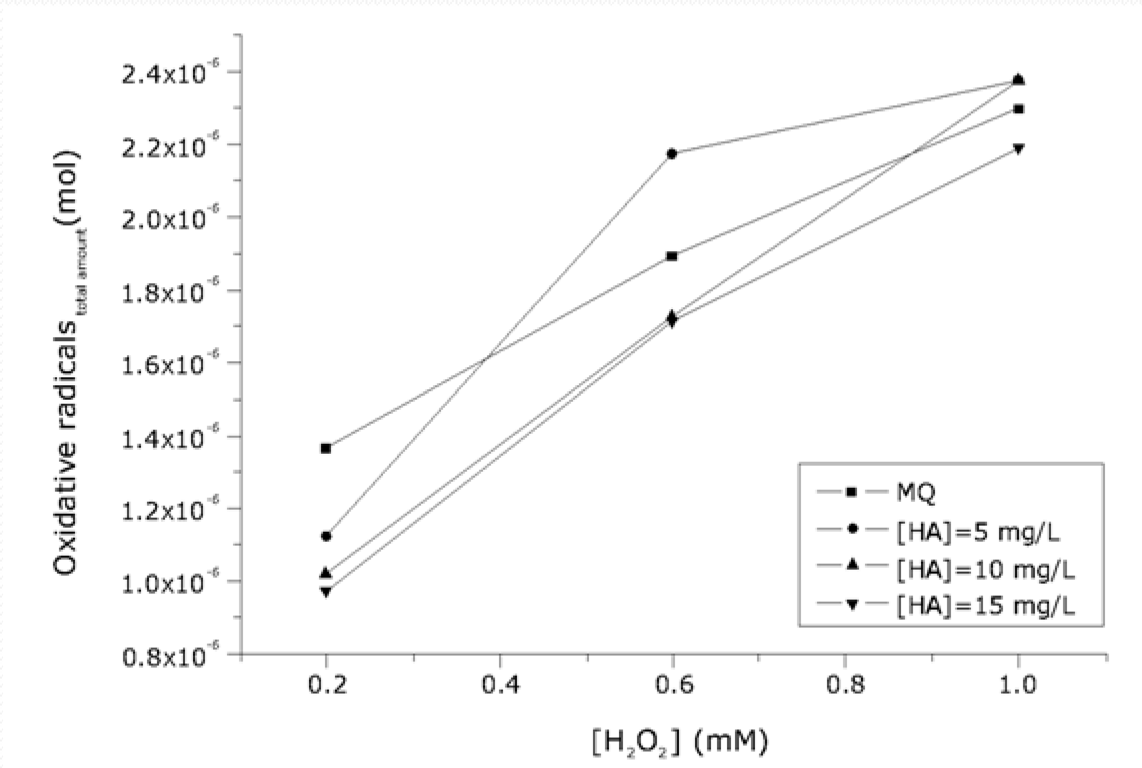
TOC consumed vs. H_2O_2 doses at different Fe(II) ratios.

Contribution of Fe(II) Species Oxidation by Hydrogen Peroxide



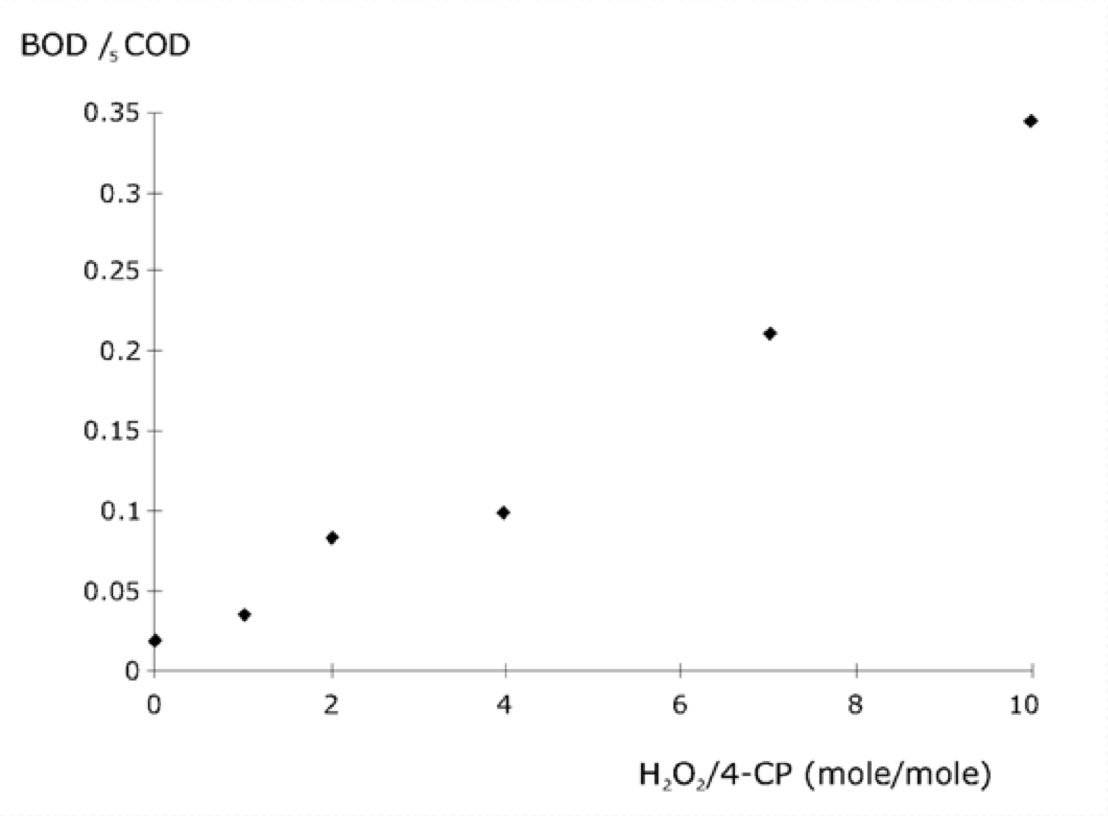
Contribution of specific Fe(II) species in total Fe(II) oxidation rate by H2O2. Calculations are for pure water with 2.0 mM NaHCO3 at 25 ºC

Hydrogen Peroxide Concentration on the Hydroxyl Radical Concentration



Influence of the hydrogen peroxide concentration on the oxidative radicals total amount: results obtained at (Fe(II))=0.365 mM

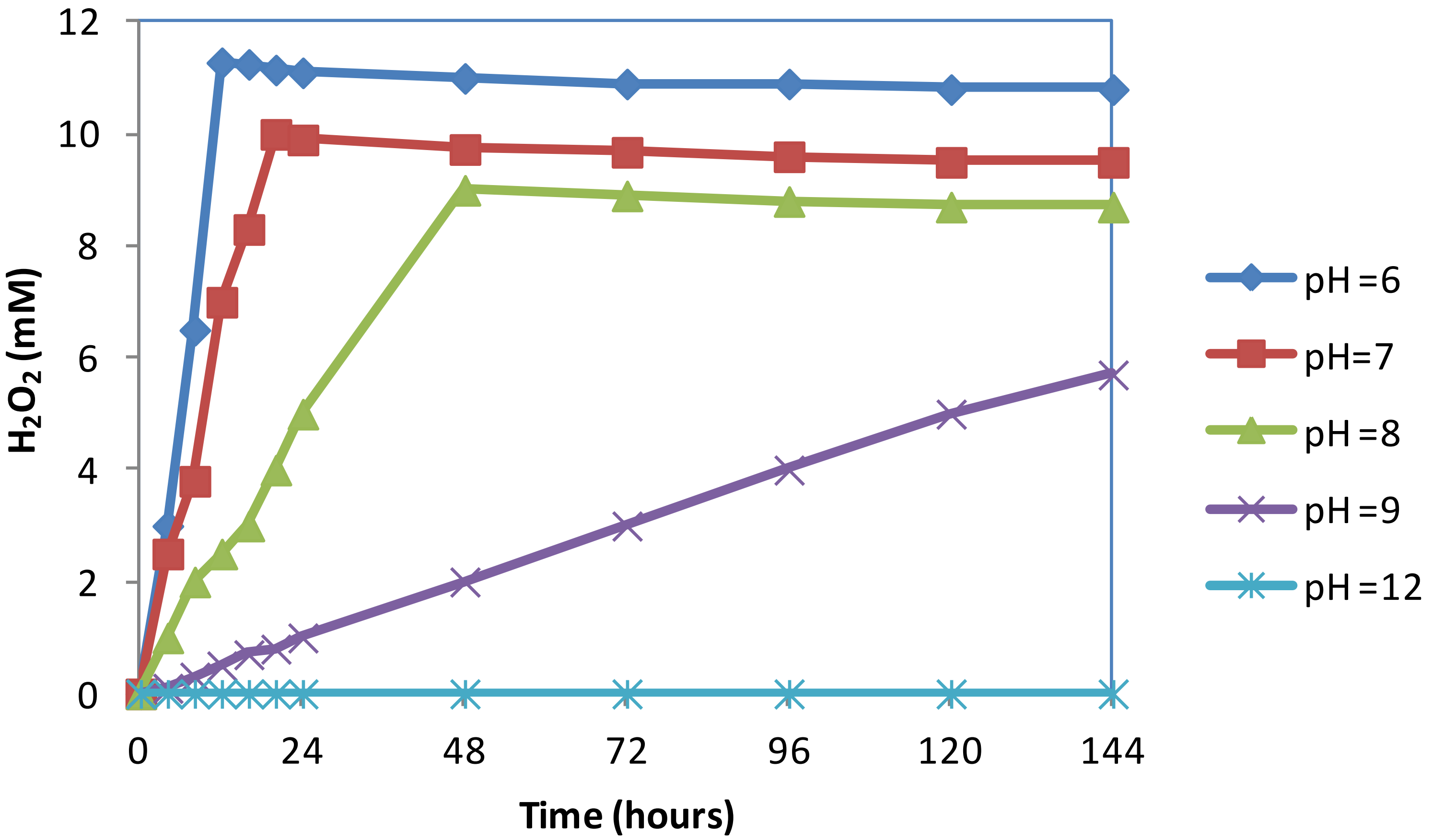
Biodegradability Increases with Hydrogen Peroxide



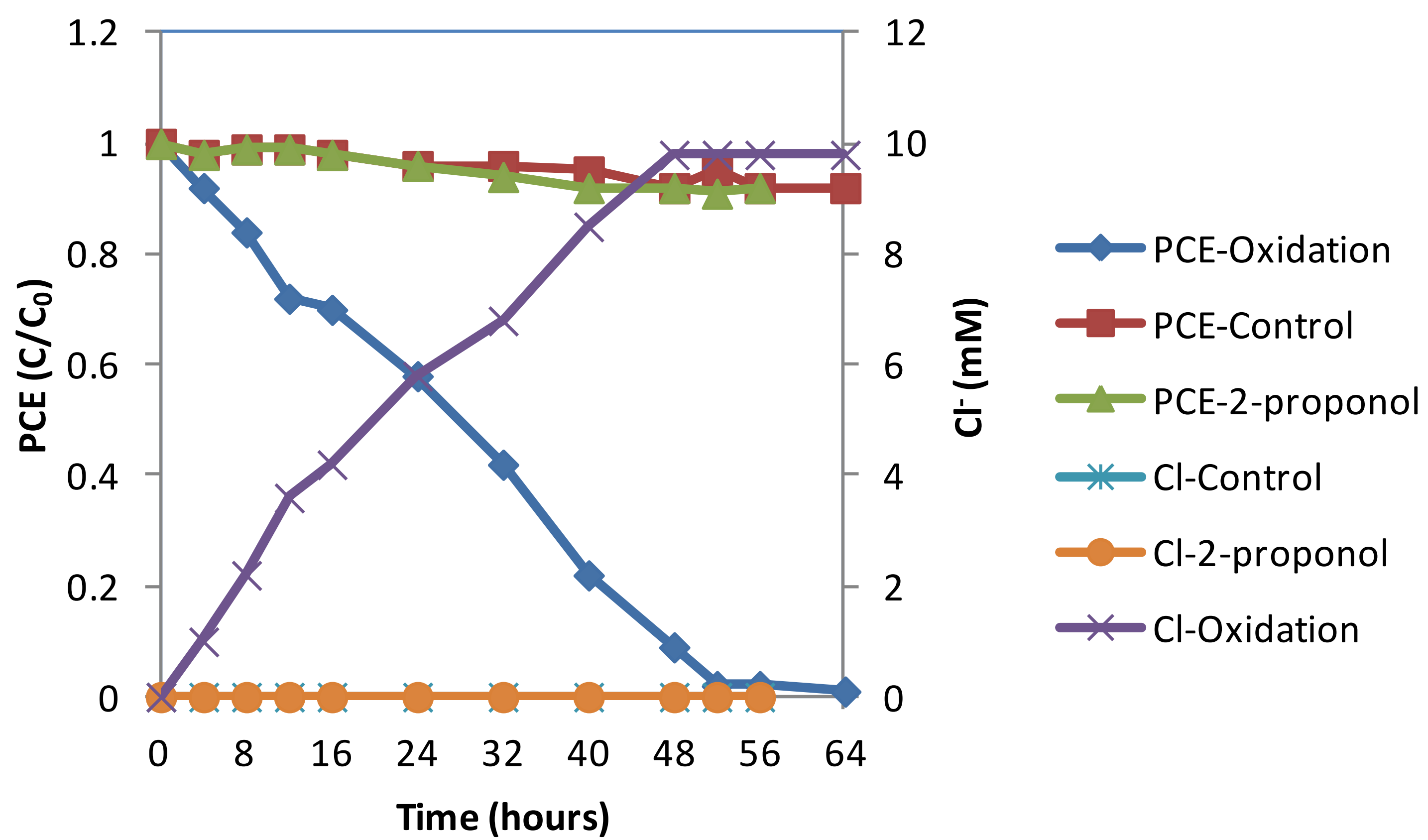
BOD_5/COD vs. H_2O_2 dose of an initial concentration of 4-CP of 300 ppm (Fe^{2+}/4-CP=1:1).

Solid Peroxides

$CaO_2(s) + \mathbf{2}H_2O == \mathbf{2}H_2O_2 + Ca(OH)_2(s)$



Ref: Northup, A. and Cassidy, D. (2008). “Calcium peroxide (CaO2) for use in modified Fenton chemistry.” Journal of Hazardous Materials, 152, 1164-1170.



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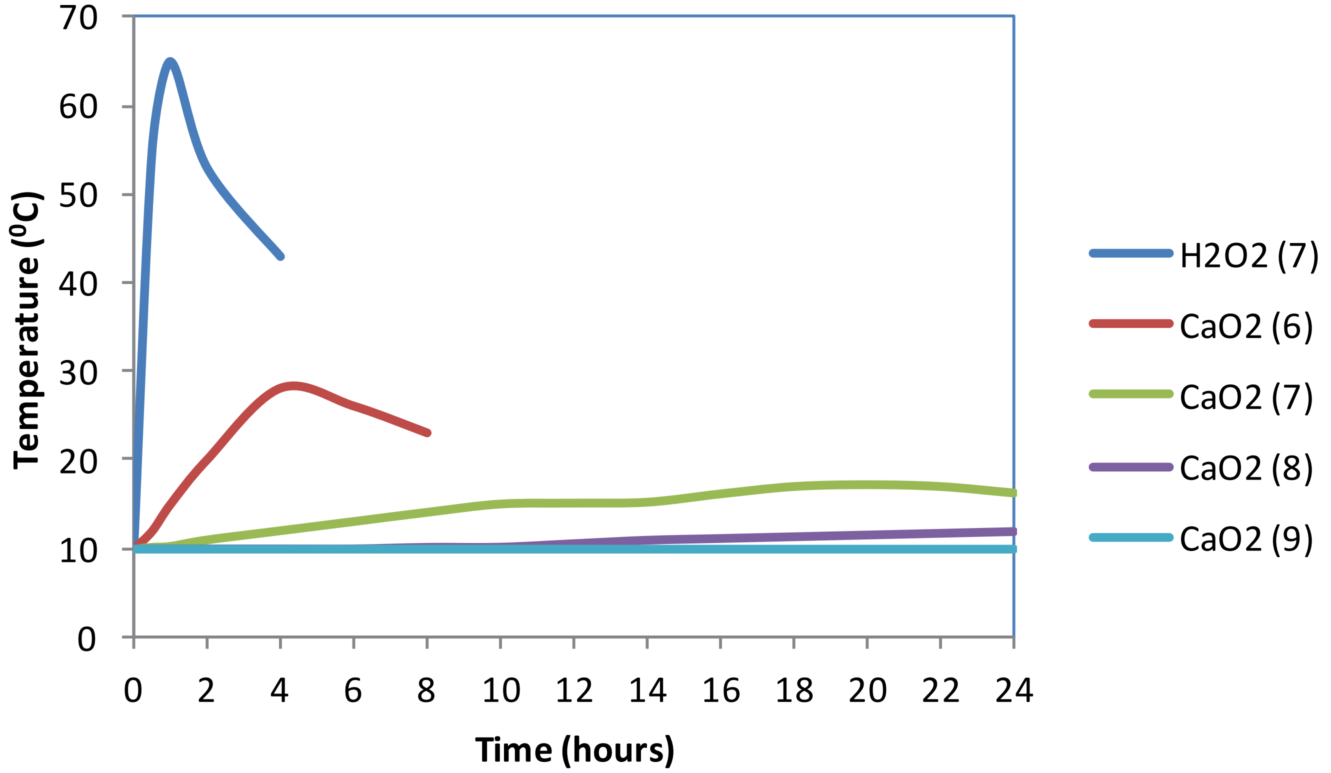

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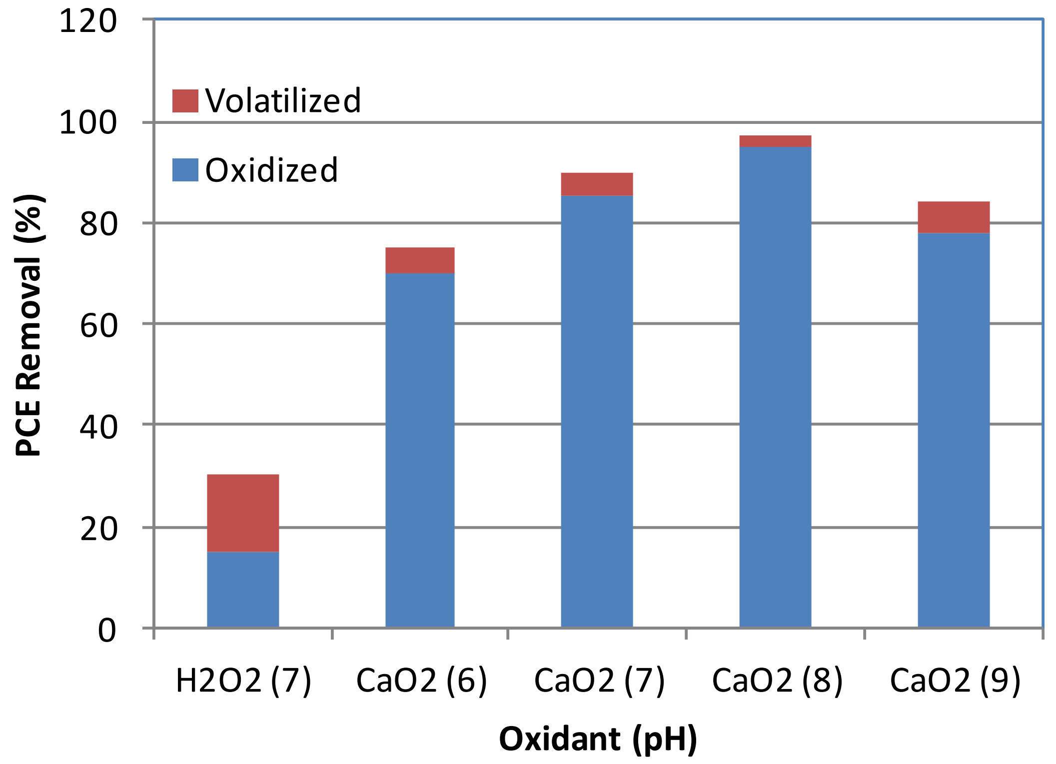


Ref: Northup, A. and Cassidy, D. (2008). “Calcium peroxide (CaO_2) for use in modified Fenton chemistry.” Journal of Hazardous Materials, 152, 1164-1170.

Objectives

- The optimal conditions of Fenton process in terms of H_2O_2/Fe^{2+}, H_2O_2/MSW(ton) will be determined to achieve the best biodegradability in terms of BOD_5/COD ratio in laboratory studies.

- Intrinsic oxidation efficiency of Fenton process η_{Oxi} will be quantified under different leachate COD loading rate (L_{COD}). A pilot bioreactor will be built for Fenton process for biodegradability enhancement and to fill the gap between theoretical relationship between η_{Oxi} and the COD loading rate (L_{COD}).

- The impact of hydrogen peroxide as an oxidant in Fenton process and a by-product, oxygen, in aerobic degradation of MSW will be quantified. Aerobic BL will be improved by Fenton pre-treatment. The enhanced aerobic degradation of leachate by Fenton process will be compared with the regular bioreactor technology in terms of leachate, gas, and waste characteristics.

- Design and operation procedures for Fenton pre-treatment of leachate for BL will be developed. Engineering design will focus on quantitative relationship between $\eta_{Removal}$, COD loading rate (L_{COD}), H_2O_2/MSW(ton), H_2O_2/Fe^{2+} and flowrate Q.

- The cost data of the Fenton enhanced BL from the laboratory studies will be used to conduct cost and benefit analysis of Fenton enhanced BL at full scale.
- Training for Fenton process as pretreatment for BL landfill operators and engineers in Florida will be provided in terms of the design, management, operation and regulations associated with Fenton enhanced BL. A technical document and a book will be developed for these purposes.

Theoretical COD Removal Efficiency

1) Theoretically, mass ratio of removable COD to H_2O_2 is 470.6/1000. In other words, 1000 mg/L H_2O_2 theoretically removes 470.6 mg/L COD by oxidation if the oxidation efficiency is 100%.

$$\eta = 100 \cdot (\Delta COD / \text{available } O_2 \text{ in } H_2O_2 \text{ added})$$

where "available O_2" is the theoretical amount of reactive oxygen equivalent to the added hydrogen peroxide.

COD Removal Efficiency

2) COD removal efficiency is defined in the following equation:

$$\eta_{oxi} = COD_{oxi}/0.417[H_2O_2] = 2.12\ COD_{oxi}/[H_2O_2]$$

where COD_{oxi} is the COD removed by oxidation $[H_2O_2]$ is the amount of peroxide added.

COD Loading

3) COD Loading (L_{COD}) is defined as:

$$L_{COD} = COD_0/0.417[H_2O_2] = 2.12\ COD_0/[H_2O_2]$$

where: COD_0 is the initial COD of leachate
$[H_2O_2]$ is the amount of peroxide added.

Our Research Team on Leachate Treatment

Our Research Team

Dr. Shrawan Singh

Ph.D. at the UF with Doctoral dissertation on pretreatment for RO system

Design, install, and operate and maintain a pilot-scale RO system for on-site landfill leachate treatment

Determined the current and future capacity of Florida Class-I landfills.

Mr. Richard Urbina

B.S. in Chemistry

M.S. candidate in the Civil and Environmental Engineering at FIU

M.S. Thesis: Fenton Oxidation of Leachate

Ms. Emma Lopez

B.S. in Environmental Engineering

M.S. candidate in the Civil and Environmental Engineering at FIU

GIS expert in our team for leachate treatment in Florida

Experiments

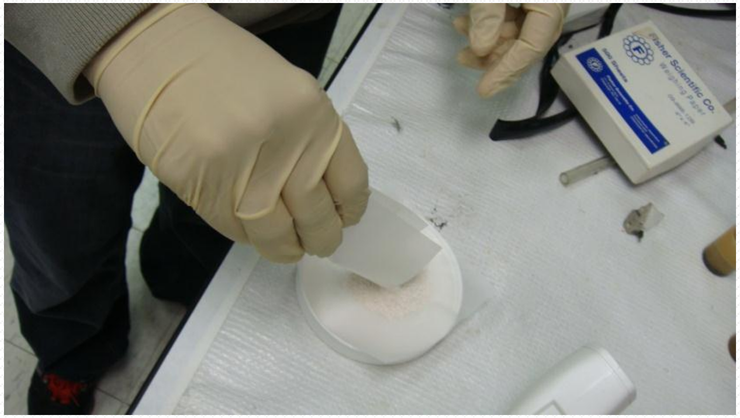
Experiments

- Leachate sample will be taken from the Miami-Dade South Dade Landfill (MDSDL) and will be placed in a beaker and magnetically stirred; its pH was adjusted to fixed values by H_2SO_4 95–97% (w/w).
- The scheduled Fe^{2+} dosage will be added the necessary amount of solid $FeSO_4(7H_2O)$.
- A known volume of 35% (w/w) H_2O_2 solution or solid CaO2 will be added in a single step.
- At the end of Fenton's treatment, stirring will be turned off and the sludge will be allowed to settle. Analysis of the treated leachate will be carried out on filtered samples.

Dr. Singh in the Laboratory

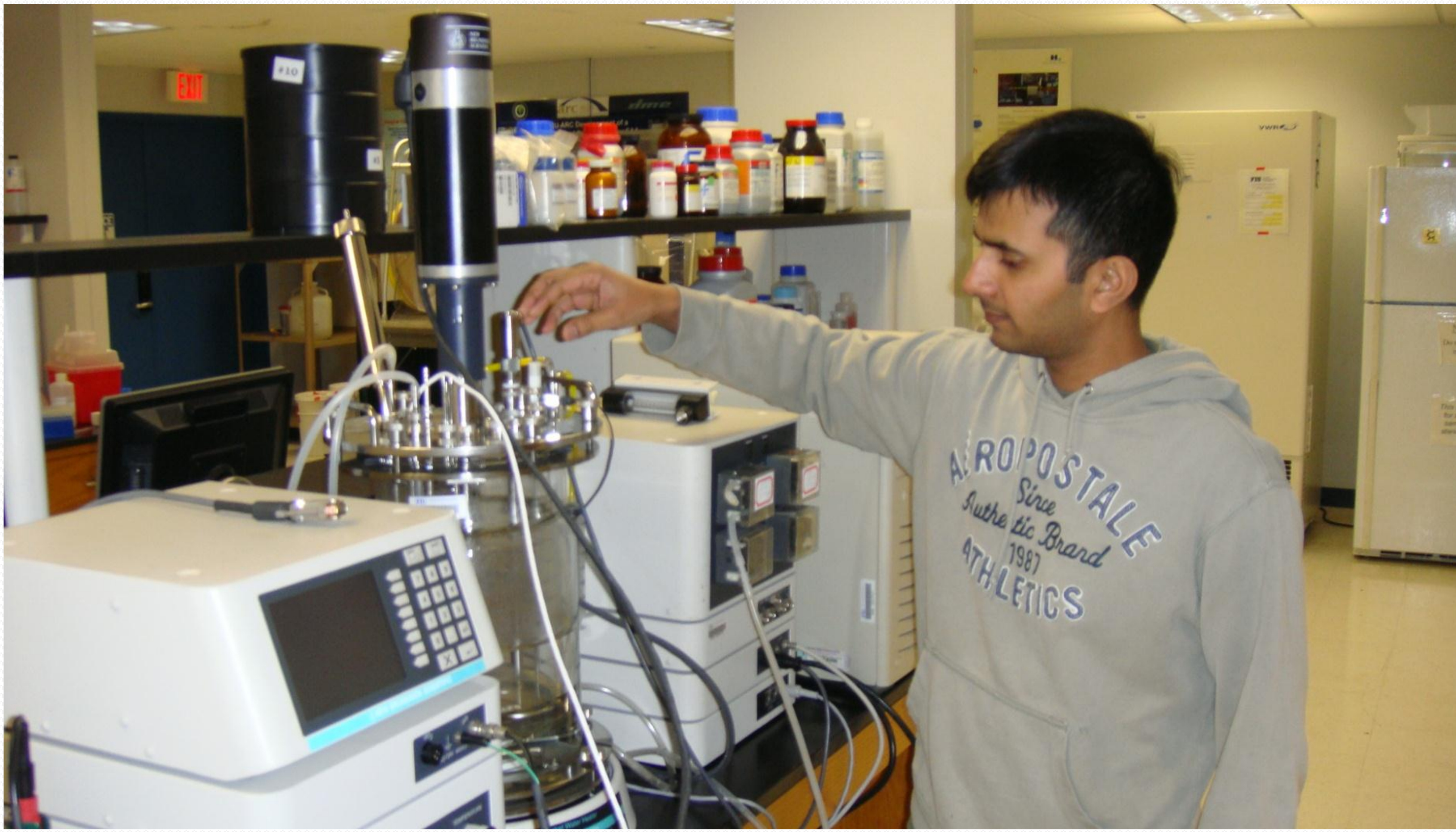
CaO_2


PFALTZ & BAUER, INC.
172 EAST AURORA STREET, WATERBURY, CT 06708
C01700
500GM
CALCIUM PEROXIDE TECH GRADE
LOT B05802




PFALTZ & BAUER, INC.
500GM
CALCIUM PEROXIDE TECH GRADE
LOT B05802

Modern Batch Reactor



Batch Reactor with Automatic Control

Batch vs. Column Reactor

Other Analytic Instruments

Research Topics

To increase biodegradability in terms of BOD_5/COD:

- What is the Optimal ratio between H_2O_2 and Fe^{2+} ?
- What are the loading factors H_2O_2 and Fe^{2+}?
- What is the impact on the amount of air injected due to the addition of H_2O_2?
- What are the best injection modes of H_2O_2 and Fe^{2+}, e.g., on site vs. offsite?
- What are the cost and benefits in dollar term?
- Which form of peroxide is the most efficient?

Deliverabls

Deliverables 1: Optimal Conditions of Fenton Process

- A universal method to unveil the intrinsic relationship between COD loading and COD removal efficiency will be developed. The experimental and simulated data will be compared with the theoretical data.
- Laboratory studies will be carried out to determine optimal conditions of Fenton process in terms of H_2O_2/Fe^{2+}, H_2O_2/MSW(ton) to achieve the best biodegradability in terms of BOD_5/COD ratio for both off-site and in-situ using method by Tang (2004).
- Linear relationship between η_{Oxi} vs. L_{COD} at optimal H_2O_2/Fe^{2+} ratio will be established for leachate at the MDSSWL so that preliminary design of Fenton process can be conducted without experimental feasibility studies once the leachate characteristics is known.

Deliverables 2: Stochastic Engineering Design for Optimal Conditions

- Stochastic Engineering Design for optimized conditions in terms of BOD_5/COD ratio for both off-site and in-situ Fenton process in different design graphs, figures, and tables at different age of landfill leachate, namely, young, middle, and matured landfills.

- Anaerobic, aerobic, hybrid (aerobic-anaerobic), semi aerobic, as-built, and retrofit BLs will demand different design diagrams in terms of amount of water and air to be circulated with consideration of additional oxygen generated using Fenton process.

Deliverables 3: Cost and Benefit Analysis (1)

- Cost and benefit analysis of Fenton process ;
  - leachate strength and quantity, the process employed, the age of the landfill, the amount and the composition of hydroxyl scavengers.
  - construction and the operational and maintenance cost (O & M).
    - effluent quality required
    - capacity of the installation
    - O & M costs cover manpower, energy, chemicals and maintenance.

Deliverables 3: Cost and Benefit Analysis (2)

- The cost of Fenton process will estimated using the following equation:

$$\left(\frac{\$}{gallon}\right) = \left\{[TOC] \times \left(\frac{[H_2O_2]}{[TOC]} \times \frac{\$}{moleH_2O_2} + \frac{[Fe^{2+}]}{[TOC]} \times \frac{\$}{moleFe^{2+}}\right)\right\} + Z$$

- The net monetary benefits will be estimated according to the following equation:

$$\mathbf{NPV} = \sum_{t=0}^{T} [1 / (1 + r)^t] \times [\text{Benefits}(t) - \text{Costs}(t)]$$

where: NPV = Net Present Value
t = time periods
r = interest rate

Deliverables 4: Design Manual

- One technical document will be produced "Bioreactor Landfill Using Fenton Processes to Increase Biodegradability: A Guide for Development, Implementation, and Monitoring".
- Design graphs, figures, and tables will be generated so that the technical document become indispensable for engineers, consultants, constructors, and operators of the BL.

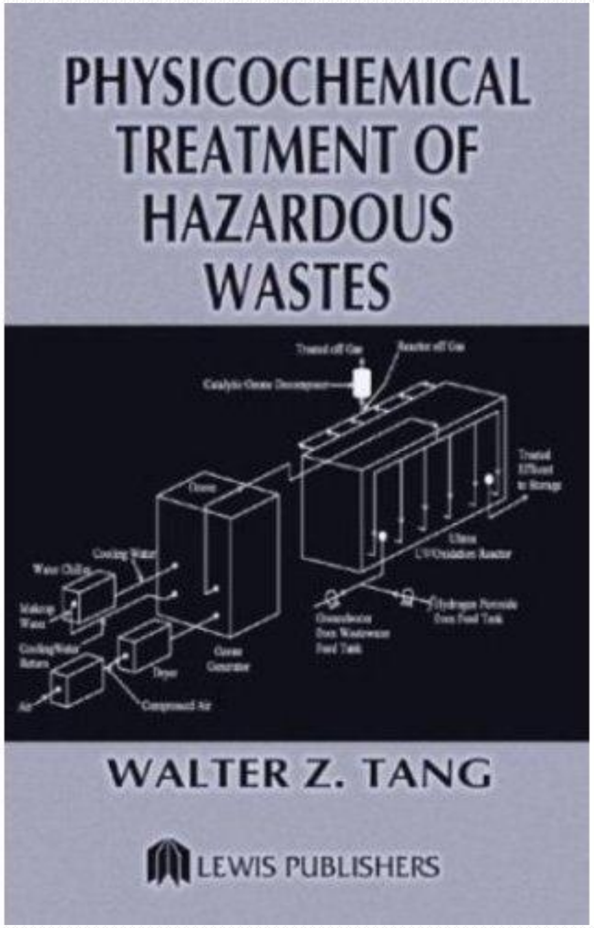
Deliverables 5: Publish a Book:
Fenton Processes of Leachate Treatment

- Real examples in terms of biodegradability enhancement by Fenton process es will be added on following topics:

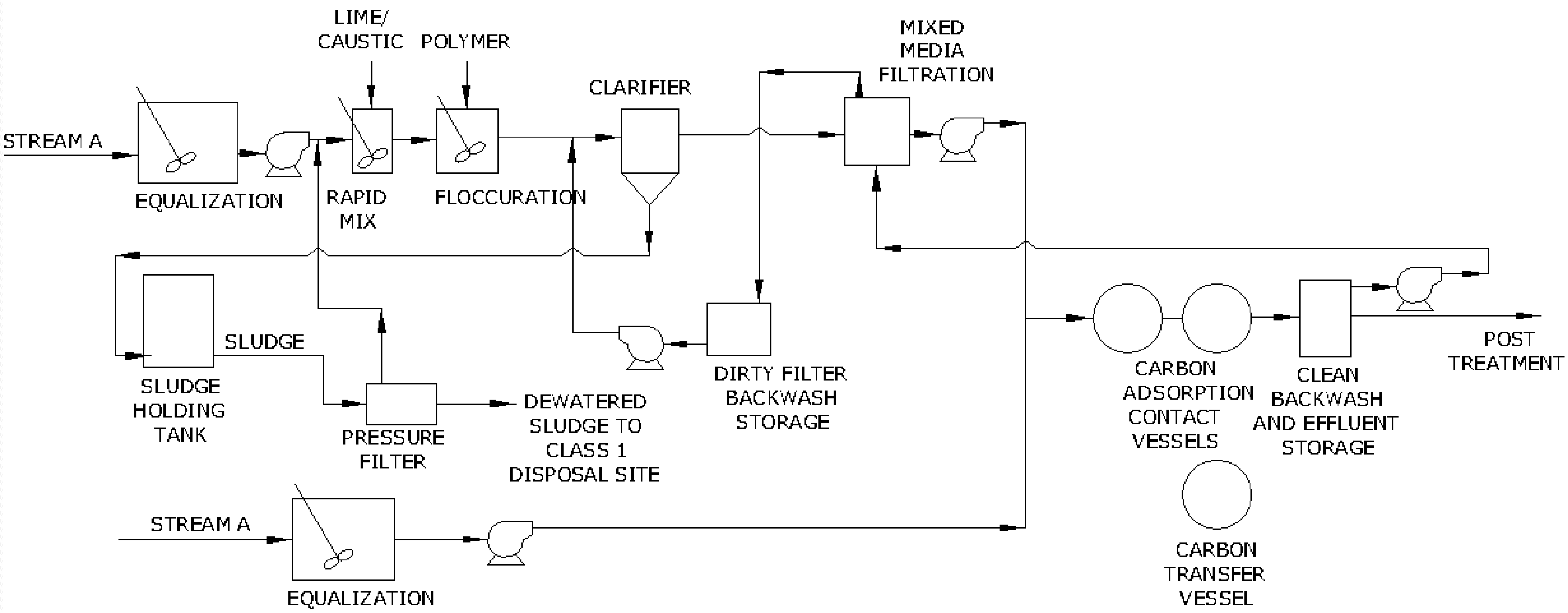
1) Optimization of H_2O_2/Fe^{2+},
2) H_2O_2/MSW(ton),
3) H_2O_2 dosage on BOD_5/COD,
4) η_{Oxi}, η_{Coag}, $L_{COD,}$
5) step wise addition of H_2O_2

The above knowledge will greatly enrich the book usefulness for both scientific researcher, engineers, consultants, and operators.

Physicochemical Treatment of Hazardous Wastes

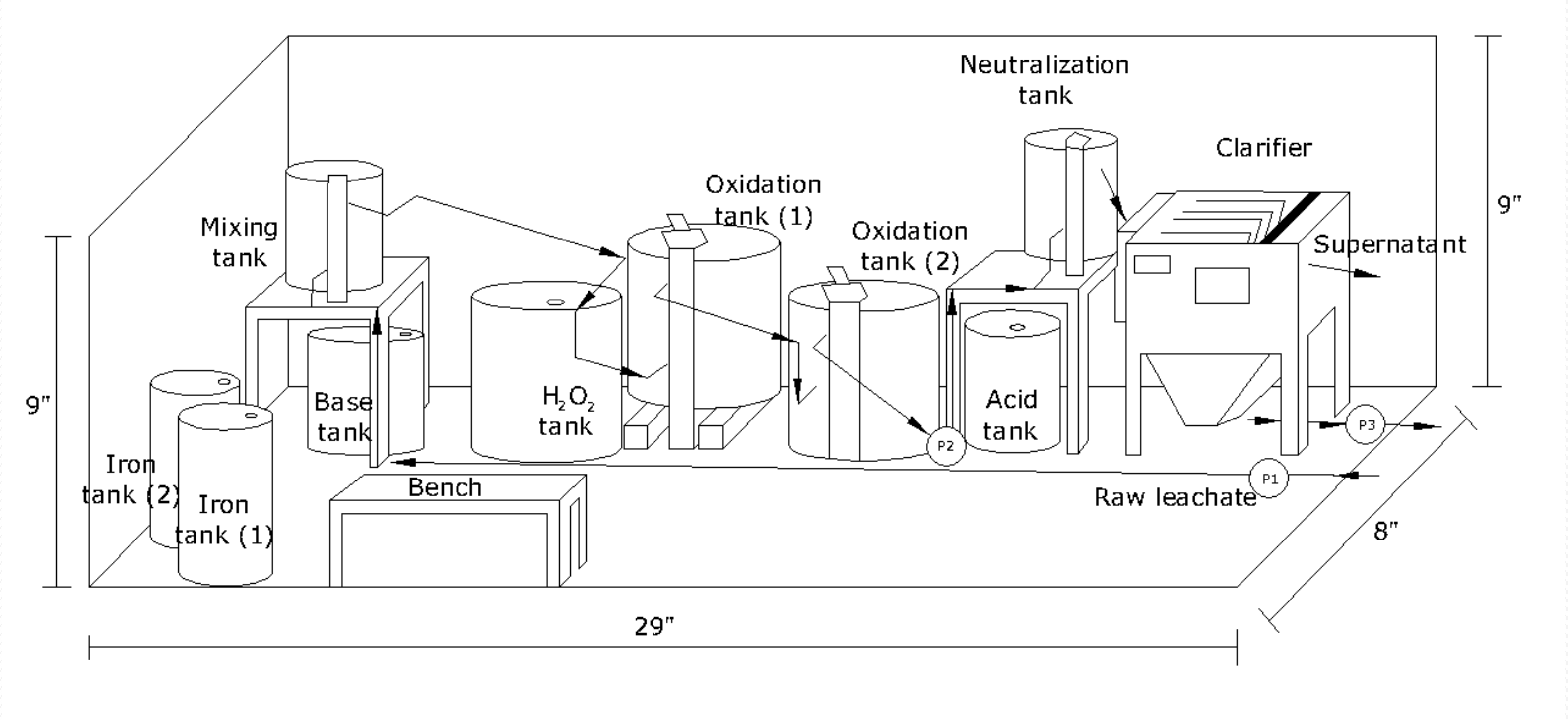


100 Graphs Have Been Developed for my second book: Fenton Process of Leachate Treatment



Typical leachate pretreatment process flow (from McArdle et al., 1988)

DSWA Pilot Plant Operation (from Roddy and Choi, 1999)



Scheduled Activities

Scheduled Activities	02/12 03/12	03/12 04/12	05/12 06/12	07/12 08/12	09/12 10/12	10/12 12/12
Kick off Meeting	X					
Literature review	X	X				
Laboratory study	X	X	X	X	X	
Data evaluation and analysis		X	X	X	X	X
Progress Report	X		X		X	
Final Report						X

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Thank You !