



WaterTech 2010

Ozone-Based Advanced Oxidation Processes in Water and Wastewater Treatment

Pamela Chelme-Ayala and Mohamed Gamal El-Din

**Department of Civil and Environmental Engineering
University of Alberta, Edmonton, Canada**

April 23, 2010

1. Process Fundamentals

2. Application in Water Treatment

3. Application in Wastewater Treatment

4. Concluding Remarks



1. Process Fundamentals

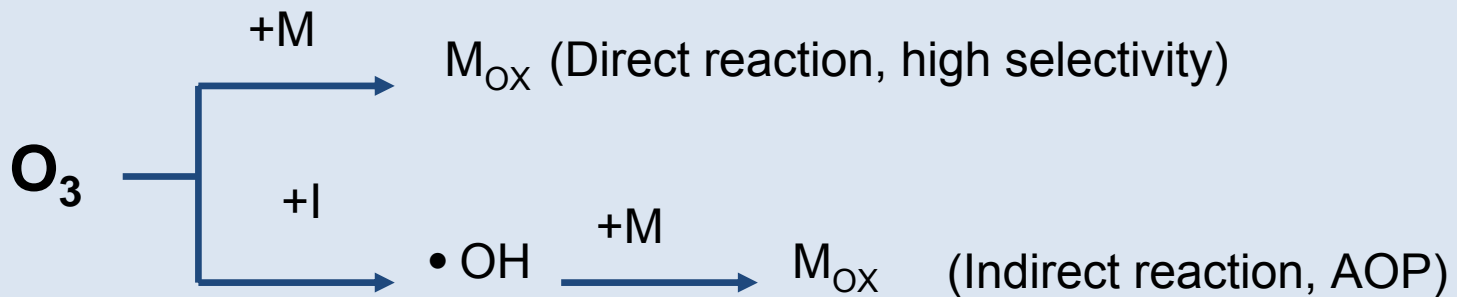
Advanced Oxidation Processes

Ozone-Based Process	Non-Ozone-Based Processes
Ozonation	Ultraviolet light (UV)/H ₂ O ₂
Ozone (O ₃)/hydrogen peroxide (H ₂ O ₂)	Vacuum UV
O ₃ /UV	TiO ₂ /hν
O ₃ /H ₂ O ₂ /UV	Photo-Fenton (UV/H ₂ O ₂)
O ₃ / Titanium dioxide (TiO ₂)	Anodic Fenton (iron electrode)

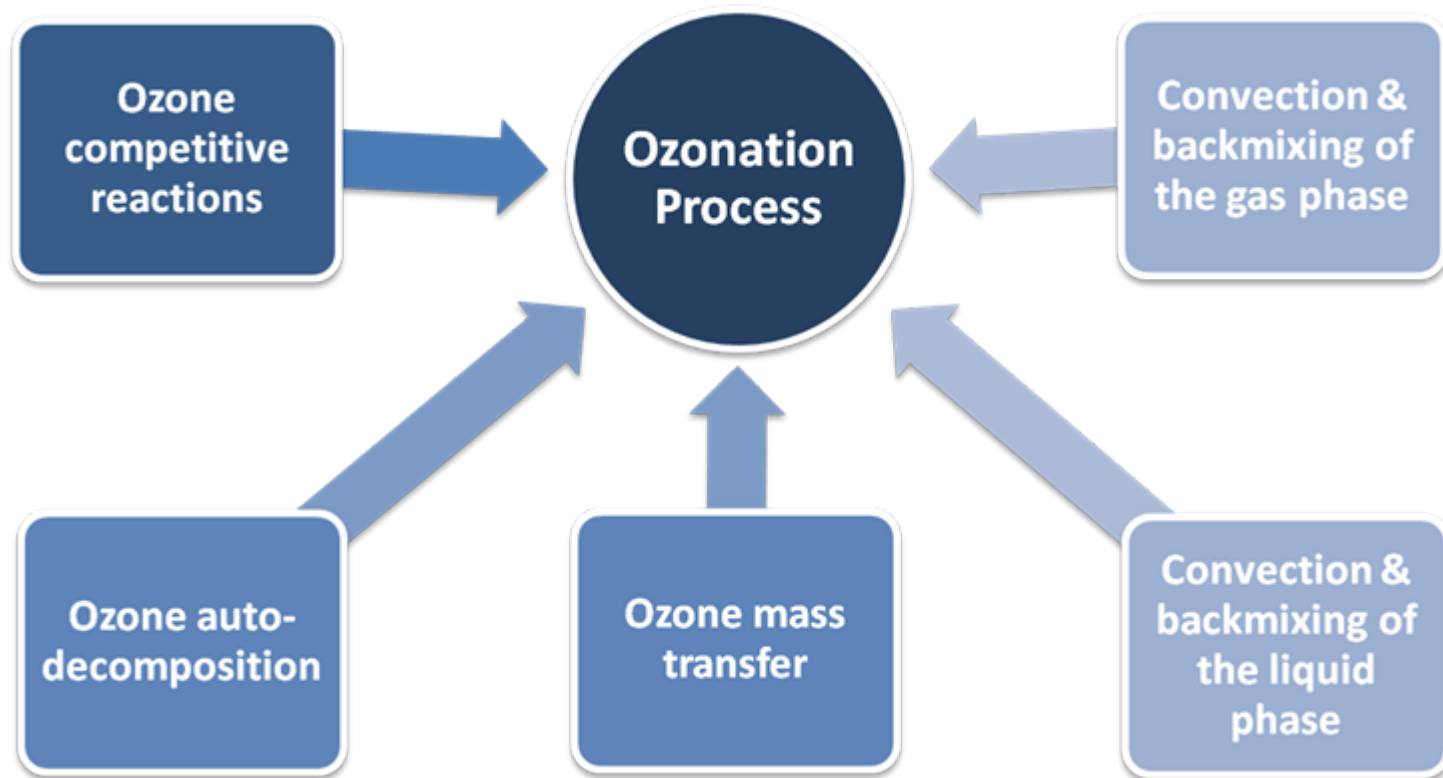
Ozone Chemistry

	O_2	ClO_2	Cl_2	MnO_4^-	H_2O_2	O_3	$\cdot OH$
E_o (V)	1.23	1.27	1.36	1.67	1.77	2.07	2.80

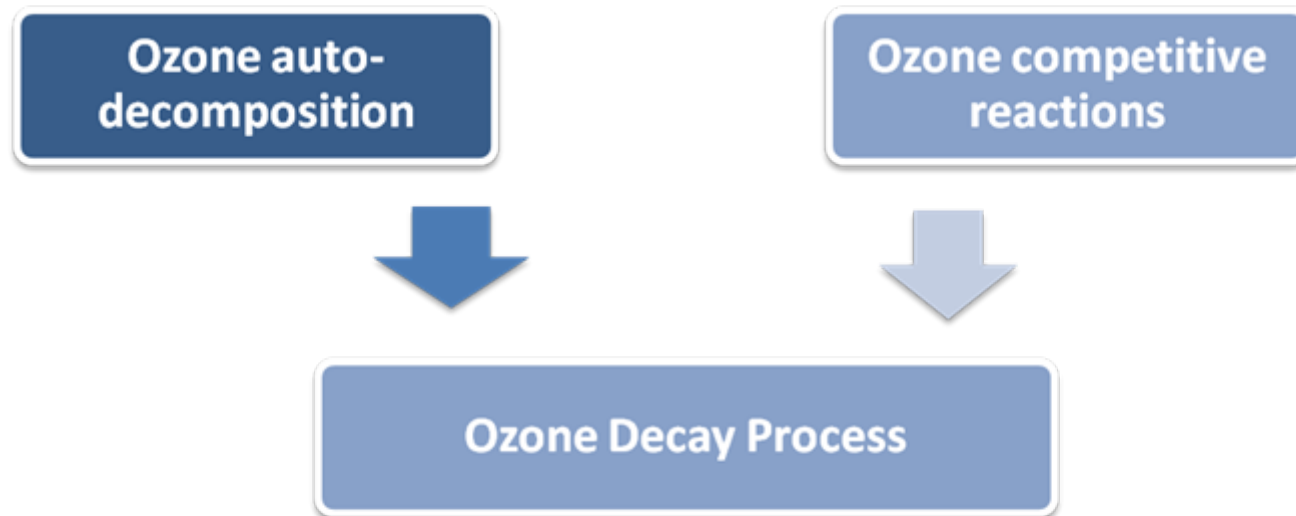
Mechanisms



Ozone Process



Ozone Decay Process



Ozonation Kinetics

Homogeneous Kinetics

Concentration of reactants

Rate constant

Reaction order

Heterogeneous Kinetics

Chemical reaction parameters

Mass transfer

Reactivity and Kinetic Regimes

Wastewater	Specific contaminant	Kinetic Regime	Pathway	Treatment
Swine Manure	Odor compounds	Fast regime	Direct Ozone reaction	AOP not recommended
Petrochemical	Benzoic acid	Very slow regime	Indirect Reaction	AOP recommended
Municipal	Ammonia	Very slow regime	Indirect Reaction	AOP recommended
Textile	Azoic dyes	Fast regime	Direct Ozone reaction	AOP not recommended



2. Application in Water Treatment

Enhancement of
Coagulation-
Flocculation

Taste and Odor
Removal

Disinfection

Removal of
Micropollutants



Degradation of Pesticides in Natural Water



Application in Water Treatment:

Degradation of Pesticides in Natural Water

Degradation of Pesticides in Natural Water

Concerns

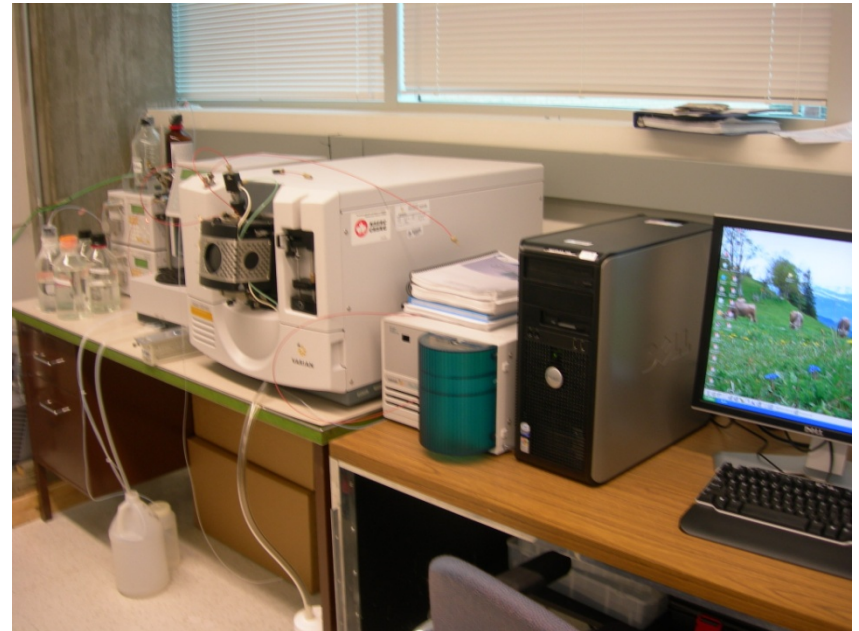
- Less than 1% of pesticides used reach their target organisms

Pesticides

- Bromoxynil
- Trifluralin

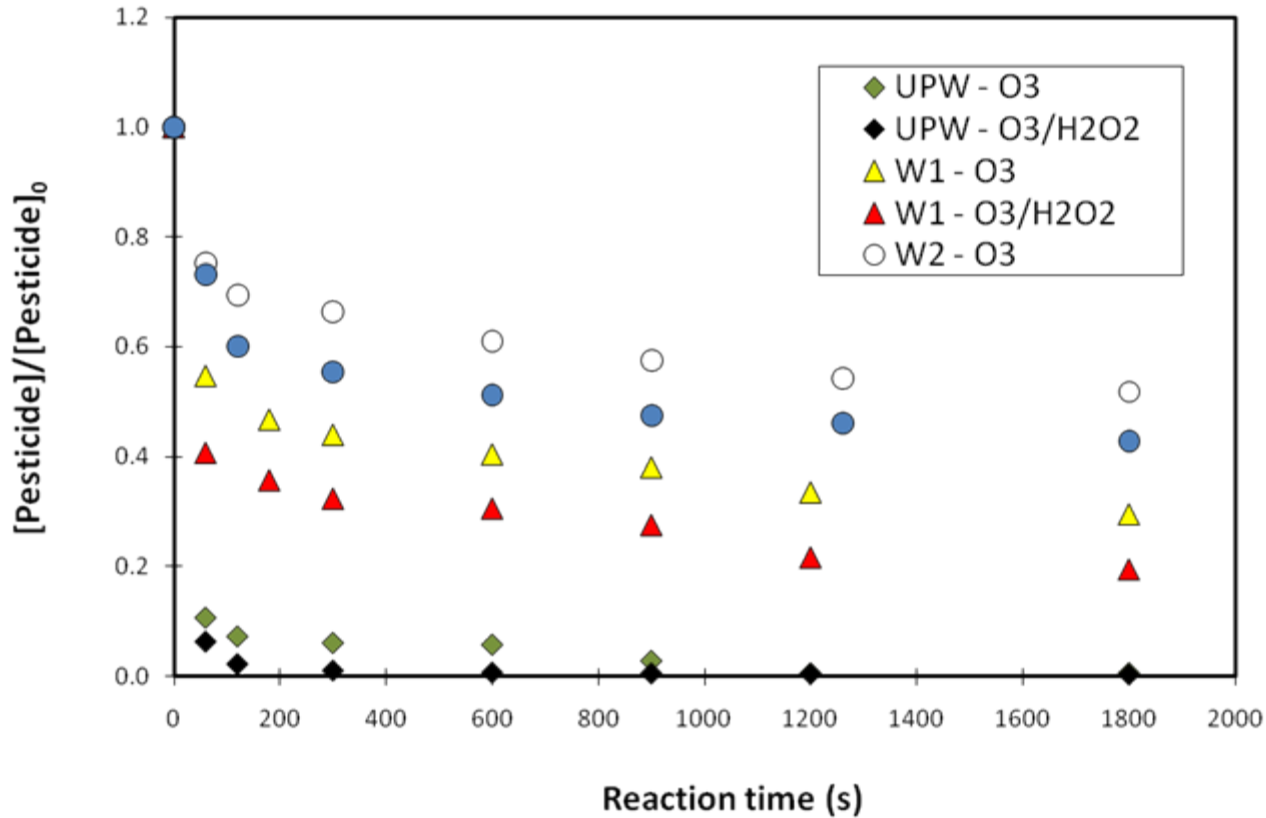
Degradation of Pesticides in Natural Water

- Pesticide degradation in river water and irrigation return flow water
- Toxicity assessed using Microtox[®] bioassay
- By-product identification



Degradation of Pesticides in Natural Water

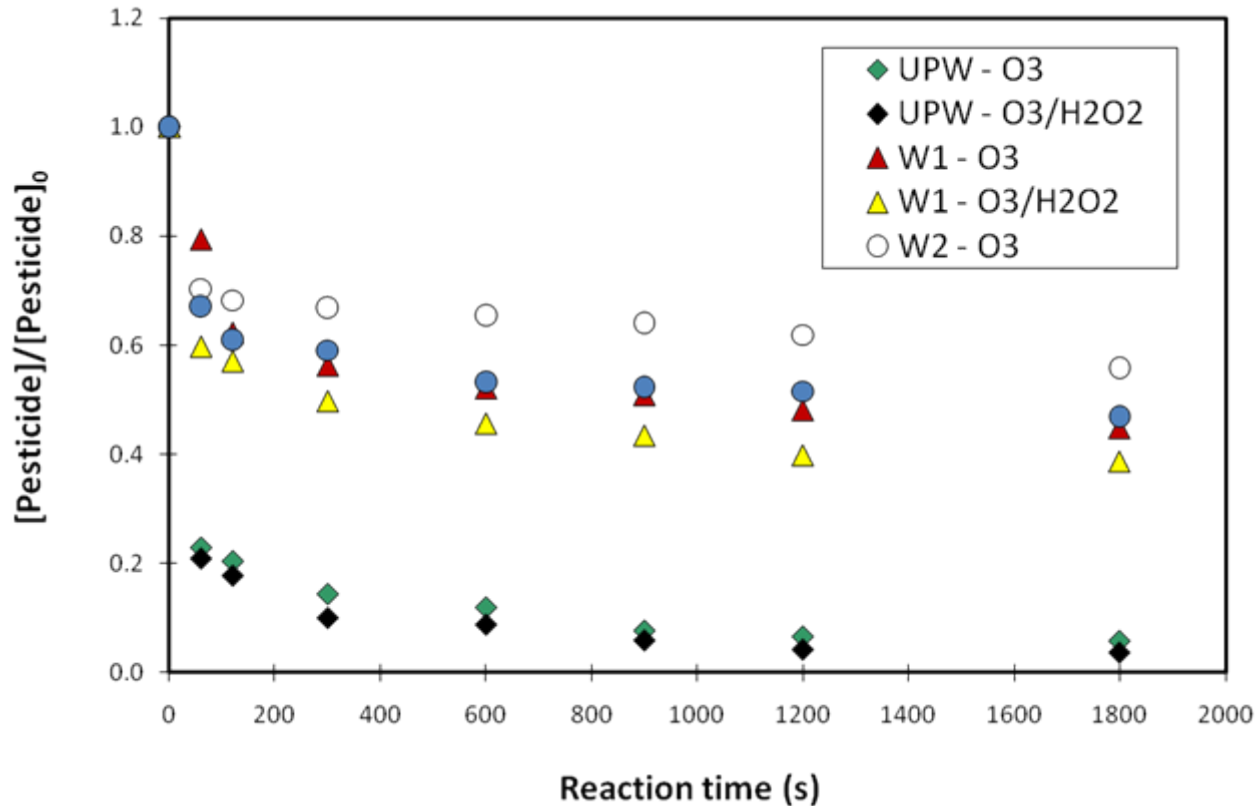
Bromoxynil decay



UPW: Ultrapure water
W1: Saskatchewan River water
W2: Irrigation return flow water flowing into the Redwater River

Degradation of Pesticides in Natural Water

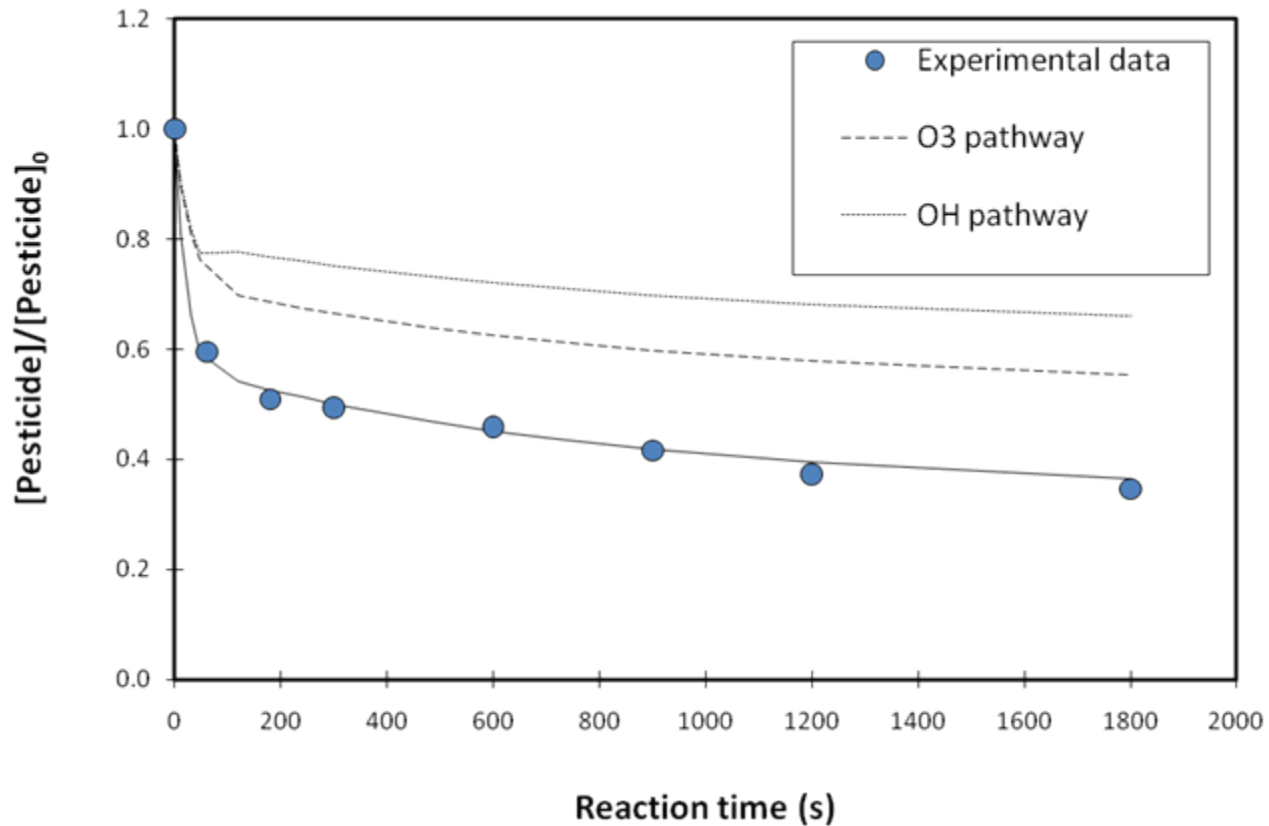
Trifluralin decay



UPW: Ultrapure water
W1: Saskatchewan River water
W2: Irrigation return flow water flowing into the Redwater River

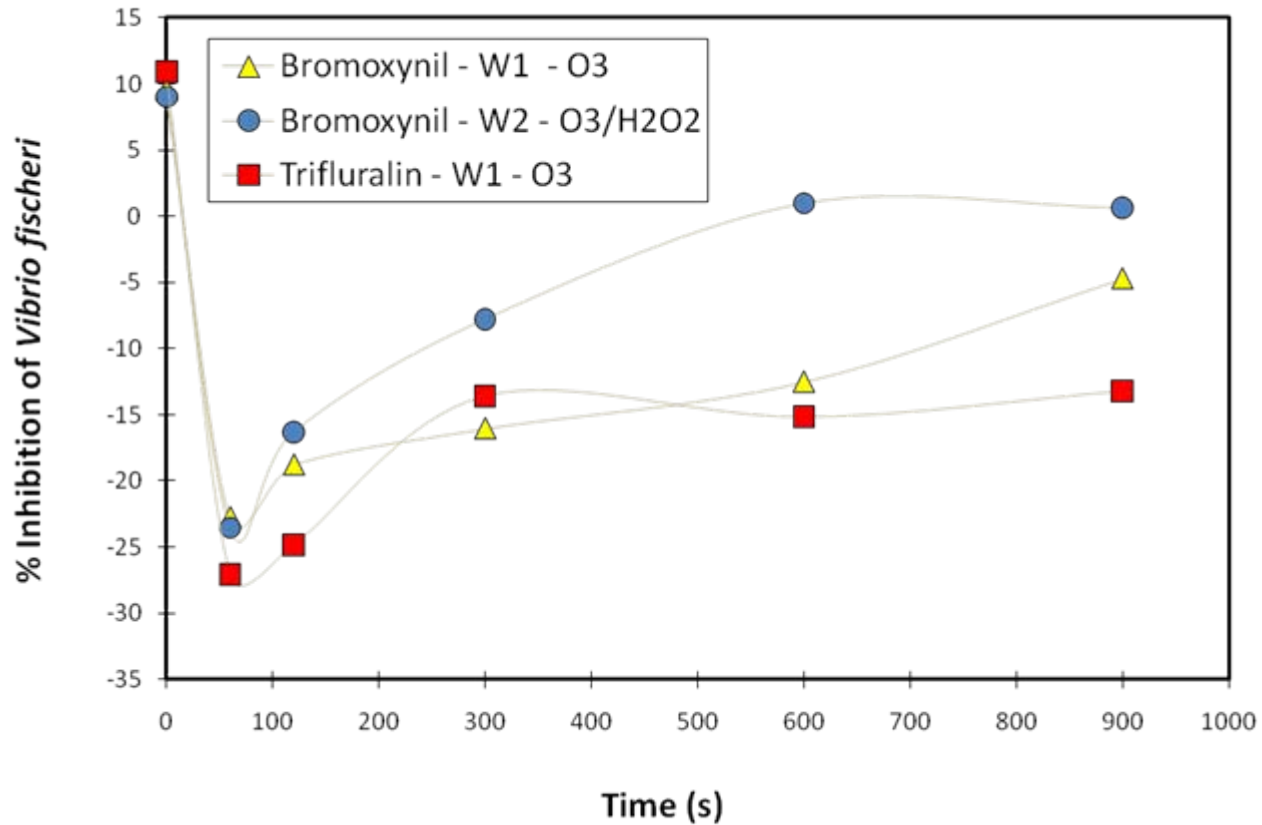
Degradation of Pesticides in Natural Water

Predicted bromoxynil oxidation by O_3 and $\cdot OH$ pathways



Degradation of Pesticides in Natural Water

Toxic effects of bromoxynil and trifluralin on *Vibrio fischeri*



W1: Saskatchewan River water

W2: Irrigation return flow water flowing into the Redwater River

Degradation of Pesticides in Natural Water

By-product identification

Bromoxynil

3,5 dibromo-2,4-dihydroxybenzonnitrile

3-bromo-4,5-hydroxybenzonnitrile

3-bromo-4-hydroxybenzonnitrile

4-hydroxybenzonnitrile

Trifluralin

α,α,α -trifluoro-4,6-dinitro-5-(dipropylamino)-*o*-cresol

α,α,α -trifluoro-2,6-dinitro-*N*-dipropyl-*p*-toluidine

2,6-dinitro-4-trifluoromethylaniline

4-trifluoromethylaniline

Degradation of Pesticides in Natural Water

Summary

- Bromoxynil and trifluralin could not be significantly degraded during conventional ozonation in natural water.
- Toxicity bioassay indicated a decrease in toxicity during the first minutes of reaction. However, an increase in toxicity was observed in the following minutes of reaction.



3. Application in Wastewater Treatment

Disinfection After
Secondary
Treatment

Removal of
Refractory and/or
Toxic Compounds

Sewage Treatment

Reuse Applications



Ozonation of Oil Sands Process-Affected Water



Application in Wastewater Treatment:

Ozonation of Oil Sands Process-Affected Water

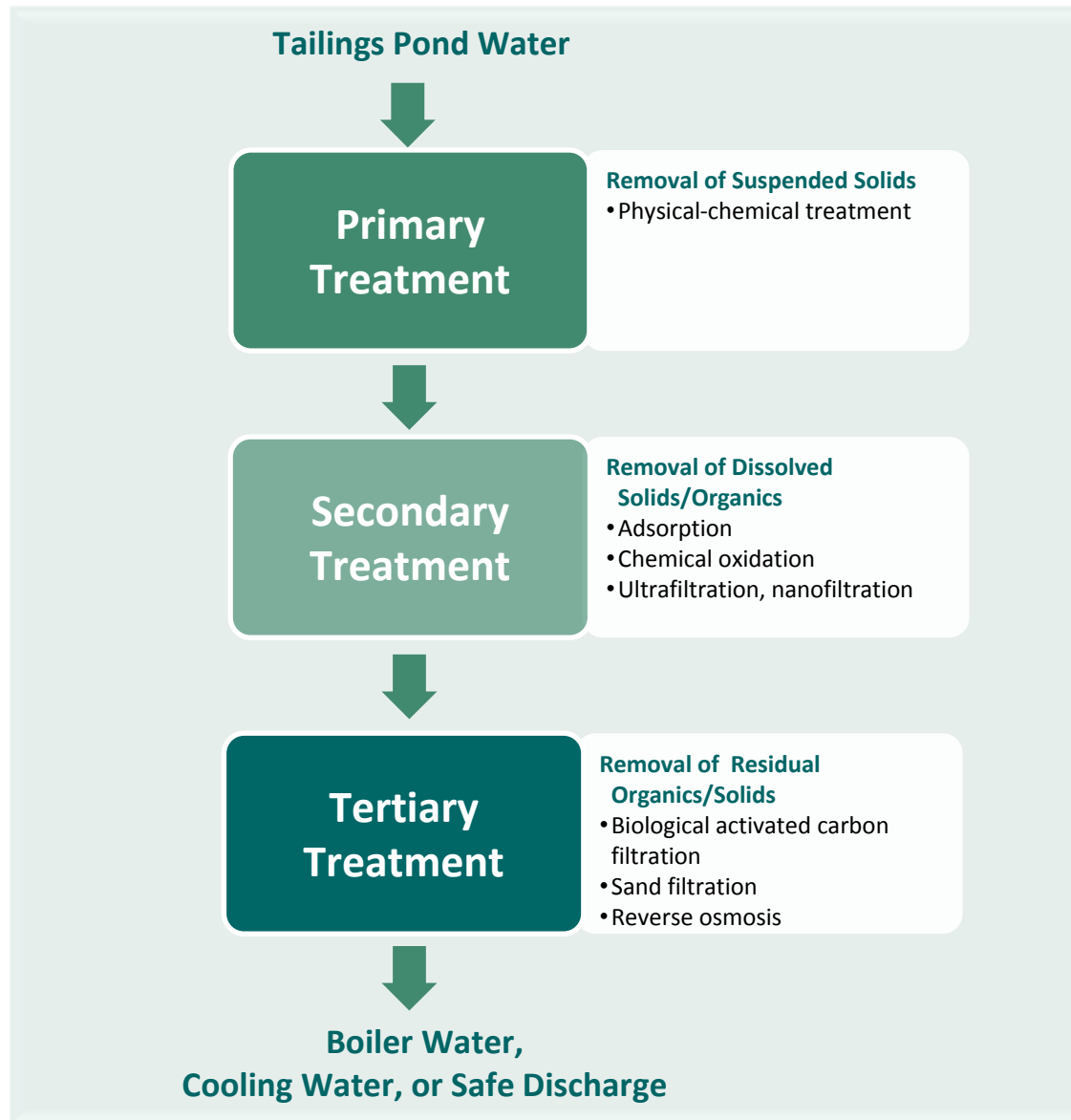
Ozonation of OSPW

Characteristics

- OSPW is estimated to be 1 billion m³ in the Athabasca oil sands region by 2025

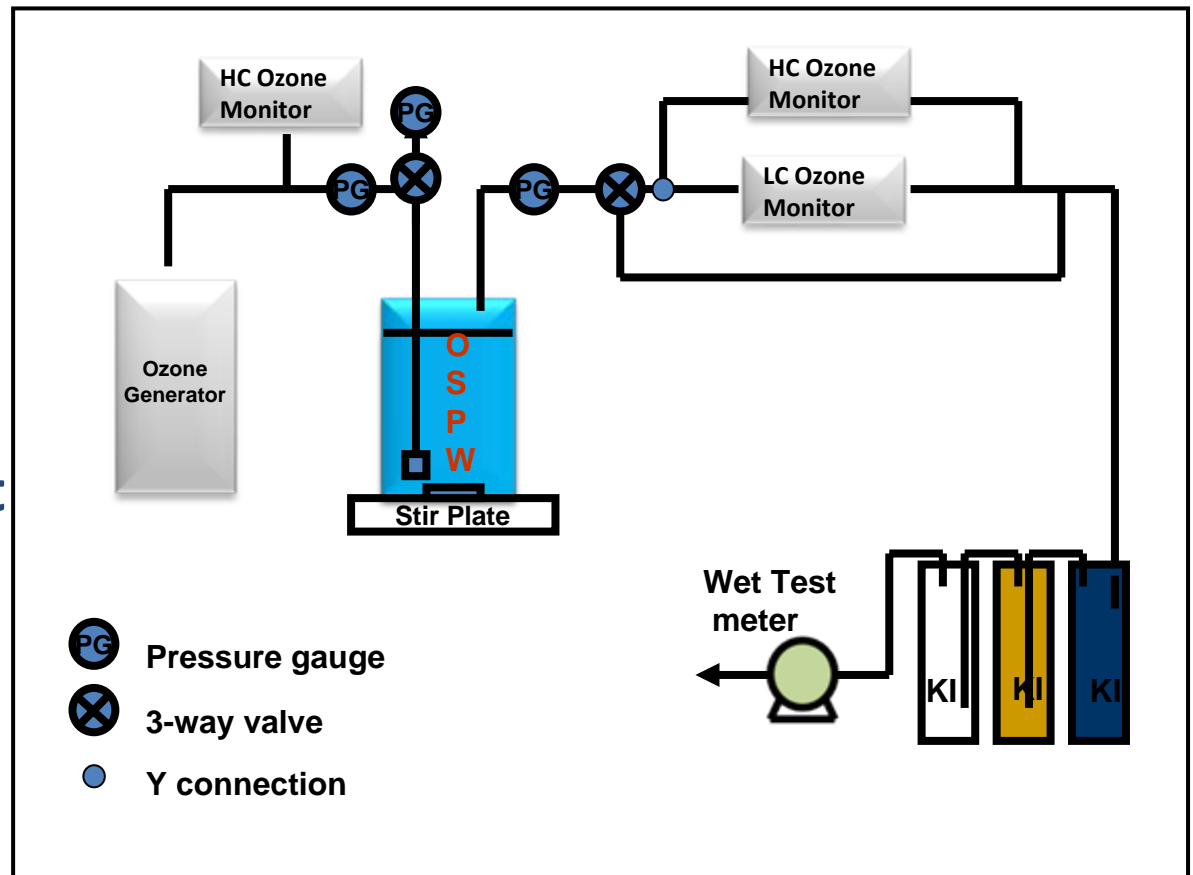
Concerns

- Naphthenic acids (NAs) are natural low molecular weight surfactants released from bitumen during extraction of oil sands ore.



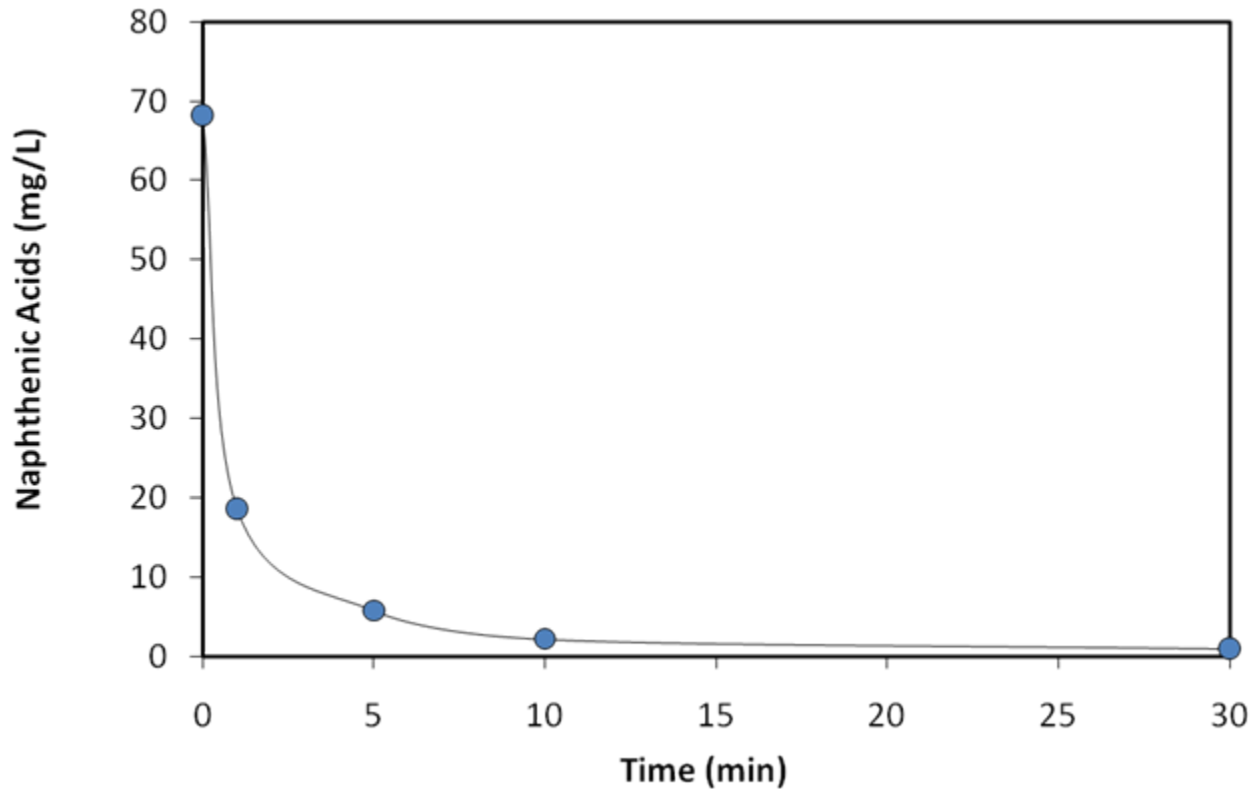
Ozonation of OSPW

- Degradation levels
- Biodegradability
- Toxicity assessment



Ozonation of OSPW

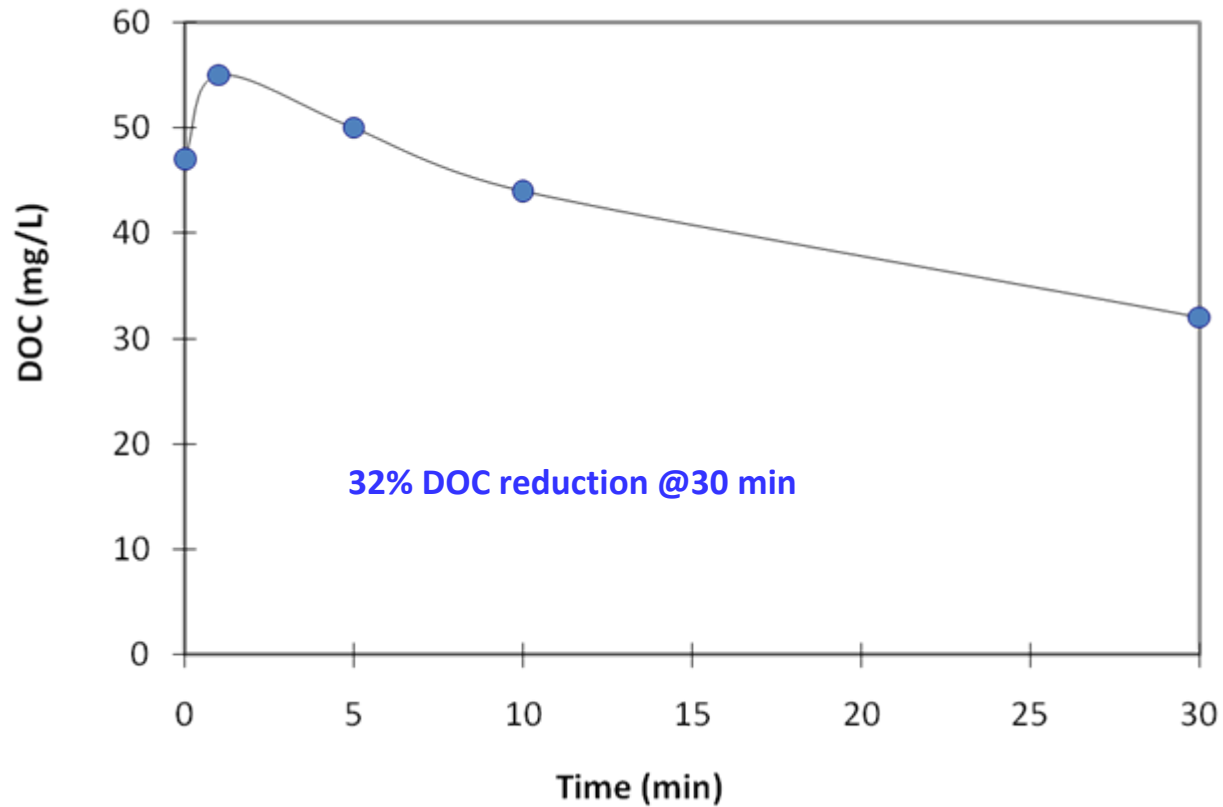
Degradation of Naphthenic Acids



- ozone contactor with a capacity of 1000 mL (222 × 56 mm i.d.)
- gas flow rate: 2 L/min
- ozone concentration in the feeding gas: 25 g/m³.

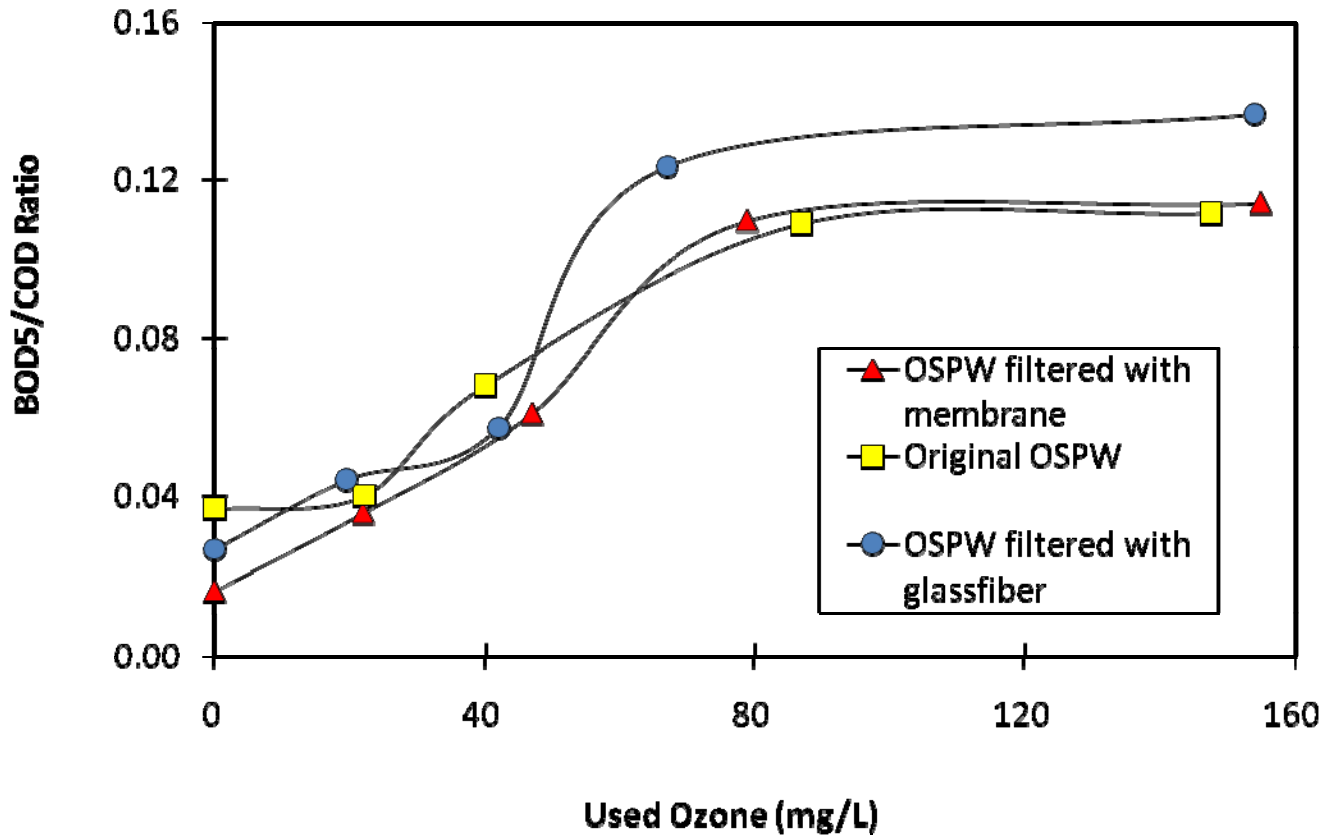
Ozonation of OSPW

Effect of ozonation on DOC



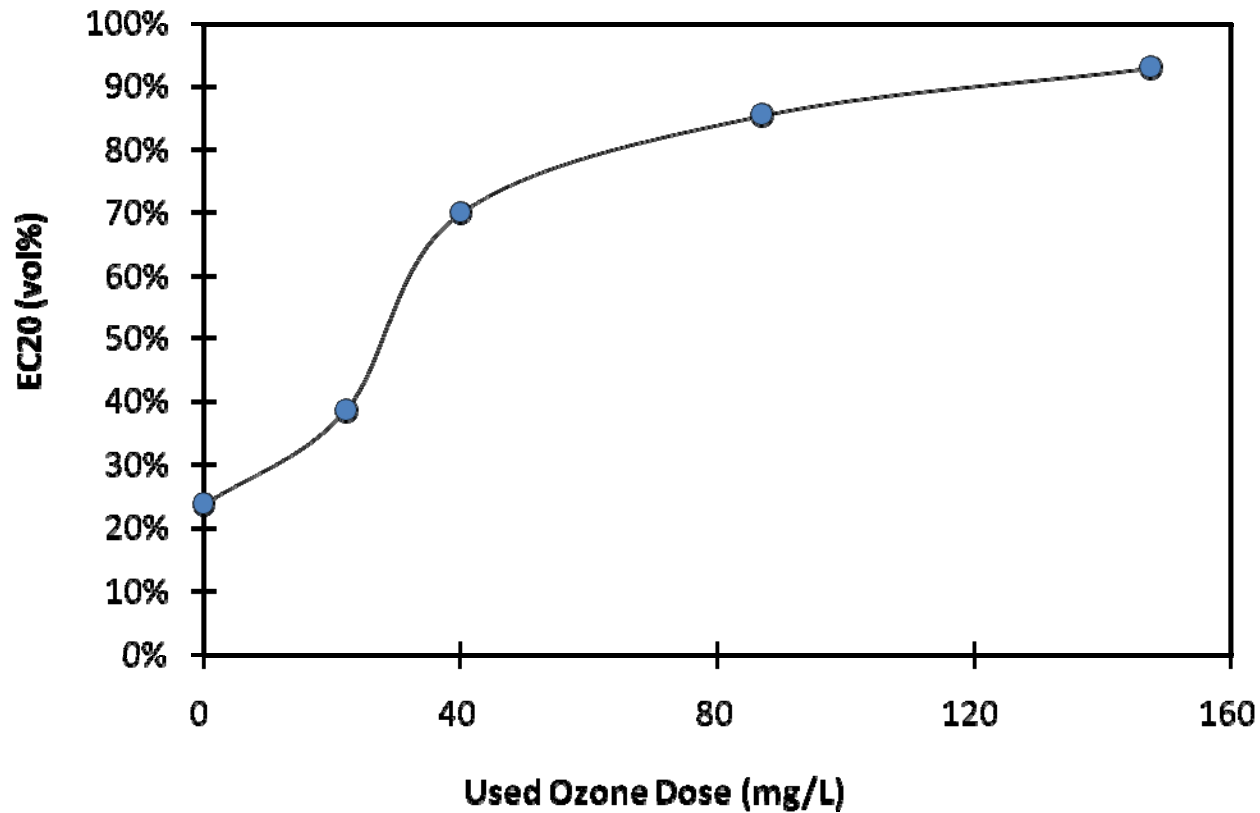
Ozonation of OSPW

Effect of ozonation on BOD₅/COD ratio



Ozonation of OSPW

Toxicity of ozonated OSPW



Ozonation of OSPW

Summary

- **Ozone is a promising advanced treatment technology for the naphthenic acids removal from OSPW (>99% removal).**
- **Ozone treatments increase the biodegradability of OSPW.**
- **OSPWs have less toxicity after ozone treatments.**

Future Works

- ✓ **Enhance the ozone use efficiency**
- ✓ **Assess process scalability**
- ✓ **Apply AOPs**
- ✓ **Understand the mechanism of degradation**
- ✓ **Characterization of by-products**



4. Concluding Remarks

4. Concluding Remarks

- ✓ **Ozone-based AOPs are effective technologies in removing many organic, inorganic and microbiological pollutants.**

- ✓ **Areas that require further development:**
 - **By-product toxicity**
 - **Energy efficiency**

Acknowledgements

- ✓ Daniel W. Smith, Ph.D., P.Eng.
- ✓ Helen Fu, Ph.D.

- ✓ Technical staff of the Environmental Engineering Program at the University of Alberta

- ✓ Financial support provided by:
 - Alberta Ingenuity Center for Water Research (AICWR)
 - Natural Sciences and Engineering Research Council of Canada (NSERC)
 - Canada Foundation for Innovation (CFI)
 - Alberta Ingenuity Fund (AIF)



Thank You For Your Attention!

For More Information

Pamela Chelme-Ayala, Ph.D., E.I.T.

chelmeayala@ualberta.ca

