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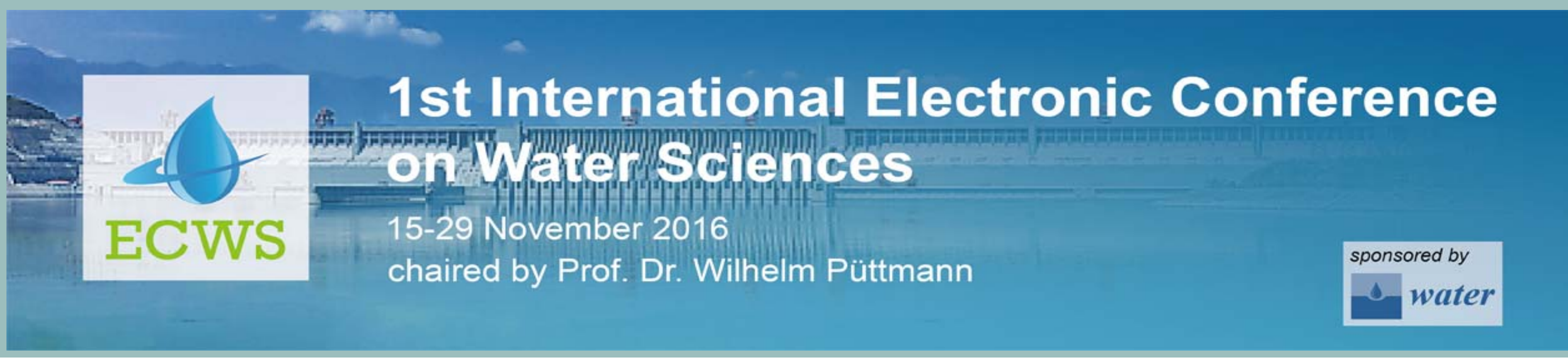
Comparison of advanced oxidation processes for emerging contaminants removal



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OUTLINE

- Introduction
- Background
  - Emerging Contaminants
  - Advanced Oxidation Processes
- Analytical Methods and Techniques
- Results
  - Process Engineering Parameters
  - Environmental Parameters
  - Economic and Social Parameters
- Discussion

INTRODUCTION

- Emerging contaminants are difficult to remove using traditional water and wastewater treatment methods
  - EDCs and PPCPs are potentially harmful to humans and wildlife
  - Advanced oxidation processes have been proven successful
- Multiple parameters must be considered when choosing the best method
  - Technical competence is not the only essential element
- Various AOPs were compared by ranking numerous parameters
  - The processes with the highest average ranking indicates most rational options

BACKGROUND

EMERGING CONTAMINANTS

- Relatively unknown
- Limited regulations
- Difficult to remove from water and wastewater
- Pose threat through introduction to aquatic environments and drinking water
- Occur on ng/L to µg/L scale

ENDOCRINE DISRUPTING COMPOUNDS (EDCS)

Table 1: Examples of EDCs

Contaminant	Description
Bisphenol A	Preservative, Plastic Component
Butylated Hydroxyanisole	Food Preservative
DDT	Pesticide
Atrazine	Pesticide
17β-estradiol	Steroid Hormone
Estrone	Steroid Hormone
Testosterone	Steroid Hormone
Cadmium	Heavy Metal
Mercury	Heavy Metal
Lead	Heavy Metal
Arsenic	Heavy Metal
Musk Ketone	Fragrance
Hexabromocyclododecane	Flame Retardant
Caffeine	Stimulant

- Effect humans and aquatic wildlife
  - Reproduction
  - Growth
  - Metabolism
- Cause birth defects and tumors
- Introduced through urban and agricultural runoff, landfill leachates, and concentrated animal feeding operations

PHARMACEUTICAL AND PERSONAL CARE PRODUCTS (PPCPS)

- Widespread use
- Include:
  - Pharmaceutical drugs
  - Cosmetics
  - Fragrances
  - Food supplements
- Introduced mainly through sewage effluent and hospital and animal wastes
- Effects:
  - Chronic effects unknown
  - Antibiotic resistance

Table 2: Examples of PPCPs

Contaminant	Description
Acetaminophen	Analgesic
Ketoprofen	Analgesic
Carbamazepine	Anticonvulsant
Ibuprofen	Anti-Inflammatory
Triclosan	Antibacterial
Ciprofloxacin	Antibiotic
Acridine	Antiseptic
Bezafibrate	Fibrate Drug
Dilantin	Antiepileptic
Nicotine	Stimulant, Insecticide

ADVANCED OXIDATION PROCESSES (AOPS)

- Effective in degrading emerging contaminants
  - Theoretically broken down into harmless components
  - Must consider degradation products
- Organic compounds are oxidized into CO_2, H_2O, and mineral acids
- Production of hydroxyl radicals that react easily with organic compounds due to unpaired electron
- Common oxidants
  - Ozone (O_3)
  - UV
  - Hydrogen peroxide (H_2O_2)

ADVANCED OXIDATION PROCESSES (AOPS)

O_3

H_2O_2/O_3

O_3/UV

H_2O_2/UV

TiO_2 photocatalysis

Fenton reaction

ANALYTICAL METHODS AND TECHNIQUES

Table 3: Ranking System

Ranking System	
Value	Description
5	Very High
4	High
3	Moderate
2	Low
1	Very Low

- In order to accurately compare each process, performance was quantified
- Rankings were assigned to each process for each parameter
- Higher values indicate improved performance
- Rankings were then averaged across each parameter category

RESULTS

Process Engineering
Environmental
Economical and Social

PROCESS ENGINEERING PARAMETERS

MECHANICAL RELIABILITY

- Mechanical soundness
  - Least number of “moving parts”
- Ozone
  - Ozone generator and ozone gas diffuser require routine cleaning and inspection
  - Sparger fouling
- UV
  - Lamp replacement
  - Routine inspection
- Photocatalysis, Fenton
  - High maintenance
    - pH
    - Mixing
    - TiO_2, iron

Table 4: Mechanical Reliability Ranking

Mechanical Reliability	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	3
H_2O_2/UV	3
TiO_2	2
Fenton	2

PROCESS RELIABILITY

Table 5: Process Reliability Ranking

Process Reliability	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	4
TiO_2	2
Fenton	2

- Ability to consistently produce adequate effluent
- Older techniques have a proven history of reliability
- Photocatalysis and Fenton process are more modern and less tested
  - TiO_2 slurry and precipitated iron effect effluent (requires removal)

FLEXIBILITY

- Ability to adjust to influent flow rate
- Older technologies have experience in adjusting conditions
  - Factor of safety has been implemented
- Chemical dosages can easily be adjusted
- Semi-batch reactors in photocatalysis and Fenton

Table 6: Flexibility Rankings

Flexibility	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	4
TiO_2	3
Fenton	3

ADAPTABILITY

Table 7: Adaptability Rankings

Adaptability	
AOP	Ranking
O_3	3
H_2O_2/O_3	3
O_3/UV	2
H_2O_2/UV	2
TiO_2	3
Fenton	3

- Ability to adjust to influent water quality
- Turbidity can effect UV penetration
- Ozone diffusers and UV lamp sleeves are subject to scaling
- Nitrate and iron reduce degradation efficiency of UV processes
- Photocatalysis produces hydroxyl radicals quickly
  - Adapts well
- Fenton process is pH sensitive

ENERGY CONSUMPTION

- Large contributor to total cost
- Relation to resource depletion, CO_2 emissions
- UV lamps
  - Energy intensive
  - Can be mitigated with proper chemical additions
- Onsite O_3 generation
- Fenton process only includes simple pumping requirements

Table 8: Energy Consumption Rankings

Energy Consumption	
AOP	Ranking
O_3	2
H_2O_2/O_3	3
O_3/UV	2
H_2O_2/UV	4
TiO_2	2
Fenton	5

AOT	Source/Water	Initial Concentration (µg/L)		Specific Energy Consumption (kWh/m^3)		Reference
		Geosmin	MIB	Geosmin	MIB	
UV/O_3	Fish Farm (spiked)	0.0042-0.0067	0.0032-0.0087	19.00	8.00	Klausen & Gronborg
UV/H_2O_2	Fish Farm (spiked)	0.0042-0.0068	0.0032-0.0088	16.00	13.00	Klausen & Gronborg
		Oxalic Acid	Dichloroacetic Acid	Oxalic Acid	Dichloroacetic Acid	
TiO_2/O_3	Synthetic	126	129	17.0	50.0	Mehrjouei, et al.
TiO_2/UVA/O_2	Synthetic	126	129	63.0	350.0	Mehrjouei, et al.
TiO_2/UVA/O_3	Synthetic	126	129	7.0	24.0	Mehrjouei, et al.
O_3	Post MBR Wastewater	-	-	11.93		Chong, et al.
O_3/UV	Post MBR Wastewater	-	-	6.15		Chong, et al.
H_2O_2/UV	Post MBR Wastewater	-	-	0.23		Chong, et al.
Photocatalysis	Post MBR Wastewater	-	-	7.09		Chong, et al.
				80W Lamp	40W Lamp	
UV/HOCl	Tap Water	1.00		0.32	0.16	Sichel, et al.
UV/ClO_2	Tap Water	1.00		0.32	0.16	Sichel, et al.
UV/H_2O_2 (UV mp lamps)	Tap Water	1.00		0.5		Sichel, et al.
UV/H_2O_2 w/ RO	MF/RO Permeate	-	-	0.62		James, et al.
UV/H_2O_2 w/ MF	MF/RO Permeate	-	-	0.93		James, et al.
UV/H_2O_2 w/ AC	MF/RO Permeate	-	-			James, et al.
$O_{3\ (2\ mg/l)}$	WWTP Effluent	0.001-0.503		0.03		Kim & Tanaka
$O_{3\ (4\ mg/L)}$	WWTP Effluent	0.001-0.503		0.06		Kim & Tanaka
$O_{3\ (6\ mg/L)}$	WWTP Effluent	0.001-0.503		0.09		Kim & Tanaka

$O_{3\ (2\ mg/l)}/UV_{65W}$	WWTP Effluent	0.001-0.503	1.06	Kim & Tanaka
$O_{3\ (4\ mg/L)}/UV_{65W}$	WWTP Effluent	0.001-0.503	1.09	Kim & Tanaka
$O_{3\ (6\ mg/L)}/UV_{65W}$	WWTP Effluent	0.001-0.503	1.12	Kim & Tanaka
UV(10W)	Hospital WW	0.4	10.00	Kohler, et al.
UV(2.5W)	Hospital WW	0.4	6.00	Kohler, et al.
0.83 $gH_2O_2L^{-1}$	Hospital WW	0.4	2.00	Kohler, et al.
1.11 $gH_2O_2L^{-1}$	Hospital WW	0.4	2.00	Kohler, et al.
Conventional GAC	NF/GAC Plants	-	0.16	Bonton, et al.
Nanofiltration	NF/GAC Plants	-	0.55	Bonton, et al.

OVERALL PROCESS ENGINEERING RESULTS

Table 9: Process Engineering Summary

	AOPs					
Process Engineering Parameters	O_3	H_2O_2/O_3	O_3/UV	H_2O_2/UV	TiO_2	Fenton
Mechanical Reliability	4	4	3	3	2	2
Process Reliability	4	4	4	4	2	2
Flexibility	4	4	4	4	3	3
Adaptability	3	3	2	2	3	3
Energy Consumption	2	3	2	4	2	5

Table 10: Process Engineering Average Rankings

AOP	Average Ranking
O_3	3.4
H_2O_2/O_3	3.6
O_3/UV	3
H_2O_2/UV	3.4
TiO_2	2.4
Fenton	3

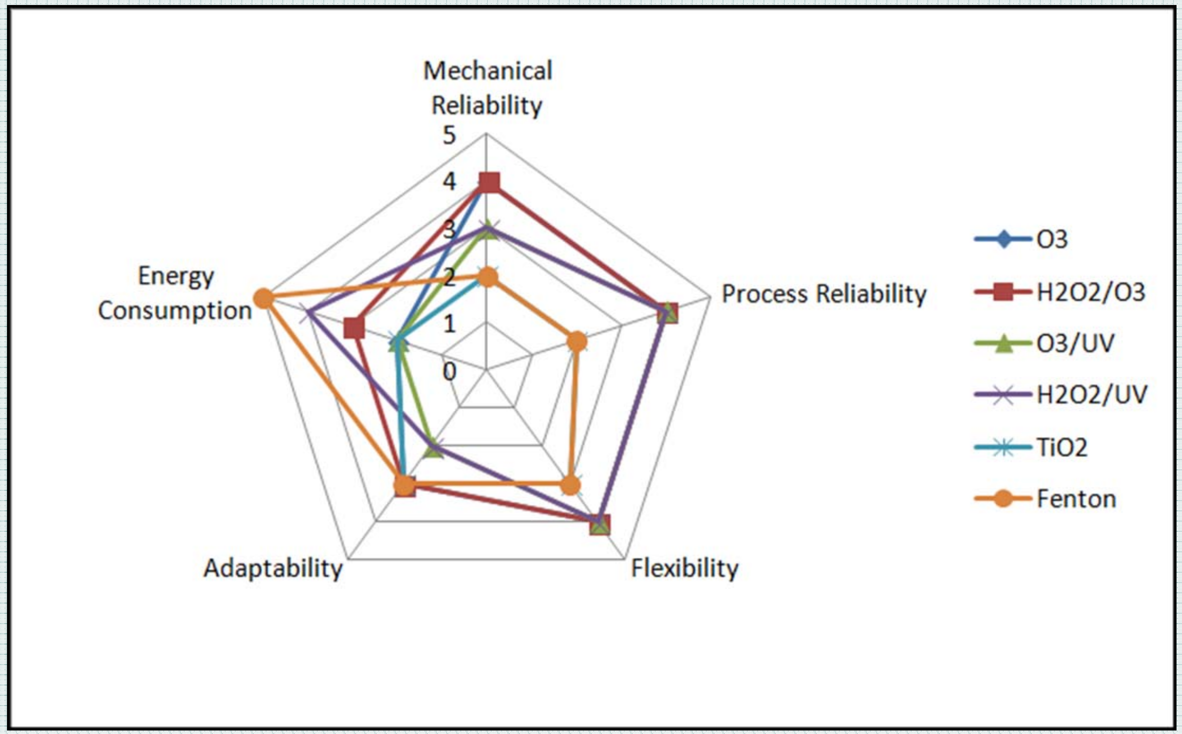

Figure 1: Process Engineering Parameter Summary

ENVIRONMENTAL PARAMETERS

CONTRIBUTION TO CLIMATE CHANGE

- Reduction in factors leading to climate change is essential
  - Emission of Greenhouse gases:
    - Polar melt
    - Altered wind and ocean patterns
    - Sea level rise
    - Change in seasons
- CO_2 emissions
  - Related to energy consumption
  - Also released during oxidation
- High ranking indicates low emissions

Table 11: Climate Change Ranking

Climate Change	
AOP	Ranking
O_3	2
H_2O_2/O_3	3
O_3/UV	2
H_2O_2/UV	4
TiO_2	2
Fenton	5

EUTROPHICATION

Table 12: Eutrophication Rankings

Eutrophication	
AOP	Ranking
O_3	5
H_2O_2/O_3	5
O_3/UV	5
H_2O_2/UV	5
TiO_2	5
Fenton	5

- Excess nutrients (nitrogen and phosphorus) can cause harmful aquatic conditions
  - Hypoxia, algal blooms
- All discussed processes do not release additional nutrients
- Preceded or proceeded by specific nutrient removal process

TERRESTRIAL AND AQUATIC TOXICITY/DEGRADATION PRODUCTS

- Chemicals and degradation products can influence effluent water quality
- Ozonation produces bromate
- UV has the advantage of no chemical usage
- Photocatalysis requires catalyst removal
- The Fenton process requires iron removal
- All processes potential form degradation products

Table 13: Toxicity Rankings

Toxicity	
AOP	Ranking
O_3	2
H_2O_2/O_3	3
O_3/UV	2
H_2O_2/UV	3
TiO_2	2
Fenton	2

OVERALL ENVIRONMENTAL RESULTS

Table 14: Environmental Summary

	AOPs					
Environmental Parameters	O_3	H_2O_2/O_3	O_3/UV	H_2O_2/UV	TiO_2	Fenton
Climate Change	2	3	2	4	2	5
Eutrophication	5	5	5	5	5	5
Toxicity	2	3	2	3	2	2

Table 15: Average Environmental Rankings

Average	
AOP	Ranking
O_3	2.25
H_2O_2/O_3	2.75
O_3/UV	2.25
H_2O_2/UV	3
TiO_2	2.25
Fenton	3

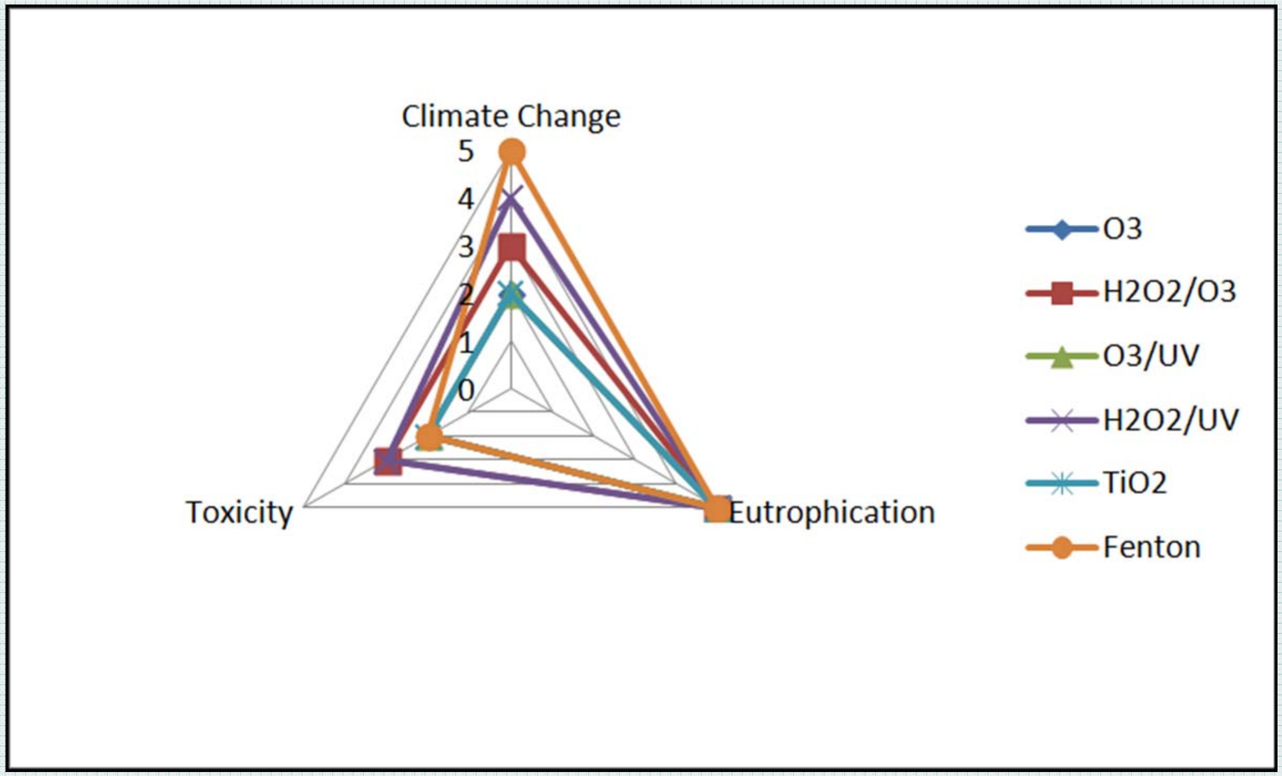

Figure 2: Environmental Parameter Summary

ECONOMIC AND SOCIAL PARAMETERS

PUBLIC ACCEPTANCE

- Approval of public is critical
- Newer technologies tend to be viewed more negatively than commonly used processes
  - Older processes have had the opportunity to prove success through pilot scale and full scale operations
  - Photocatalysis and the Fenton process introduce inorganic compounds (TiO_2 and iron) that may be viewed negatively

Table 16: Public Acceptance Rankings

Public Acceptance	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	4
TiO_2	2
Fenton	2

EASE OF USE

Table 17: Ease of Use Rankings

Ease of Use	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	4
TiO_2	2
Fenton	2

- More complicated techniques introduce more opportunity for error
- Skilled personal can increase operational costs
- Commonly used processes have had time to correct problems
- Newer technologies possess level of uncertainty
- Photocatalysis also requires difficult catalyst recovery

ECONOMIC FEASIBILITY

Table 18: Cost Summary

AOP	Cost $/1000 gal	Amortized Annual Capital Cost	Annual O&M Costs
O_3	1.2023	7.55E+04	9.16E+04
O_3/UV	38.648	1.12E+06	4.25E+06
H_2O_2/UV	308.482	2.36E+06	4.05E+07
TiO_2	8648.79	2.51E+08	9.51E+08
Fenton	14.2829	-	1.99E+06

Table 19: Capital Cost Breakdown

Factors	Percent (%)
Piping, Valves, Electrical	30
Site Work	10
Engineering	15
Contractor O & P	15
Contingency	30
Total	100

- Plant is working for the full year (52 weeks)
- Labor rate = $80/hour
- Analytical labor rate = $200/hour
- Electricity rate = $0.08/kWh
- Amortization occurs over 30 years at a rate of 7%
- Mahamuni & Adewuyi, 2014

ECONOMIC FEASIBILITY

- Can be considered one of the most important/limiting factors
- Largely related to energy consumption
- Older methods tend to be more cost efficient
- Photocatalysis shows very poor performance
  - UV lamps, expensive catalyst, maintenance

Table 20: Economic Feasibility Rankings

Economic Feasibility	
AOP	Ranking
O_3	5
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	3
TiO_2	1
Fenton	4

OVERALL ECONOMIC AND SOCIAL RESULTS

Table 21: Economic and Social Summary

	AOPs					
Economic and Social Parameters	O_3	H_2O_2/O_3	O_3/UV	H_2O_2/UV	TiO_2	Fenton
Public Acceptance	4	4	4	4	2	2
Ease of Use	4	4	4	4	2	2
Economic Feasibility	5	4	4	3	1	4

Table 22: Average Economic and Social Rankings

	Average
AOP	Ranking
O_3	4.33
H_2O_2/O_3	4.00
O_3/UV	4.00
H_2O_2/UV	3.67
TiO_2	1.67
Fenton	2.67

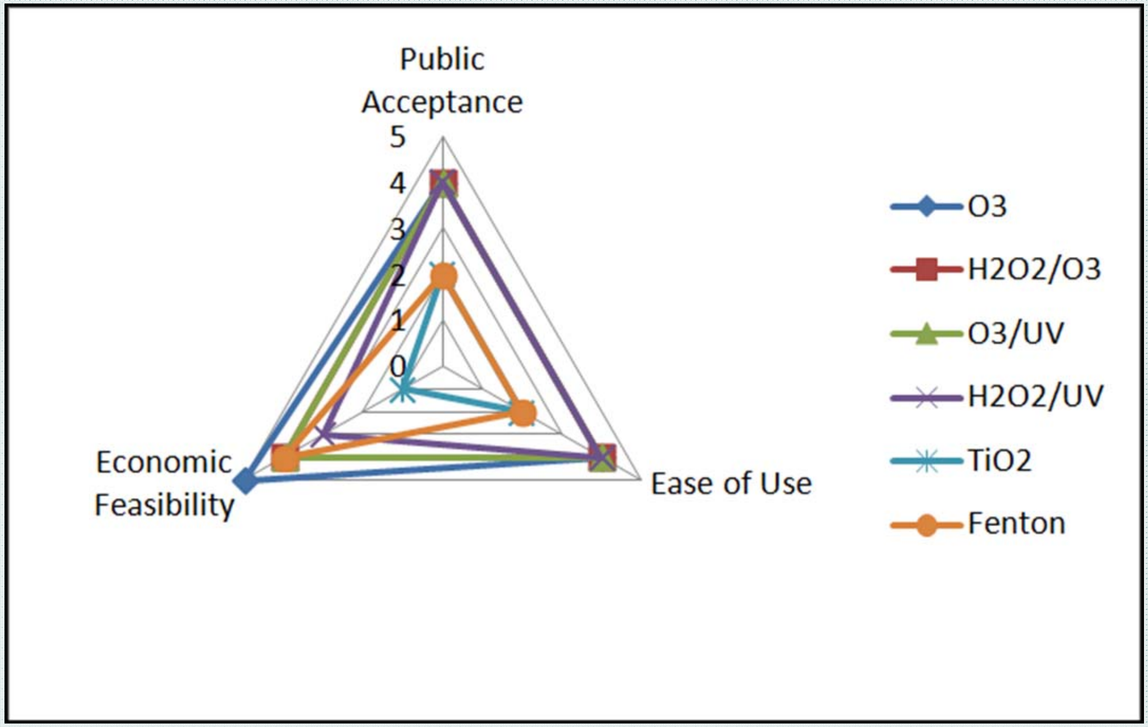

Figure 3: Economic and Social Parameter Summary

COMPREHENSIVE RESULTS

Table 23: Comprehensive Rankings and Averages

	AOPs					
Parameters	O_3	H_2O_2/O_3	O_3/UV	H_2O_2/UV	TiO_2	Fenton
Mechanical Reliability	4	4	3	3	2	2
Process Reliability	4	4	4	4	2	2
Flexibility	4	4	4	4	3	3
Adaptability	3	3	2	2	3	3
Energy Consumption	2	3	2	4	2	5
Average Engineering	3.4	3.6	3	3.4	2.4	3
Climate Change	2	3	2	4	2	5
Eutrophication	5	5	5	5	5	5
Toxicity	2	3	2	3	2	2
Average Environmental	2.25	2.75	2.25	3	2.25	3
Public Acceptance	4	4	4	4	2	2
Ease of Use	4	4	4	4	2	2
Economic Feasibility	5	4	4	3	1	4
Average Economic and Social	4.33	4	4	3.67	1.67	2.67
Comprehensive Average	3.33	3.45	3.08	3.36	2.11	2.89

COMPREHENSIVE RESULTS

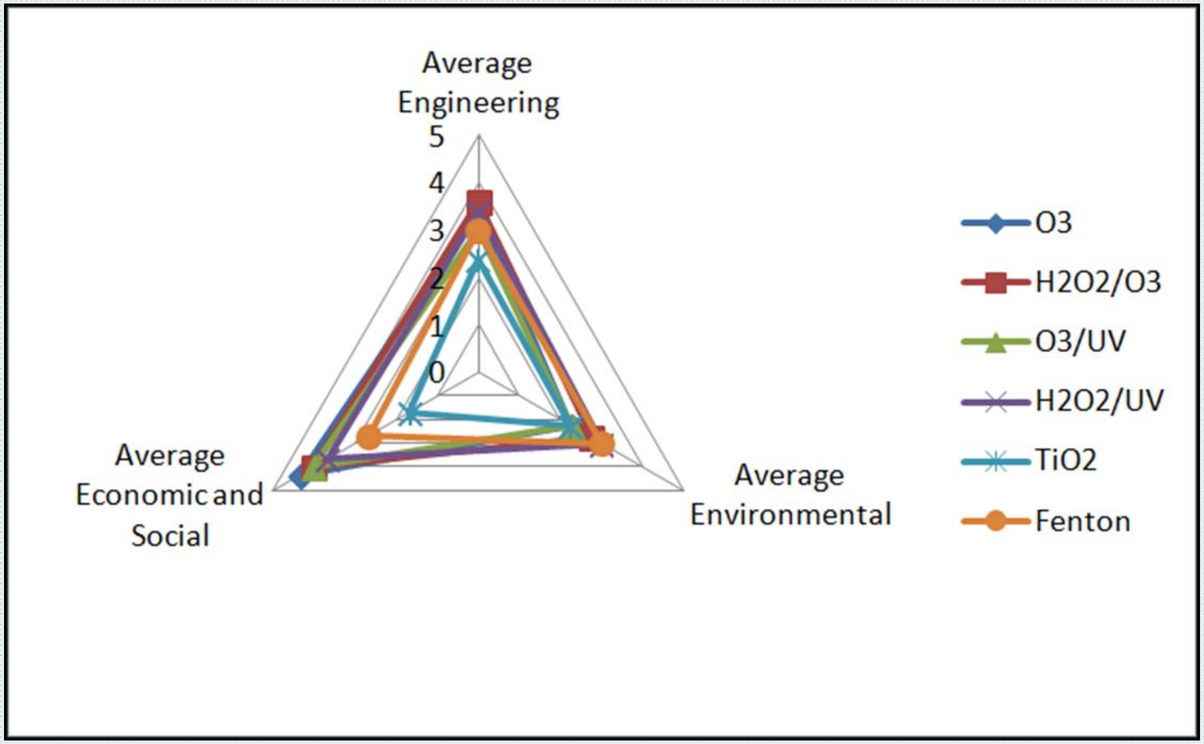

Figure 4: Comprehensive Parameter Category Comparison

DISCUSSION

POTENTIAL FOR DISPROPORTIONATE COMPARISON

- Analysis included both novel techniques and more commonly used processes
  - Older processes often had an advantage
  - The same study completed in the future could produce different results as methods progress
- Variation in constituent matrix
  - Different studies considered different contaminants
  - Some contaminants are more difficult to degrade than others
  - This gives unequal comparison
    - One process may work well for one contaminant, which should not be compared to a process degrading a more recalcitrant contaminant
- An examination of all processes with multiple sources would be advantageous

ADDITIONAL DATA REQUIREMENTS

Table 24: Cost Breakdown

O&M Cost Breakdown						
AOP	Part Replacement	Labor	Analytical	Chemical	Electrical	Total
O_3	5.10E+02	4.54E+04	4.16E+04	0.00	4.09E+03	9.16E+04
O_3/UV	1.28E+06	5.94E+04	7.28E+04	0.00	2.84E+06	4.25E+06
H_2O_2/UV	2.78E+06	3.89E+04	3.12E+04	3.15E+07	6.17E+06	4.05E+07
TiO_2	2.95E+08	3.89E+04	3.12E+04	1.56E+04	6.56E+08	9.51E+08
Fenton	0.00	4.77E+04	3.12E+04	1.91E+06	0.00	1.99E+06

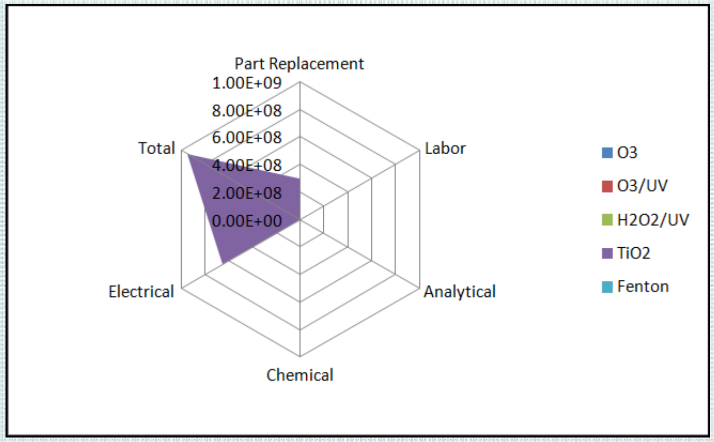

Figure 5: Comparison of O&M Costs

- Further study of economic feasibility was deemed necessary
  - Breakdown of O&M costs revealed that photocatalysis is significantly more expensive due to electricity costs
- Degradation products are also a concern
  - Limited information available
  - Additional research is needed

PROPOSED RANKING SYSTEM ALTERATIONS

- All parameters were considered to have equal worth
  - Some aspects may be more important than others (economic feasibility)
  - A study using parameters weighted for importance or relevance would be more accurate
    - Importance could vary from user to user, however
- Amount of detail was limited by five point scale
  - All rankings were relatively similar due to small numerical range
  - A ten point scale would allow for further detail and a more accurate study

CONCLUSIONS

- After comparing six AOPs across three parameter categories:
  - H_2O_2/O_3 presented the highest average ranking (3.45)
  - TiO_2 photocatalysis earned the lowest ranking (2.11)
    - This was largely due to high energy consumption and electricity costs
- The ranking system revealed both strengths and weaknesses for each process
- More established processes performed better overall
  - Reinforces need for pilot scale and full scale studies
- Confirms need for studies in energy consumption and economic feasibility
- Revealed faults in ranking system