## Suspended Fiber Biofiltration for the Treatment of Landfill Leachate. Year II. Incorporation of Advanced Oxidation and Phosphorous Removal in a Single Unit

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## Xenobiotic, Organic, Phosphorous and Iron Removal from Landfill Leachate

- Fewer Restrictions
- Municipal Solid Waste (MSW)
- Protein (0.5% of Dry MSW)
- Iron Issues of Northwest Florida





## **Research Question**

#### Advanced Oxidation Combined with Suspended Fiber Biofiltration for the Treatment of Landfill Leachate



# **Objectives**

Advanced oxidizing processes will be introduced to the leachate treatment for xenobiotic destruction. The suspended fiber biofiltration will be configured to enhance iron and phosphorous removal in addition to organic degradation.

- 1. Reactor Design, Setup and Parameter Characterization Advanced Oxidation and Suspended Fiber Biofiltration to Be Arranged in Single Unit
- 2. Reactor Operation Combined UV, Ozone and Hydrogen Peroxide for Xenobiotic Destruction; Suspended Fiber Biofiltration for Iron and Phosphorous removal and Organic Degradation
- ➢ 3. System Optimization and Cost Analysis





# **Proposed Research Setup**



# **Laboratory Setup**

#### Third Stage Fiber Reactor



#### **Fraction Collector**

Peristaltic Pump Ozone Generator Vacuum Pump



Ozone		UV	Oxidant	Standard Oxidation Potential (Volts)	Relative Strength (Oxygen = 1)
	Radicals	1	Hydroxyl Radical	2.3	1.92
	•OH	/	Ozone	2.1	1.75
			Sodium Persulfate	2.0	1.67
			Hydrogen Peroxide	1.8	1.50
	H <sub>2</sub> O <sub>2</sub>		Oxygen	1.2	1.0

System	Molecules of O <sub>3</sub> /Mole <sup>•</sup> OH	Moles of UV Photons, Einsteins/Mole •OH	Moles of H <sub>2</sub> O <sub>2</sub> /Mole <sup>•</sup> OH
$O_{3}/H_{2}O_{2}$	1.5	0	1.0
O <sub>3</sub> /UV	0.5	0.5	0
$H_2O_2/UV$	0	0.67	0.67
$O_3/H_2O_2/UV$	1.0	0.58	0.83



## **Advanced Oxidation Types**

- > Ozone + hydrogen peroxide  $(O_3/H_2O_2)$   $H_2O_2 \rightarrow HO_2^- + H^+$   $2O_3 + H_2O_2 \rightarrow 2^{\bullet}OH + 3O_2$  $HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet-}$
- ➢ Ozone-UV radiation (O<sub>3</sub>/UV)
  - $O_3 + h\nu \rightarrow O_2 + O(^1D)$
  - $O(^{1}D) + H_{2}O \rightarrow H_{2}O_{2} \rightarrow 2^{\bullet}OH$
- > Hydrogen peroxide-UV radiation ( $H_2O_2/UV$ )
  - $\begin{array}{c} H_{2}O_{2} \xrightarrow{hv} 2^{\bullet}OH \\ H_{2}O_{2} \Leftrightarrow HO_{2}^{-} + H^{+} \end{array} \qquad HO_{2}^{-} \xrightarrow{hv} \bullet OH + O^{\bullet -} \end{array}$
- > Ozone-hydrogen peroxide-UV radiation  $(O_3/H_2O_2/UV)$

The addition of  $H_2O_2$  to the  $O_3/UV$  process accelerates the decomposition of ozone, which results in an increased rate of 'OH generation.





### **Advanced Oxidation Application Dosage**

 $\sim O_3/H_2O_2$ O<sub>3</sub> 2 to 6 mg/L and H<sub>2</sub>O<sub>2</sub> 1 to 5 mg/L

### ≻ O<sub>3</sub>/UV

 $O_3$  2 to 6 mg/L and UV 10 to 100 mJ/cm<sup>2</sup> (by varying the exposure time from 0 to 15 min)

 $H_2O_2/UV$ H<sub>2</sub>O<sub>2</sub> 1 to 5 mg/L and UV 10 to 100 mJ/cm<sup>2</sup>

### $> O_3/H_2O_2/UV$

 $O_3^-$  1 to 3 mg/L, H<sub>2</sub>O<sub>2</sub> 1 to 2.5 mg/L, and UV 10 to 50 mJ/cm<sup>2</sup>





**Impact Factors** 

**Reaction time** 0, 1, 5, 10 and 15 min

**pH** 4, 5, 6, 7, 8, 9 and 10

> Alkalinity 100, 200, 300, 400, 500 and 600 mg/L as CaCO<sub>3</sub>

**Xenobiotic Destruction** 

**Organic Decomposition** 

Iron Removal





2,3,7,8-TCDD the most toxic dioxin









### **Phosphorous Adsorption on Iron Coated Fiber**



#### Low pH preferred for phosphorous adsorption

Alkalinity of 100, 200, 300, 400, 500 and 600 mg/L as CaCO<sub>3</sub>
pH of 5, 6, 7, 8, 9 and 10





#### Iron Removal as a Function of Oxidation







#### **Organic Removal as a Function of Oxidation**









## Iron Accumulation on the Fiber

HPMI





1µm

WD 5.8mm

10.0kV X20,000

SEI

### **Organic Removal as a Function of O<sub>3</sub>**



#### COD Removal with Variable H<sub>2</sub>O<sub>2</sub> Dosages at pH 7.4 and 9.6



#### COD Removal with Variable UV Radiation at pH 4.0, 7.4 and 9.6



# COD Removal with Variable UV Radiation at $H_2O_2$ Dosage of $H_2O_2$ : COD = 0.25:1 and pH 4.0, 7.4 and 9.6



### **Organic Removal as a Function of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>**



#### NH<sub>4</sub><sup>+</sup> Release as a Function of H<sub>2</sub>O<sub>2</sub> Dosage



Xenobiotics The word points out a large range of artificial components such as

#### **Drugs - Medication**

Sources:

Pharma Industries Hospitals, Medical Centres and Human and Animal wastes Chemicals

Sources:

**Chemical Industries (mainly)** 

### Pesticides

& Fungicides Sources:

Agriculture





Aromatic Hydrocarbons	Range (µg/L)HalogenatedHydrocarbons		Range (µg/L)	
Benzene	0.2-1630	Chlorobenzene	0.1-110	
Toluene	1-12300	1,2-Dichlorobenzene	0.1-32	
Xylenes	0.8-3500	1,3-Dichlorobenzene	5.4-19	
Ethylbenzene	0.22329	1,1,1-Trichloroethane	0.01-3810	
Trimethylbenzene	0.3-250	Trans-1,2- Dichloeoethylene	1.6-6582	
n-propylbenzene	0.3-16	Trichloroethylene	0.05-750	
t-Butylbenzene	2.1-21	Tetrachloroethylene	0.01-250	
o-Ethyltoluene	0.5-45	Phenols		
m-Ethyltoluene	0.3-21	Phenol	0.6-1200	
p-Ethyltoluene	0.2-10	Cresols	1-2100	
Naphthalene	0.1-260	Bisphenol A	200-240	

### **Xenobiotic Organic Compounds in landfill Leachate**







O<sub>3</sub> (mg/L)

#### **BPA** Removal as a Function of $O_3$ and $O_3/H_2O_2$

Nitrobenzene is an organic compound with the chemical formula  $C_6H_5NO_2$ . It is a water-insoluble pale yellow oil with an almond-like odor.



#### Nitrobenzene Removal as a Function of UV and UV/H<sub>2</sub>O<sub>2</sub>





2,3,7,8-TCDD the most toxic dioxin Polychlorinated dibenzodioxins (PCDDs), or simply dioxins, are a group of polyhalogenated organic compounds



#### **Cornwall Avenue Landfill**

The mountain consists of two large piles of dioxin-contaminated sediment dredged from Squalicum Harbor. It is covered with a white plastic sheet held in place with sandbags. The city and port, as coowners of the landfill, obtained approval from the Washington State Department of Ecology (DOE) to dump this material at the landfill. The public was never advised that the sediment contained dioxin.

### **Solid Components in Landfill Leachate**



10 um 251 kU 262E3 0017/00 B





LEI

2.0kV X700 10µm

WD 3.4m

#### c:\edax32\genesis\genspc.spc 14-May-2015 15:01:55 Chlorite (Nrm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28) LSecs : 50

1.9 Element Wt % At % SiKa D Ka С 23.23 38.50 0 35.63 44.34 1.5 Fe 08.80 03.14 Br 12.37 03.08 BrLa 1.1 Si 11.27 07.99 KCnt 03.76 00.78 Mo Cl 00.00 00.00 8.0 K 00.00 00.00 CaKa Ca 04.14 02.06 MoLa 0.4 00.80 00.12 Ba BaLa la. 0.03.75 8.00 12.25 16.50 20.75 25.00 29.25 33.50 37.75 Energy - keV





## **Expected Results**







# **Model Simulations**

## **Ozone Transfer**

$$\frac{d[O_3]}{dt} = k_L \alpha (\frac{P}{H} - [O_3]) - \sum k_j [S_j] [O_3]$$

 $\frac{d[O_3]}{dt} = k_L \alpha (\frac{P}{H} - [O_3]) - 2k_2 (10^{pH-pK}) [H_2O_2] [O_3] - (k_9 (10^{pH-pK}) + k_{10}) [H_2O_2] [OH] - 2k_{14} [O_3] [OH] - S_{PER} (k_{12} [HCO_3^-] + k_{13} [CO_3^{2-}]) [OH] - 3k_3 [OH^-] [O_3]$ 

$$S_{PER} = \frac{k_{15}[CO_3^{2-}][H_2O_2]}{k_{15}[CO_3^{-}][H_2O_2] + \sum k_j[CO_3^{2-}][I_j]}$$

> k<sub>L</sub> $\alpha$ : overall mass-transfer coefficient

- P: ozone partial pressure
- ➤ H: Henry's law constant for ozone

>  $[S_j]$ : concentration of all species that react with ozone with second-order rate constants  $k_j$ 

# **Model Simulations**

## **Iron Removal**

 $d[Fe^{2+}]/dt = X_{Fe^{2+}} \cdot (-\mu_{max} \cdot [Fe^{2+}]/([Fe^{2+}] + K_{Fe^{2+}})/Y_{Fe^{2+}})$ 

[Fe<sup>2+</sup>]: Ferrous iron concentration

X<sub>Fe2+</sub> : Iron oxidizing bacteria concentration

 $\mu_{max}$  : Iron oxidizing bacterial maximal specific growth rate

 $K_{Fe2+:}$  Michaelis-Menten constant for ferrous iron oxidation

Y<sub>Fe2+</sub>: Yield coefficient for iron oxidizing bacteria





# **Model Simulations**

# **Organic Decomposition**



S: Organic Concentration X: Bacterial cell concentration

 $\mu_m$ : Bacterial maximum specific growth rate t: Time

K<sub>s</sub>: Half saturation constant Y: Yield coefficient





# **System Comparison**

Operation parameters to be optimized based on individual and overall treatment results

- Treatment costs
- Effluent quality

Cost benefits analysis and comparison with conventional treatment processes



# **Timeline of Milestones**

Activity (Monthly)	1-3	3 - 6	7 - 9	9 - 12
Reactor Design, Setup and Parameter Characterization				
Consortia Cultivation				
Reactor Operation				
System Optimization and Cost Analysis				
Model Simulations				
Reporting	Quarterly	Quarterly	Quarterly	Final





# **Questions?**



