# LANDFILL LEACHATE TREATMENT USING FENTON PROCESS: COD LOADING vs TREATMENT EFFICIENCY

Shrawan Singh, PhD

Post-doctoral Research Associate
Department of Civil and Environmental Engineering
Florida International University
Miami, FL

TAG meeting at University of Central Florida, Orlando, FL

7/13/2012

# OUTLINE

- Background
- Objectives
- Methodology
- Results
- Project outcomes

# FENTON OXIDATION

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$$

$K_1 = 76\ M^{-1}s^{-1}$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+$$

$K_2 = 10^{-3}$ to $10^{-2}\ M^{-1}s^{-1}$

$$RH + OH^\bullet \rightarrow H_2O + R^\bullet$$

$K_3 = 10^{7}$ to $10^{10}\ M^{-1}s^{-1}$

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$$

$K_4 = 1.2 \times 10^{7}$ to $4.5 \times 10^{7}\ M^{-1}s^{-1}$

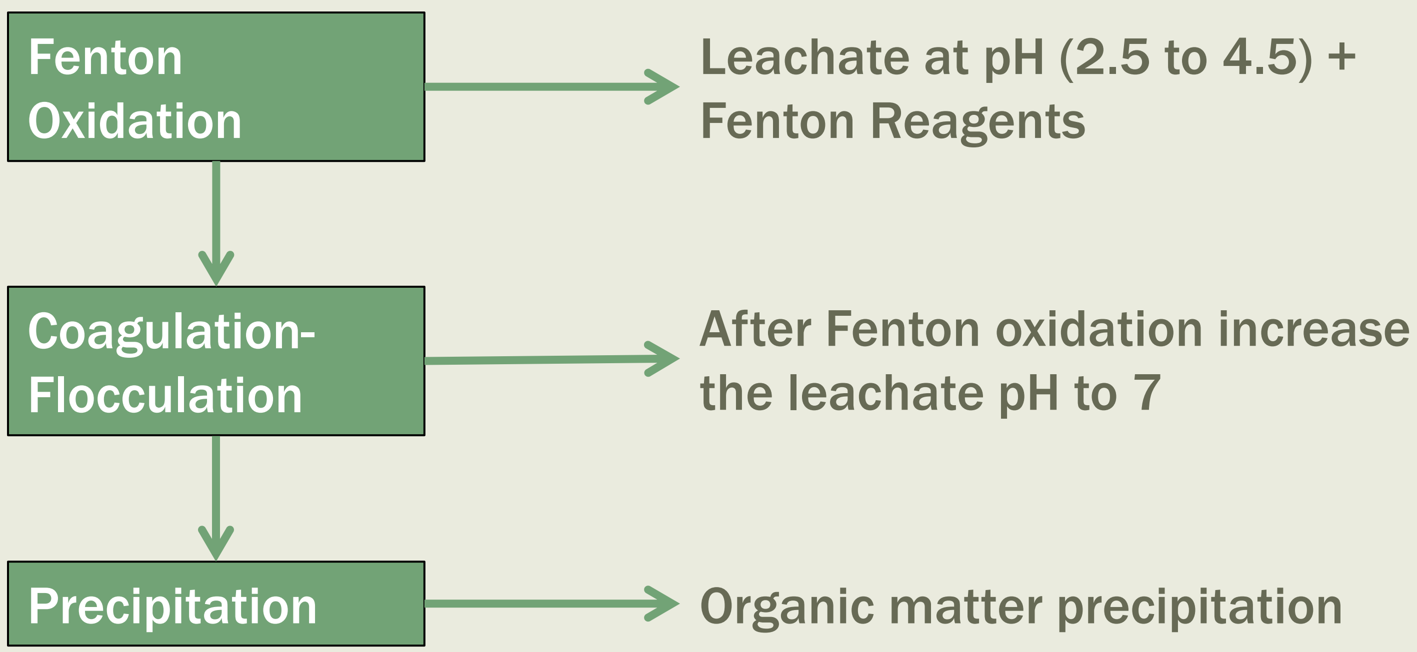
$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^-$$

$K_5 = 3 \times 10^{8}\ M^{-1}s^{-1}$

# IMPORTANT PARAMETERS OF FENTON PROCESS

- Characteristics of leachate
- Operating pH condition
- Fenton reagents ($H_2O_2$ and $Fe^{2+}$) dose ratio
- Fenton reagents absolute dose
- Reaction time
- Reaction temperature

# FENTON PROCESS

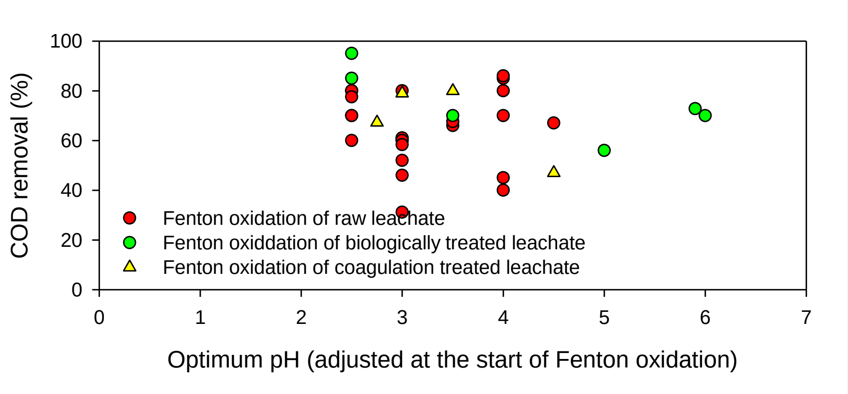


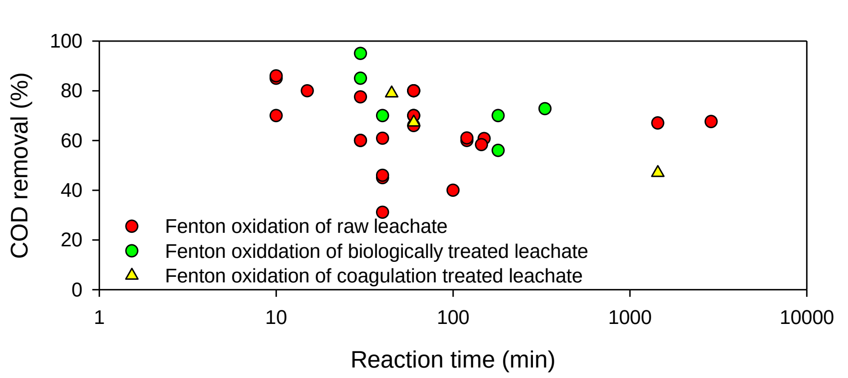
# LITERATURE REVIEW

**Primary objective:**

To determine optimum operating conditions for a specific leachate based on maximum organic matter removal

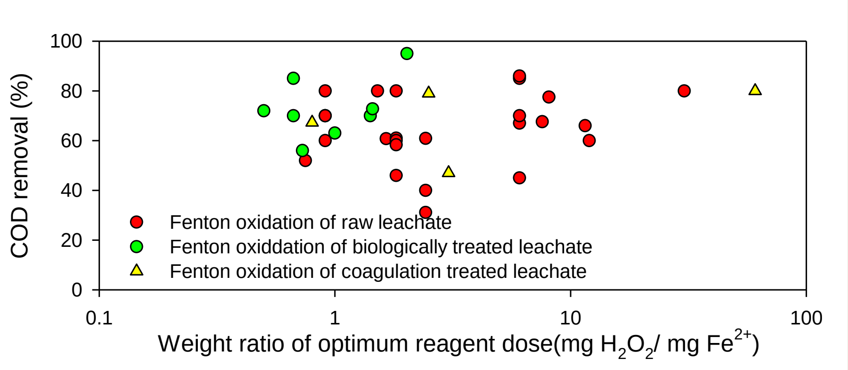
# LITERATURE REVIEW: OPTIMUM FENTON PROCESS CONDITIONS

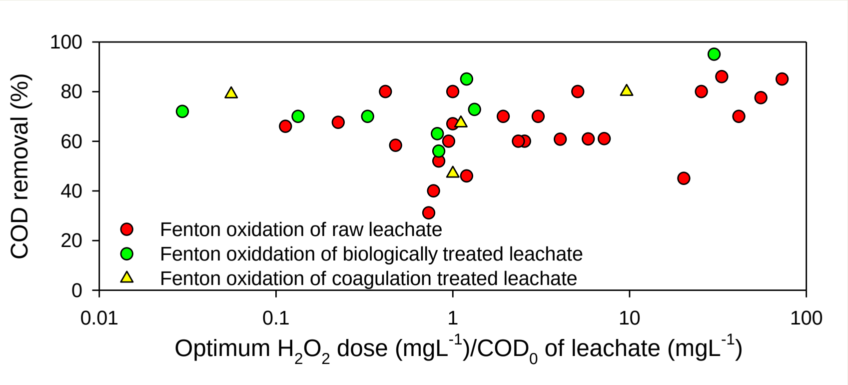



| Parameter | Optimum pH | Optimum reaction time (minutes) |
|---|---|---|
| Number of studies | 35 | 33 |
| Average | 3.4 | 241 |
| Max | 6.0 | 2,880 |
| Min | 2.5 | 10 |
| Standard deviation | 0.9 | 582 |
| Median | 3.0 | 60 |

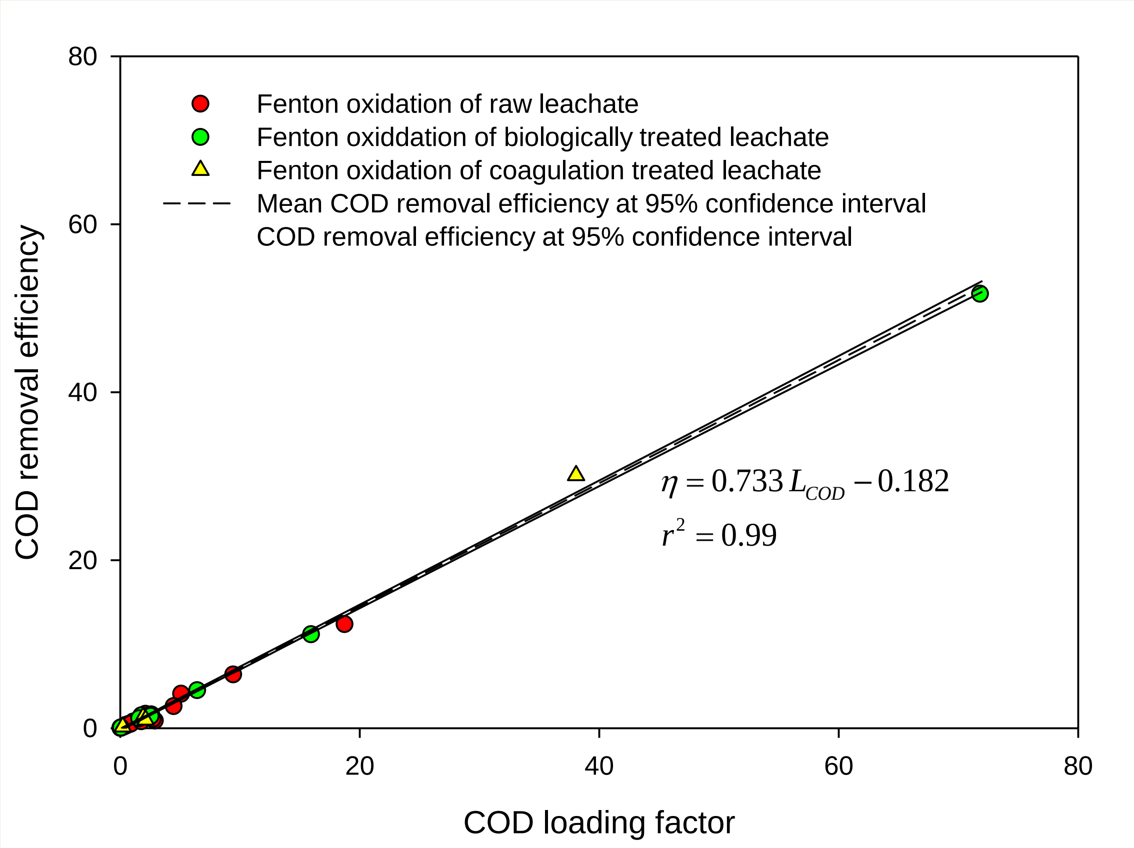
# LITERATURE REVIEW: OPTIMUM FENTON PROCESS CONDITIONS




| Parameter | $H_2O_2/Fe^{2+}$ | $H_2O_2/COD_0$ |
|---|---|---|
| Number of studies | 37 | 37 |
| Average | 5.4 | 9.1 |
| Max | 60.7 | 73.1 |
| Min | 0.5 | 0.01 |
| Standard deviation | 10.8 | 17.0 |
| Median | 1.8 | 1.2 |

# COD LOADING vs TREATMENT EFFICIENCY




## COD loading factor

$$L_{COD} = COD_0/\text{available } O_2$$
$$= COD_0/0.47\ H_2O_2$$

## COD removal efficiency

$$\eta = COD_{removed}/\text{available } O_2$$
$$= COD_{removed}/0.47\ H_2O_2$$

**'available $O_2$' is the theoretical amount of reactive $O_2$ equivalent to the added $H_2O_2$.**

# PROJECT OBJECTIVES

- To determine generalized Fenton oxidation operating conditions for landfill leachate treatment.
- To determine the effect of Fenton oxidation on biodegradability of landfill leachate.

# METHODOLOGY

Landfill leachate collection and characterization

↓

Determine Fenton oxidation experimental condition

↓

Design experiments

↓

Perform experiments

↓

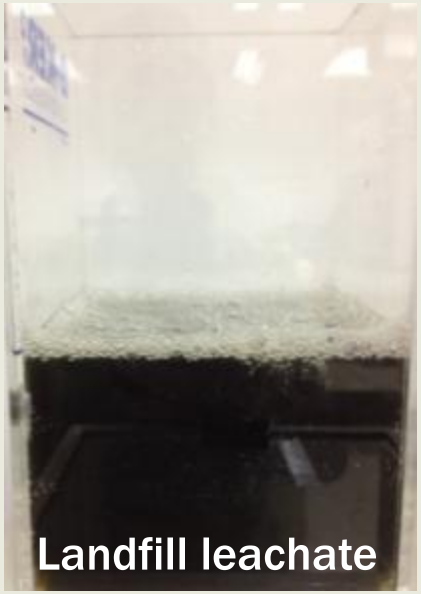
Analyze samples

# LEACHATE COLLECTION


Pump Station A at Solid waste Authority Landfill Palm Beach County

# LEACHATE CHARACTERIZATION

| Parameter | Concentration |
|---|---|
| pH | 7.52 |
| DO (mg/L) | 2.64 |
| Conductivity (mS/cm) | 28.6 |
| Total dissolved solids (mg/L) | 19,066±757 |
| Alkalinity (mg/L as $CaCO_3$) | 2,345±57 |
| TOC (mg/L) | 777±73 |
| COD (mg/L) | 2,183±50 |
| $BOD_5$ (mg/L) | 151±50 |
| $BOD_5$/COD | 0.07 |


Landfill leachate

# EXPERIMENTAL CONDITIONS

- Experimental pH:
  - 2.0, 3.5, and 6.0
- Reagent dose ratio ($H_2O_2/Fe^{2+}$)
  - 1.8
- Different initial COD
  - Leachate at different dilutions (1:8; 1:4; 1:2, and 1:1)
- Reagent absolute doses based on COD Loading factor ($L_{COD}$)
  - 0.25, 0.50, 0.75, 1.0

# EXPERIMENTAL PROCEDURE

1 L Leachate sample
Adjust pH to desired value (using 10 M $H_2SO_4$)
Start mixing at 100 rpm
Add desired $FeSO_4.7H_2O$ and $H_2O_2$.

→ **Oxidation** →

Sample collection after 0.5, 1, 5, and 10 min from the start of experiment. pH of each sample adjusted to >12 using 10 M NaOH

Leachate
Adjust pH to 7.0 (using 10 M NaOH)
Mixing at 100 rpm

→ **Coagulation** →

Sample collection after 15 min from the start of experiment. pH of sample adjusted to >12 using 10 M NaOH

Leachate
Mixing at 30 rpm

→ **Flocculation** →

Sample collection after 30 min from the start of experiment. pH of sample adjusted to >12 using 10 M NaOH

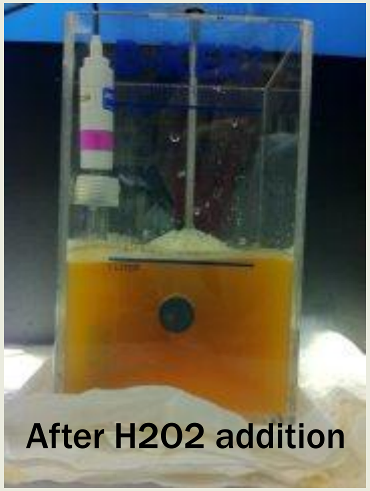
Leachate
No mixing

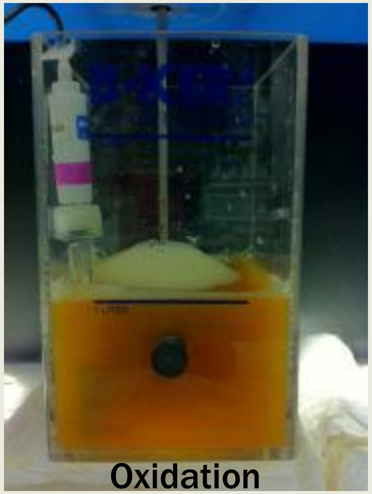
→ **Precipitation** →

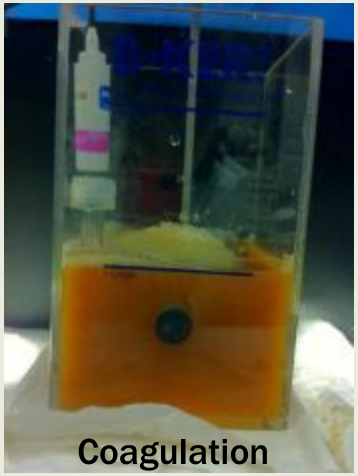
Supernatant and sediment samples collection after 75 min from the start of experiment. pH of sample adjusted to >12 using 10 M NaOH

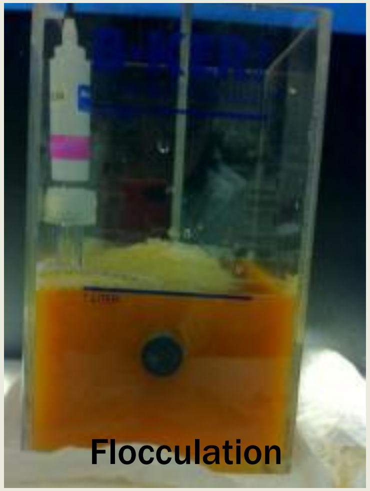
# EXPERIMENT

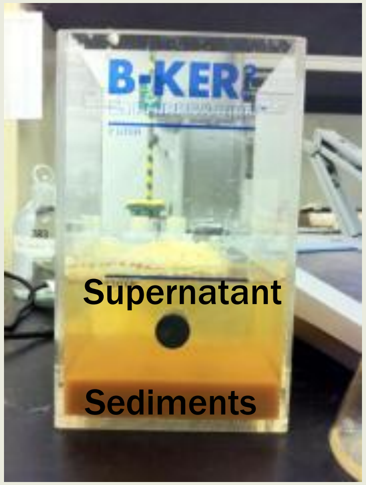

Raw leachate


After H2O2 addition


Oxidation


Coagulation


Flocculation


Supernatant

Sediments

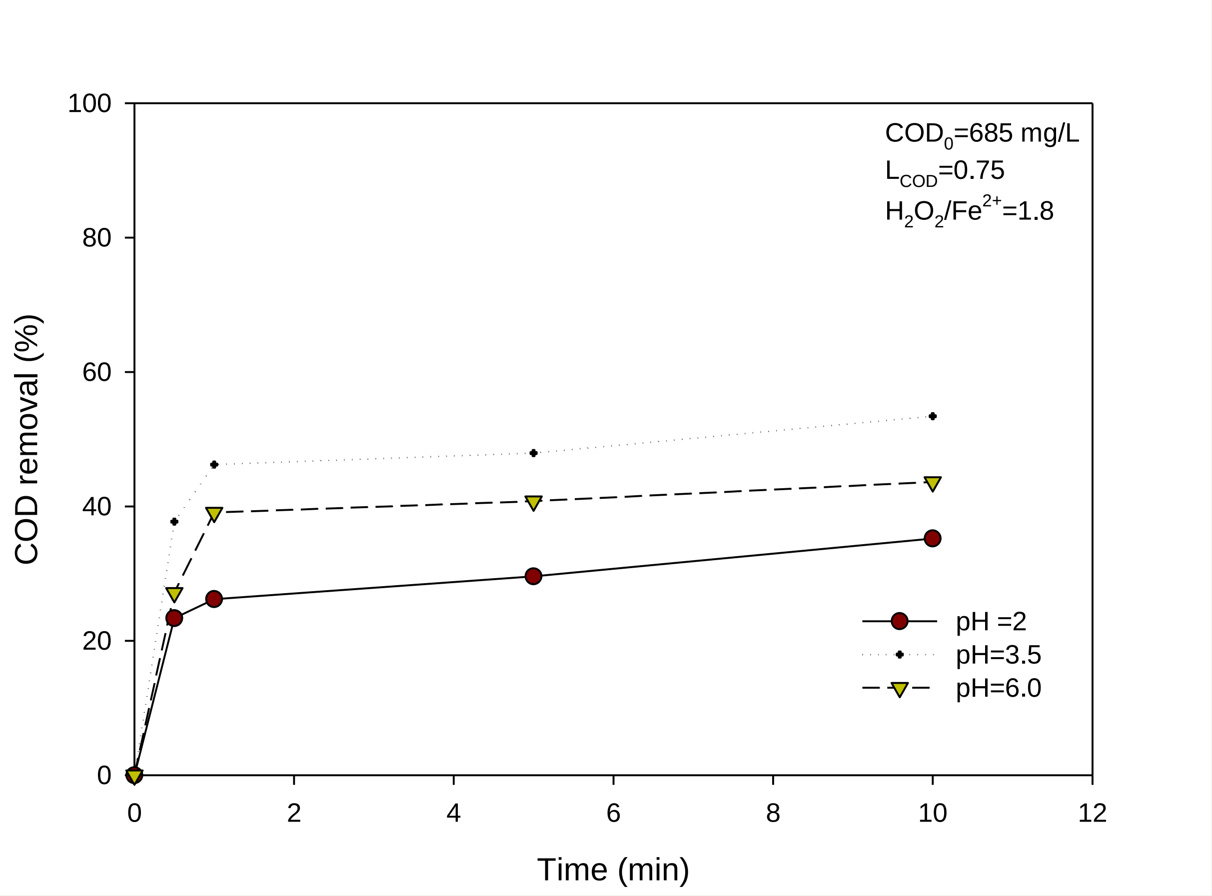
# SAMPLE ANALYSIS

Shimadzu TOC-$V_{CPH}$
Total Organic Carbon Analyzer

HACH COD digester and HACH-DR/850 Colorimeter

BOD analysis

# RESULTS

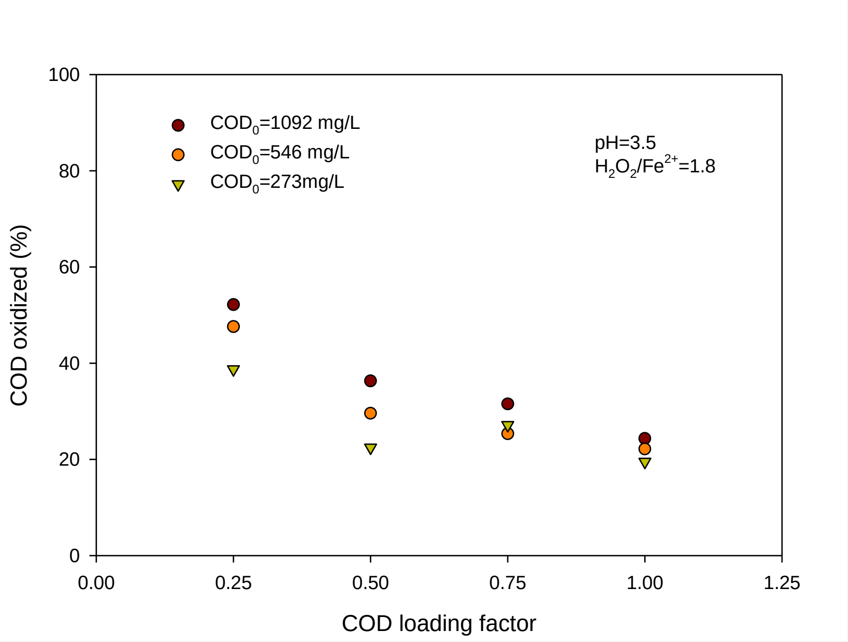



**Impact of initially adjusted pH on COD removal efficiency during Fenton oxidation**

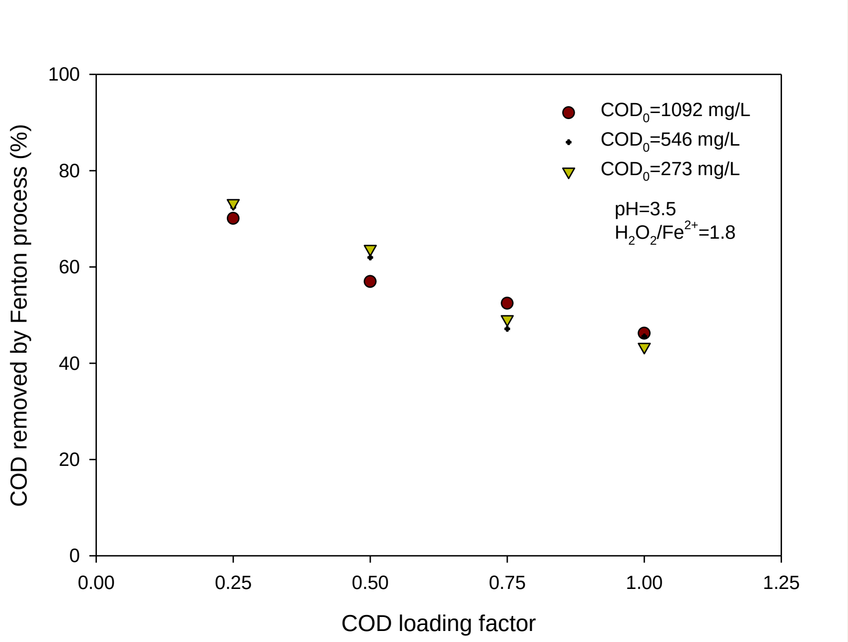
## COD loading factor

$$L_{COD} = COD_0/\text{available } O_2$$
$$= COD_0/0.47\ H_2O_2$$

# RESULTS

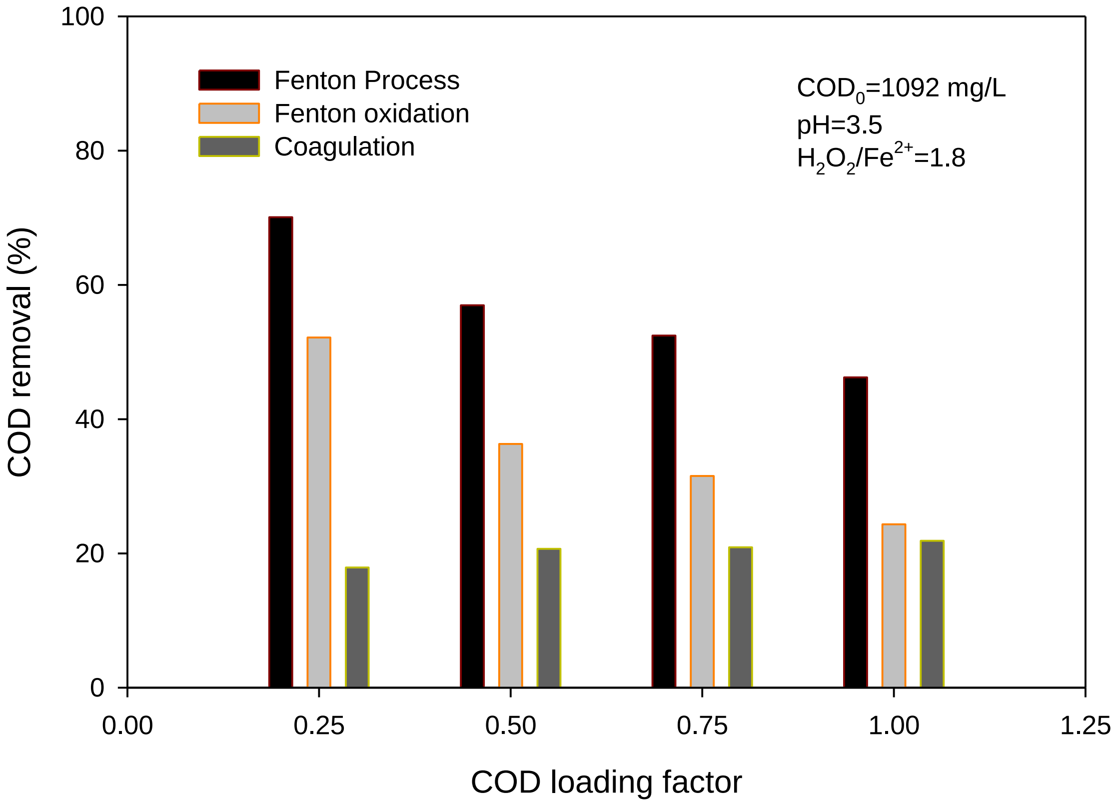



Impact of $L_{COD}$ on COD removal by oxidation



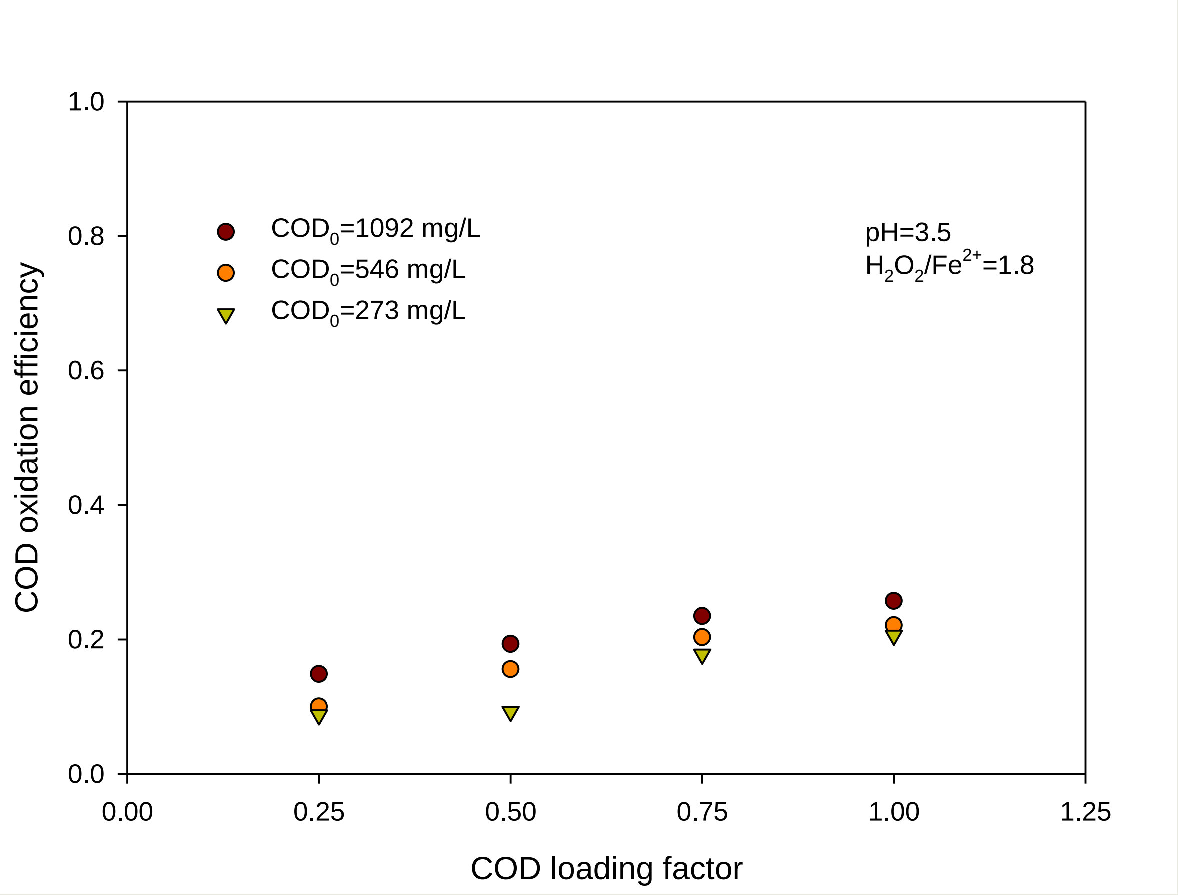

Impact of $L_{COD}$ on COD removal by Fenton Process

# RESULTS



100
80
60
40
20
0
COD removal (%)
Fenton Process
Fenton oxidation
Coagulation
COD0=1092 mg/L
pH=3.5
H2O2/Fe2+=1.8
0.00
0.25
0.50
0.75
1.00
1.25
COD loading factor

# RESULTS

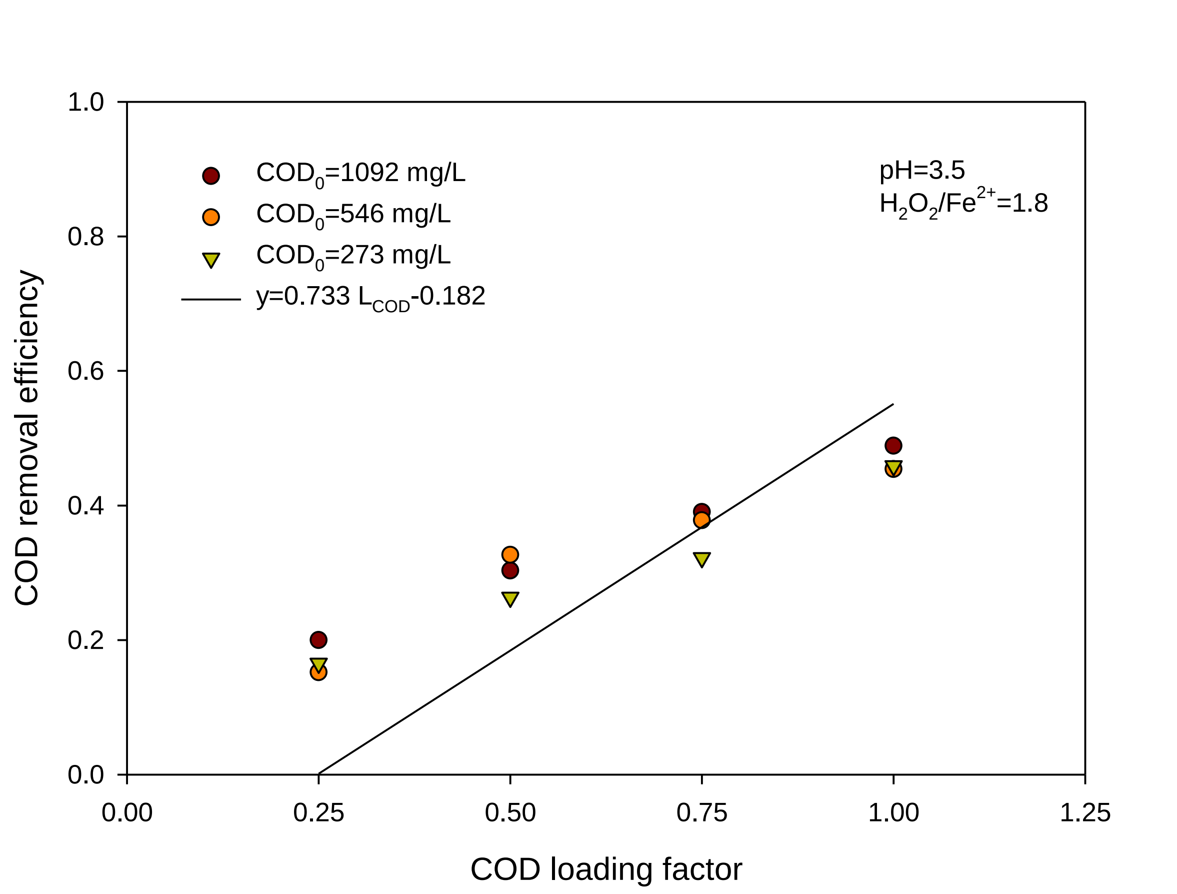



**Effect of $L_{COD}$ on COD oxidation efficiency**

## COD oxidation efficiency

$$\eta = COD_{oxidized} / \text{available } O_2$$
$$= COD_{oxidized} / 0.47\ H_2O_2$$

# RESULTS

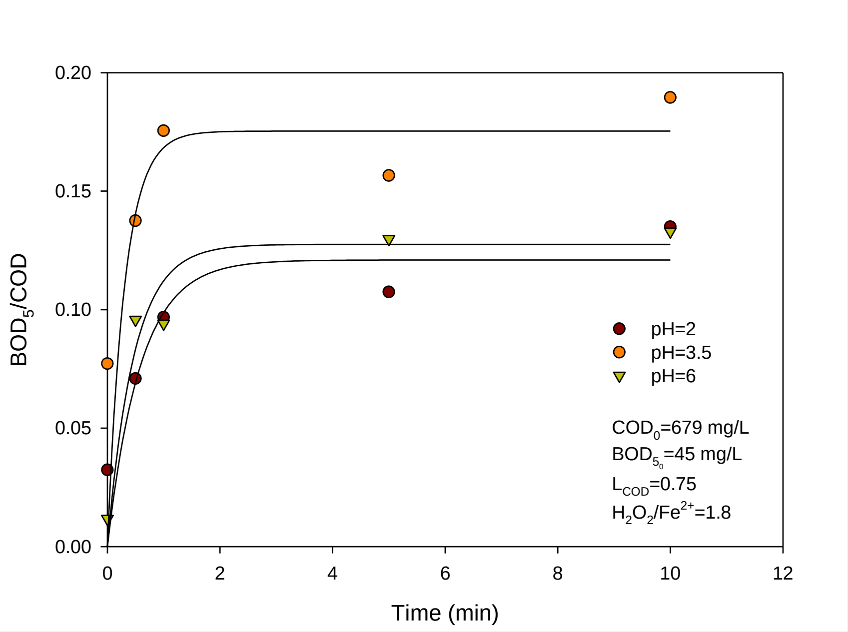



**Effect of $L_{COD}$ on COD removal efficiency**

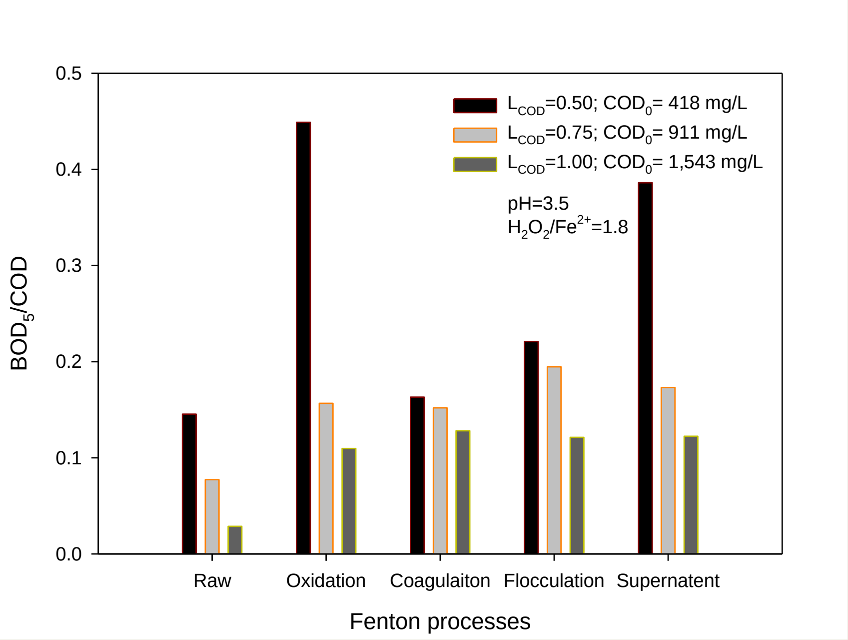
## COD removal efficiency

$$\eta = COD_{removed}/\text{available } O_2$$
$$= COD_{removed}/0.47\ H_2O_2$$

# RESULTS




Effect of Fenton oxidation on biodegradability of leachate




Effect of Fenton processes on biodegradability of leachate

# CONCLUSIONS

- $L_{COD}$ can provide a significant information for determining the Fenton reagent dose.
- The relationship $\eta = 0.733\ L_{COD} - 0.182$ can be used to determine COD removal efficiency from landfill leachate at optimum Fenton process conditions without performing multiple experiments.
- Fenton process can quickly remove organic matter from landfill leachate. Approximately 50% COD was removed within 1 minute of Fenton oxidation at favorable conditions.
- $L_{COD}$ of 0.75 provided optimum operating dose for leachate treatment using Fenton process.
- Fenton process significantly improves biodegradability of leachate.
- $BOD_5/COD$ linearly increases at the start of Fenton oxidation.
- Fenton oxidation showed greater increase in $BOD_5/COD$ than complete Fenton process.

# PROJECT BENEFITS

- The results of the study will help the leachate treatment practitioners for determining Fenton reagent doses without performing multiple experiments on a specific landfill leachate.
- Practitioners can use $L_{COD}$ of 0.75 as a Fenton reagent dose for optimum organic matter removal.
- If low biodegradability of landfill leachate is a major issue in a wastewater treatment facility, Fenton oxidation can provide a significant improvement in treatment performance.

# ACKNOWLEDGEMENTS


- Hinkley Center for Solid and Hazardous Waste Management
- Ron Schultz, SWA, Palm Beach County, Florida
- Anna Bricker, PhD, FIU
- Richard Urbina, FIU
- Emma Lopez, FIU
- Allison Vo

# QUESTIONS

Walter Tang, PhD, PE

tangz@fiu.edu

Shrawan Singh, PhD

shrawan.singh@fiu.edu

Project website:

http://www.tang.fiu.edu/hinkley-center-projects/