Review of Advanced Oxidation Technologies for the Removal of Emerging Contaminants

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Impaired Water Quality

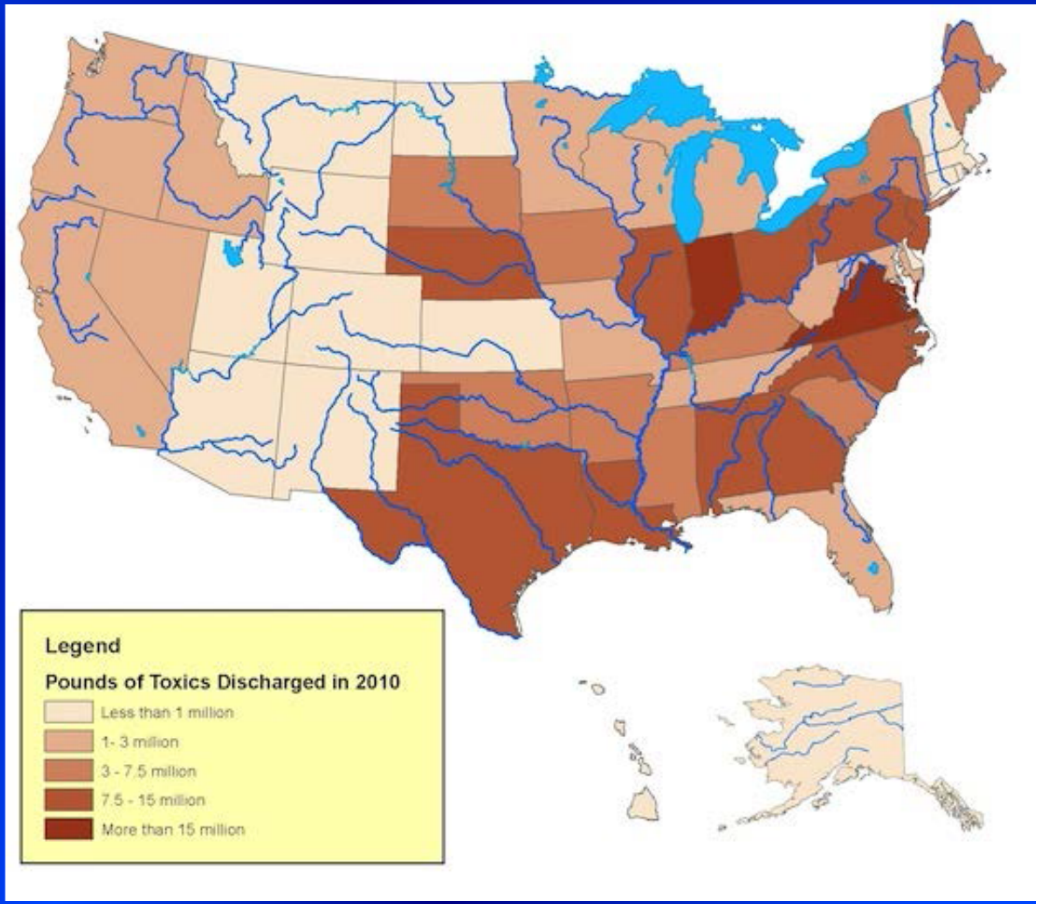
In 80 percent of the 139 streams sampled by USGS in 2001, one or more of the 95 organic wastewater contaminants were detected. Mixtures of the chemicals were common; 75 percent of the streams had more than one, 50 percent had 7 or more, and 34 percent had 10 or more."

Coastal Waters and Estuaries have not improved. In fact there is evidence that they are getting worse due to:

– Increasing population and development

– Slow build-up of polluted sediments (anoxia, metals, PCBs, pesticides)

National Coastal Condition Report, EPA-620/R-01/005



Graphic courtesy of Environment America: Wasting our Waterways 2012

USGS Survey of Surface Waters

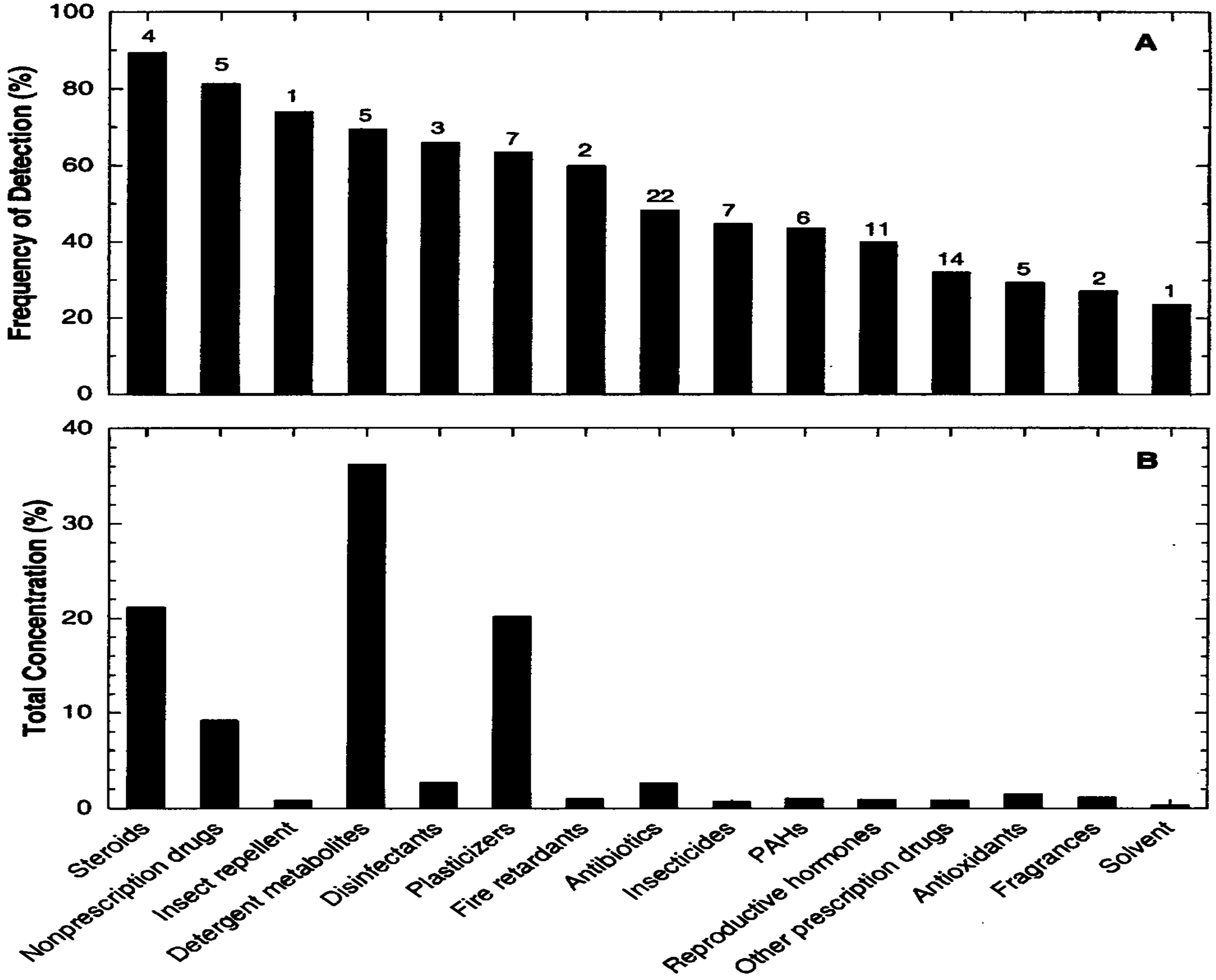


FIGURE 4. Frequency of detection of organic wastewater contaminants by general use category (4A), and percent of total measured concentration of organic wastewater contaminants by general use category (4B). Number of compounds in each category shown above bar.

Koplin et al., ES&T 36:6:1202-1211

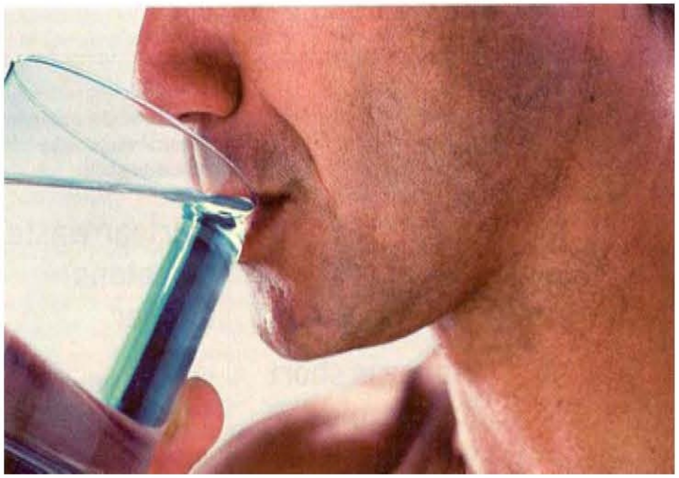
The Chemical Universe (~2014)

❖ Chemicals registered by Chemical Abstracts Services	~20 million
❖ TSCA Chemical inventory (> 10,000 lbs/yr) CAS (2011)	84000
❖ Chemicals with High Production Volume (HPV) exceeding 10^6 lbs/year (2005)	2800
❖ Chemicals in Toxics Release Inventory (TRI) (2014)	683
❖ Priority Pollutants, Clean Water Act (40 CFR, part 423, Appendix A) (~2014)	129
❖ Organic chemicals/groups regulated under the federal SDWA (2013)	53
❖ US EPA’s Contaminant Candidate List Chemicals(CCL1, 2, 3)	196

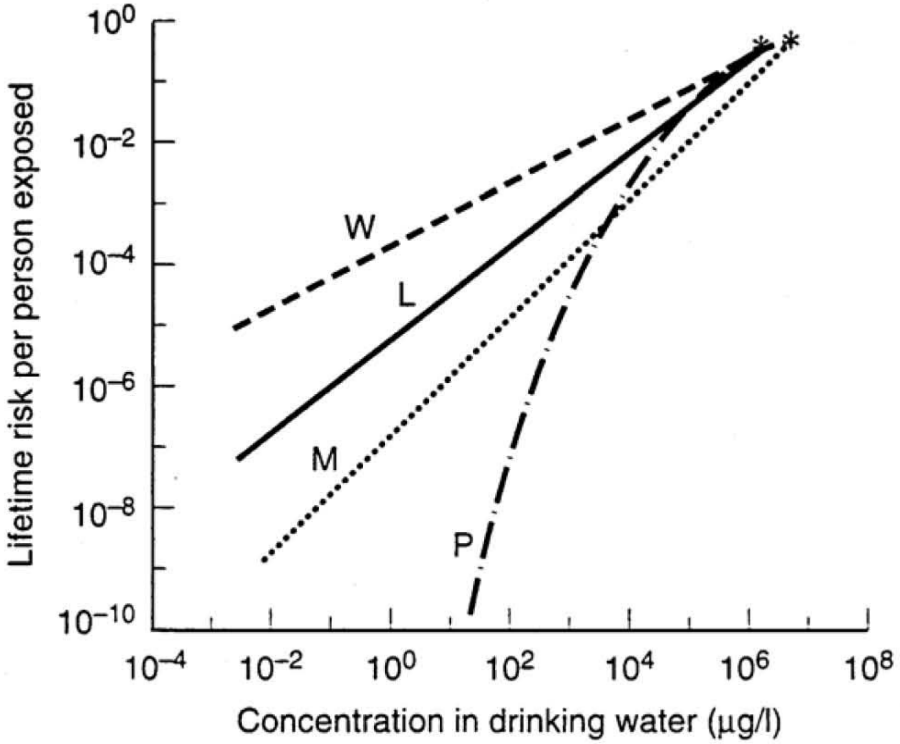
Examples from Contaminants Candidate List

Compound Class	CCL 1 in 1998 (Total 50)	CCL 2 in 2005 (Total 42)	CCL 3 in 2009 (Total 104)
Volatile organics	2,4-dinitrophenol 2,4,6-trichlorophenol	1,2-diphenylhydrazine 1,3-dichloropropane	1,1-Dichloroethane 2-Methoxyethanol
Gasoline additives	MTBE	Methyl bromide	Benzyl chloride Methyl tert-butyl ether
Industrial additives	Naphthalene Hexachlorobutadiene	2-methyl-Phenol (o-cresol) Bromobenzene	1,4-Dioxane Perchlorate
Inorganics	Manganese Sodium	Aluminum Boron	Strontium Germanium
Surfactants/residues	EPTC Methyl bromide	Nitrobenzene Fonofos	Estriol Ethinyl Estradiol
Pesticide/herbicide organic compounds	Bromobenzene Disulfoton	Acetochlor DDE	Acrolein Formaldehyde

Dose Response Relationships



- Uncertainty in the dose-response relationship for *carcinogens* can be huge (up to 10,000 times) for extrapolation of high doses in animals to low doses in humans
- <u>Example:</u> Drinking water and health; TCE in drinking water is difficult to estimate a dose response (MCL = 5 ppb)
- *How to handle mixtures?*
- *Multiple exposures, multiple diseases & target organs, endocrine effects?*
- *Is Toxicogenomics the answer?*

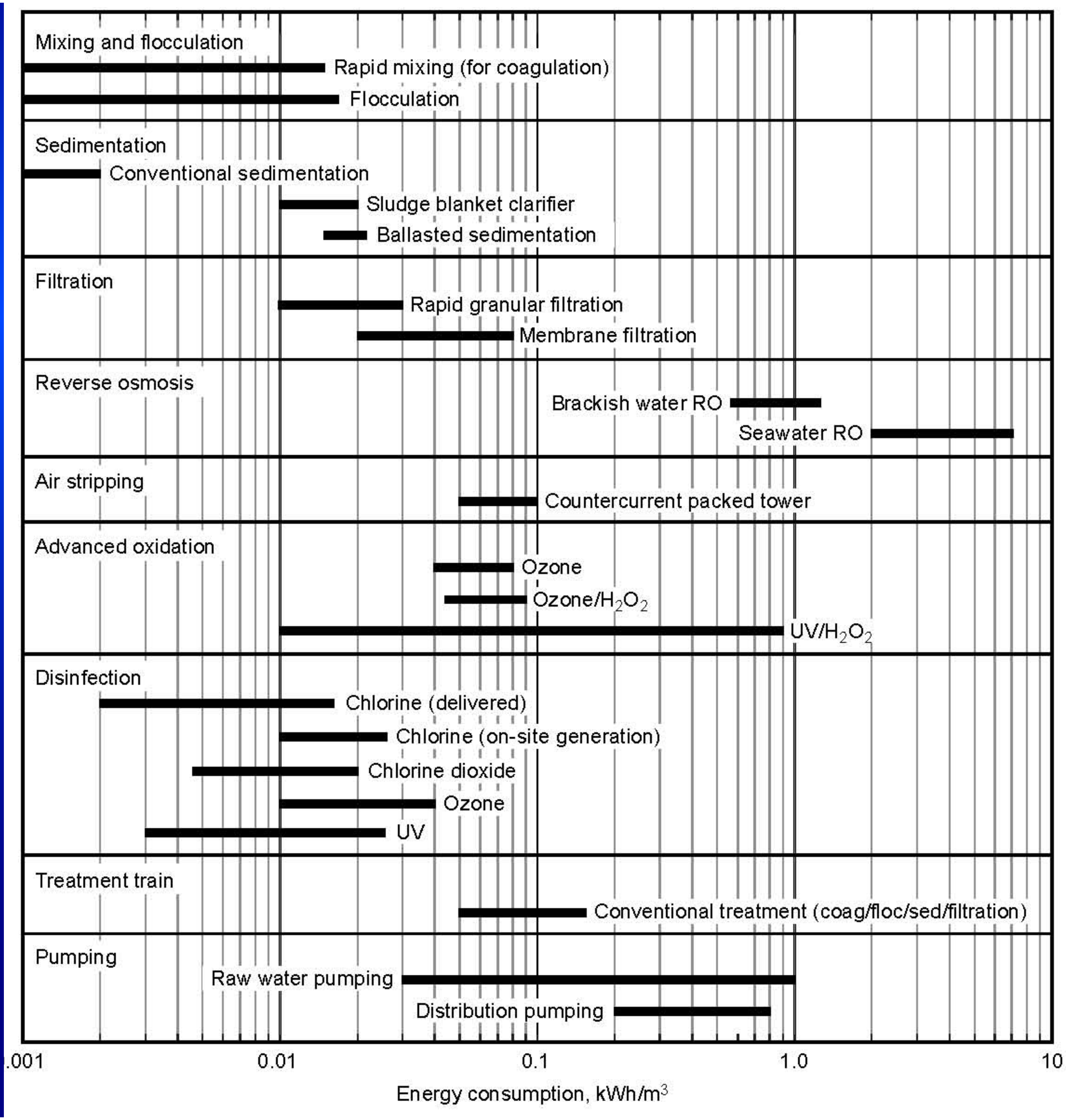


Current Treatment Processes for Removal of Emerging Contaminants

- **Adsorption** is effective to organic compounds which are large (MW> 300-150) and /or have low solubility (<1 mM).
- **Stripping** is effective for organic compounds which have low solubility and intermediate vapor pressure (H=0.01). We have to control the contaminants of off gas, gas phase adsorption and incineration.
- **AOPs** is effective for organic compounds which have second order rate constants 10^8 , k_R.

$$\boxed{r_R = -k_R C_R C_{\mathrm{HO\bullet}}}$$

Follow the Energy



Introduction - What are AOPs? 1/2

- **Advanced Oxidation Processes (AOPs) that produce hydroxyl radicals (HO• radicals) at ambient temperature and atmospheric pressure are promising water treatment technology.**
- **HO• radicals are highly reactive electrophiles, that react rapidly and non-selectively with the electron-rich sites of compounds.**
- **HO• radicals are capable of mineralizing organic compounds into carbon dioxide CO_2 and water.**

What are AOPs? 2/2

- **According to Bolton and Carter (Bolton and Cater, 1994), the following general pattern of oxidation is observed for AOPs.**

Organic pollutant → Aldehydes → Carboxylic acids → Carbon dioxide and mineral acids

- **The most significant observed by-products are the carboxylic acids, due to the fact that the second order rate constants for these compounds are much lower than those for most organics. However, if adequate reaction time is provided, all by-products (>99% as measured by a TOC mass balance) are destroyed.**

Factors Affecting AOP Performance 1/5

- Destruction rate of targeted compound R by HO•

$$r_R = -k_R C_R C_{HO\bullet}$$

Typical k_R: 10^7–10^9 $M^{-1}s^{-1}$,
C_R: μM or nM, $C_{HO\bullet}$: 10^{-11} ~ 10^{-9} M

- Rate raw for HO• that reacts with an organic compound

$$HO\bullet + R \longrightarrow \text{byproducts}$$

$$r_R = -k_R C_{HO\bullet} C_R$$

- Half-life of an organic compound for CMBR

$$t_R = \frac{\ln(2)}{k_R C_{HO\bullet}}$$

Compound	$k_{HO\bullet}$ $M^{-1}s^{-1}$	Halflife, min $[HO\bullet]=10^{-9}$ M	 $[HO\bullet]=10^{-10}$ M	 $[HO\bullet]=10^{-11}$ M
MtBE	1.6×10^{9}	0.01	0.1	1
Oxalic acid	1.4×10^{6}	8	83	825
Acetate ion	7×10^{7}	0.2	2	17
Trichloromethane	5.0×10^{6}	2	23	231
1,1,2-Trichloroethane	1.1×10^{8}	0.11	1	11
Chloroform	5×10^{6}	2	23	231
Chloroacetic cid	4.3×10^{7}	0.3	2.7	27
Glycolic acid	6×10^{8}	0.02	0.2	2
1,1,1-Trichloroethane	4×10^{7}	0.3	3	29
Benzene	7.8×10^{9}	0.001	0.01	0.1
Phenol	6.6×10^{9}	0.002	0.02	0.2

Various AOP Technologies

H_2O_2/UV

Advantages

- Long stability and can be preserved prior to use of H_2O_2.
- $H_2O_2 + UV \rightarrow 2HO\cdot$

Disadvantages

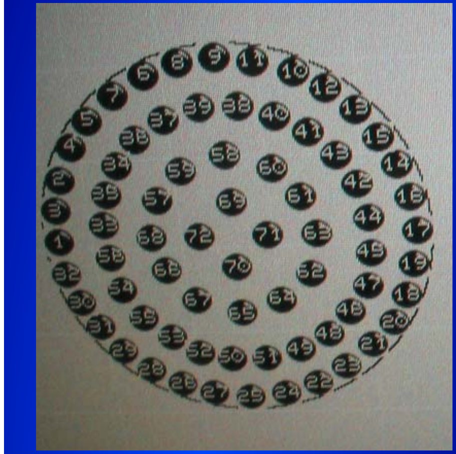
- Poor UV absorption of H_2O_2
- Interface of UV with the water matrix
- Special reactors required for UV illumination
- H_2O_2 Residuals

H_2O_2/UV

Low Pressure UV system (UV/H_2O_2) Trojan Tech

Performance:

- 24 reactors
- H_2O_2 10 mg/L
- Chemical 600lb/d
- 21300 kWh/d
- Total Cost $3029/d

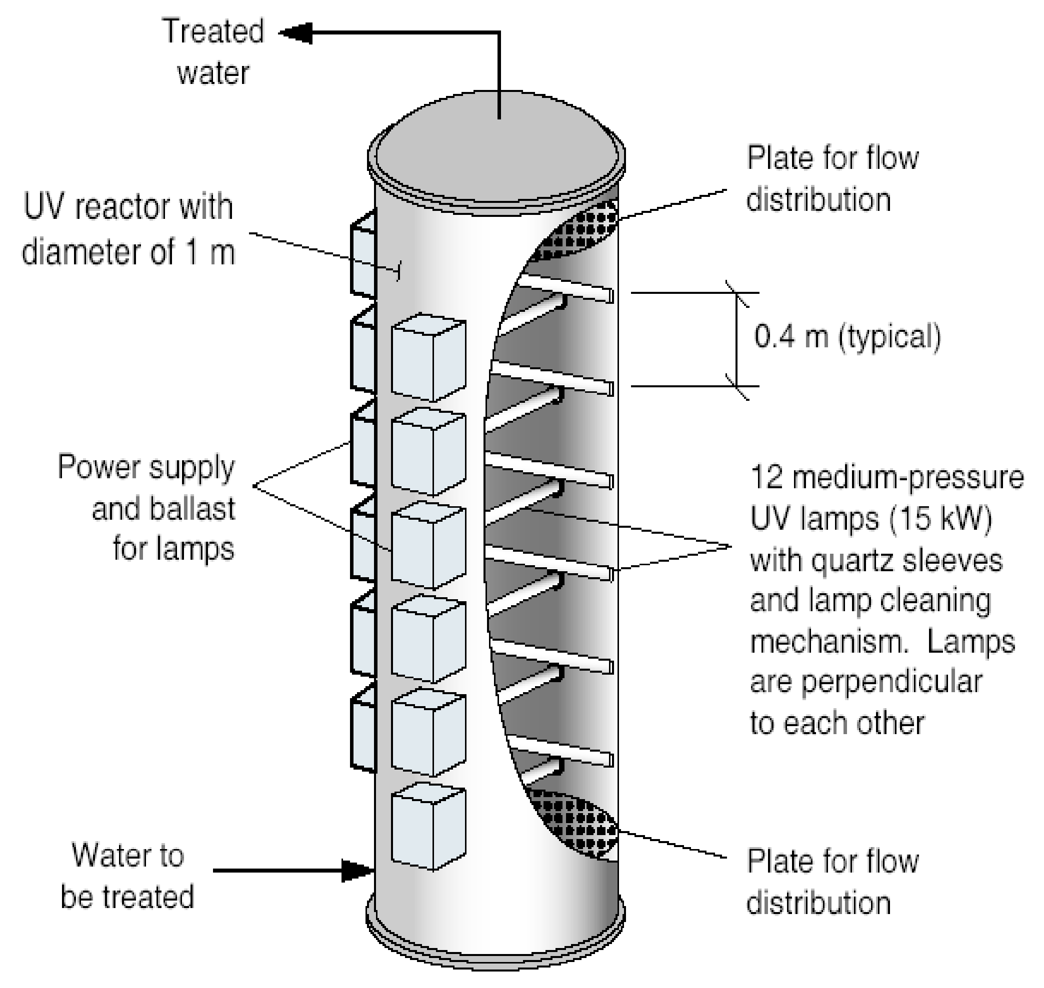


Lamp Configuration

Median Pressure UV system (UV/H_2O_2) Trojan Tech

Performance:

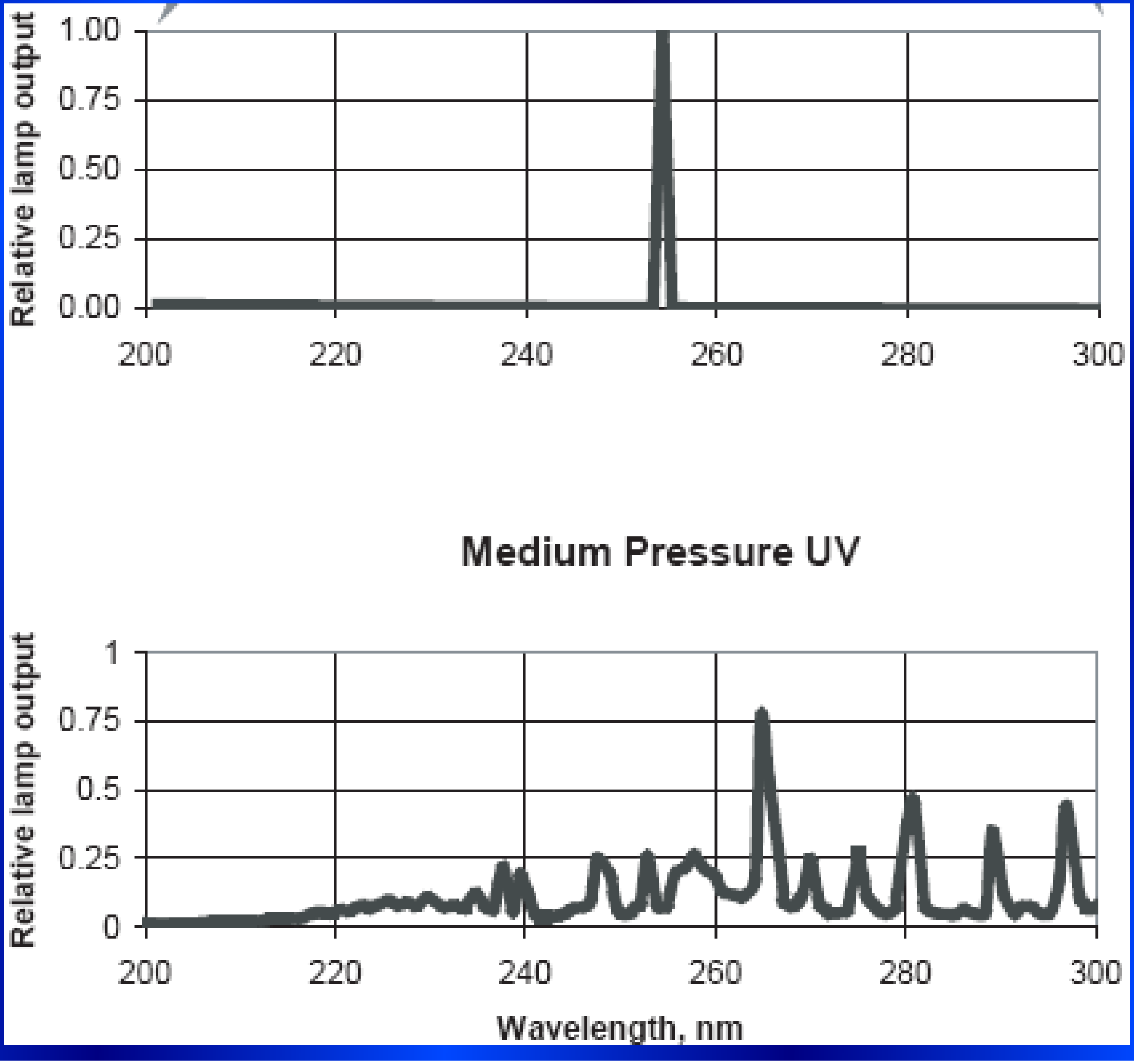
- 10 reactors
- H_2O_2 10 mg/L
- Chemical 600lb/d
- 10800 kWh/d
- Total Cost $11699/d



H_2O_2/UV

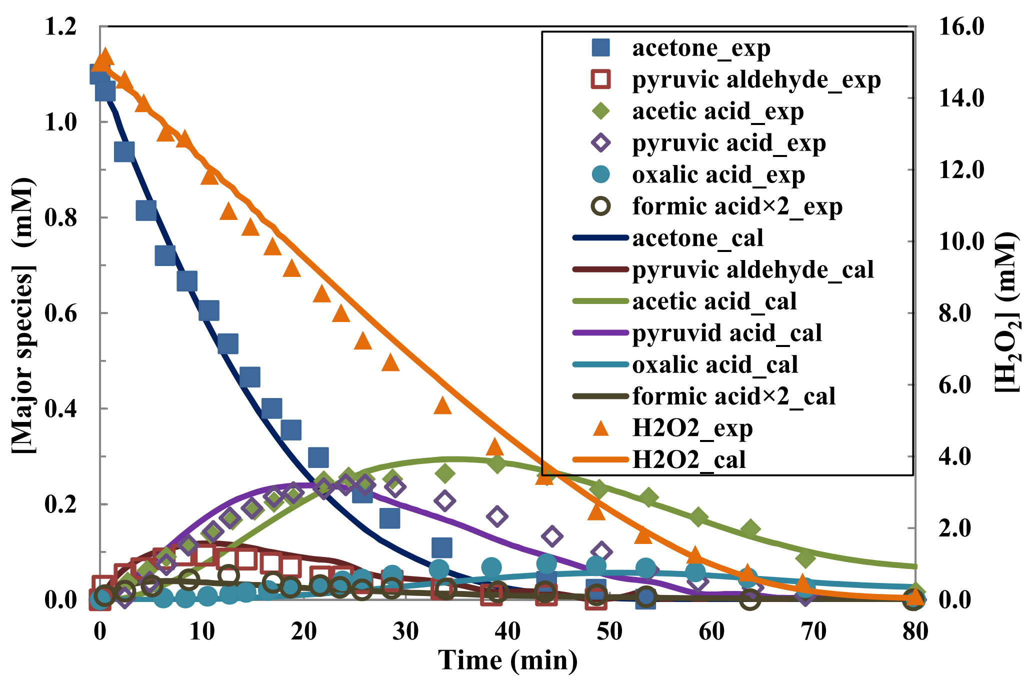
Light Sources

Low Pressure UV



Predicted Concentration Profiles of Acetone and Stable-byproducts in UV/H_2O_2 AOP

Comparison of concentration profiles of major species for experimental data (Stefan, Hoy, Bolton, 1999 ES&T 33, 870-873) and simulations results



Type of mechanism	Number of species	Number of reactions
Full mechanism	285	3639
Reduced mechanism	59	103

The criterion for DRG method is 0.1%.

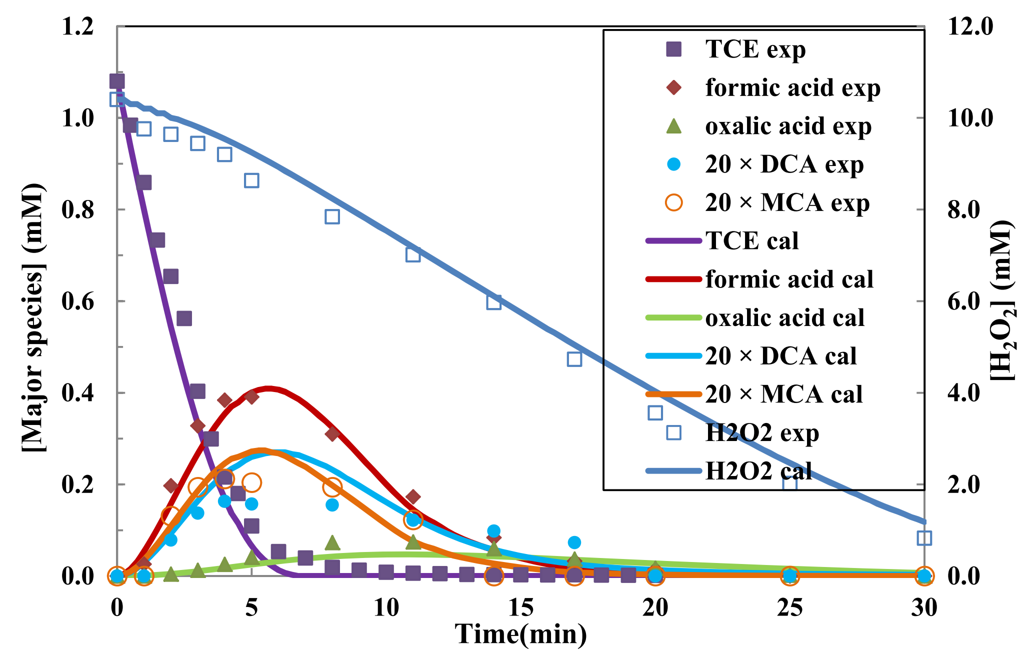
Initial concentration of acetone	1.02 mM
Initial concentration of O2	2.2 mM
Initial concentration of H2O2	15.6 mM
Initial pH	5.9
Wave length of UV	200~300 nm
Light intensity	7.79×10^{-6} Einstein/L·s
Reactor type	Completely mixed batch reactor
Reaction time	80 min

Reaction rate constants are obtained from group contribution method (Minakata et al., 2009 ES&T 43, 6220-6227) and literature including:
Nate et al., 1990 J. Phys. Chem. Ref. Data. 19, 413-513.
Nate et al., 1995 J. Phys. Chem. Ref. Data. 25, 709-1050.
Buxton et al., 1988 J. Phys. Chem. Ref. Data. 17, 513-886.
von Sonntag et al., 1991 Angeuz. Chem. Int. Ed. Engl. 30, 1229-1253.
Li et al., 2009 ES&T 43, 2831-2837.
Stefan et al., 1996 ES&T 30, 2382-2390

The reaction between pyruvic acid and hydrogen peroxide was added manually because it is not included in this version of the pathway generator. ($CH_3COCOOH + H_2O_2 = CH_3COOH + CO_2 + H_2O$)

Predicted Concentration Profiles of Trichloroethene (TCE) and Stable-byproducts in UV/H_2O_2 AOP

Comparison of concentration profiles of major species for experimental data (Li, Stefan, Crittenden, 2007 ES&T 41, 1696-1703) and simulation results



Initial concentration of TCE	1.08 mM
Initial concentration of O2	2.2 mM
Initial concentration of H2O2	10.4 mM
Initial pH	5.9
Wave length of UV	200~300 nm
Light intensity	7.79×10^{-6} Einstein/L·s
Reactor type	Completely mixed batch reactor
Reaction time	30 min

Type of mechanism	Number of species	Number of reactions
Full mechanism	120	370
Reduced mechanism	41	89

The criterion for DRG method is 1%.

The photolysis of TCE was added manually because it is not included in this version of the pathway generator.

Reaction rate constants are obtained from group contribution method (Minakata et al., 2009 ES&T 43, 6220-6227) and literature including:

Nate et al., 1990 J. Phys. Chem. Ref. Data. 19, 413-513.
Nate et al., 1995 J. Phys. Chem. Ref. Data. 25, 709-1050.
Buxton et al., 1988 J. Phys. Chem. Ref. Data. 17, 513-886.
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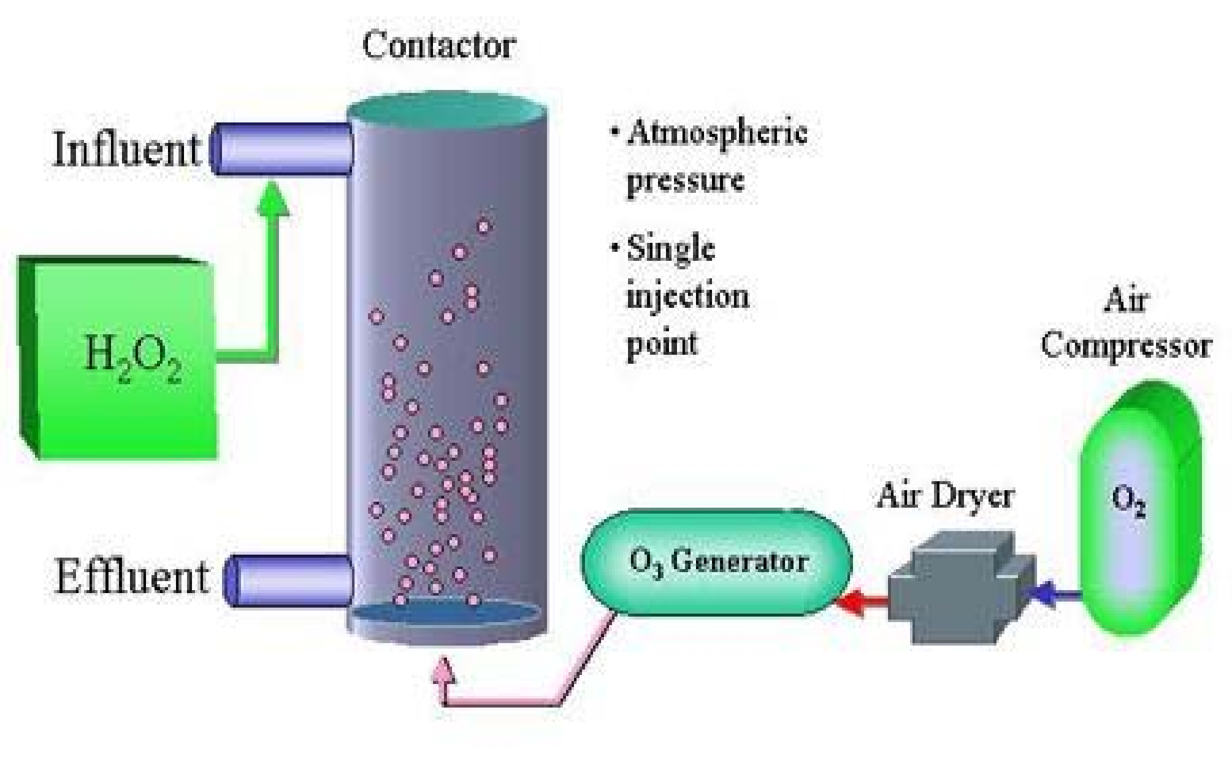
Li et al., 2009 ES&T 43, 2831-2837.
Li et al., 2007 ES&T 41, 1696-1703.

H_2O_2/O_3

Advantages	Disadvantages
• Suitability for waters with poor UV light transmission • Special reactors requirement for UV illumination2 • $2O_3+H_2O_2 \rightarrow 2HO\cdot+3O_2$	• Stripped volatile organics • Expensive and inefficient to produce O_3 • Residues of gaseous O_3 • Difficulty of maintenance (O_3/H_2O_2 dosages) • Low pH is detrimental • When only ozonation is used, bromate formation is of concern if source water contains bromide ion.

H_2O_2/O_3



- Atmospheric pressure
- Single injection point

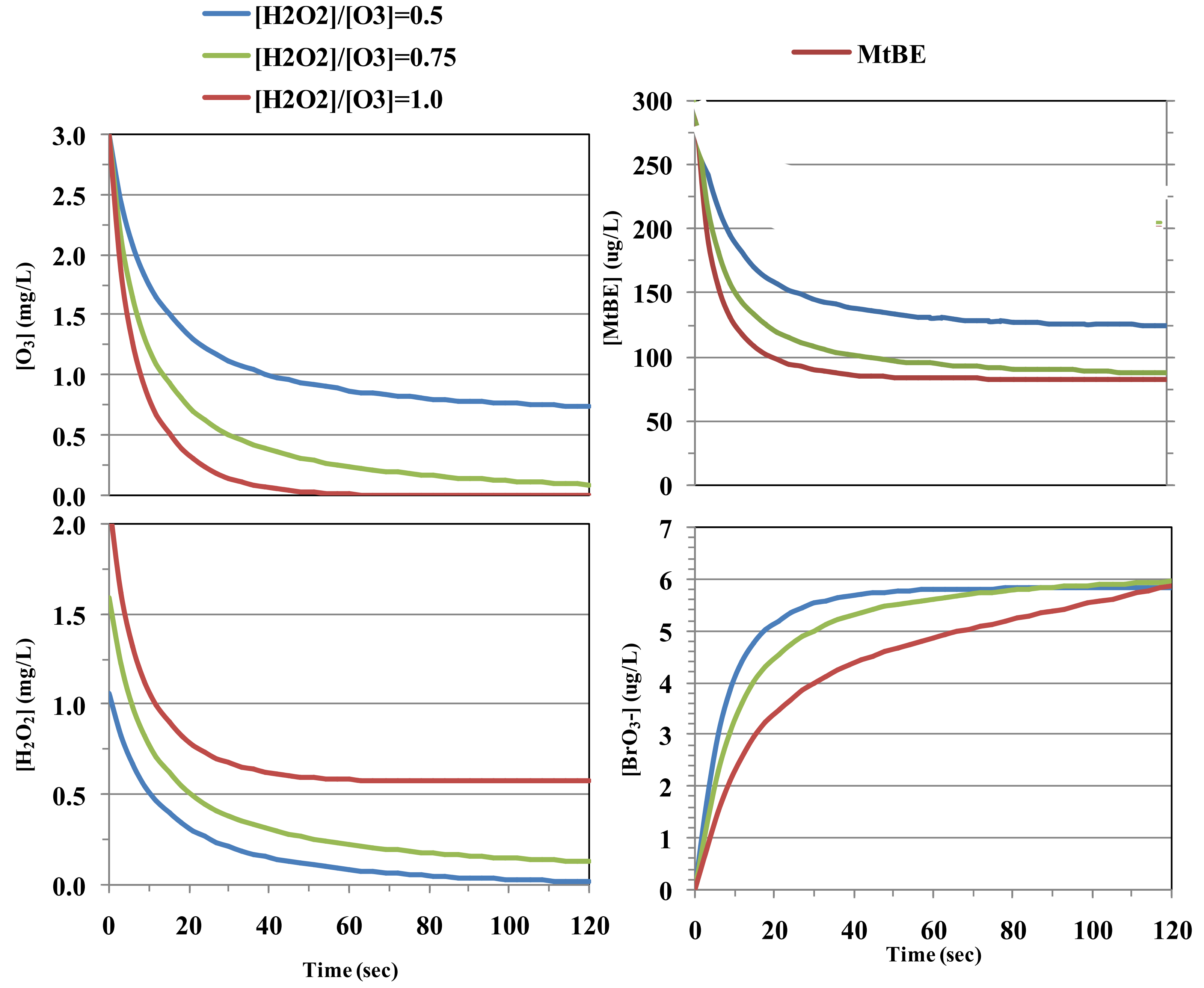
HiPOx (H_2O_2/O_3)
Performance: 180-200 gallons/minute
Treating 1, 4-Dioxane industrial wastewater as high as 65 ppm
Applied Process Technologies, Inc

Simulation – O_3 with H_2O_2 process–

Simulation parameters

- MtBE = 300 ug/L
- pH = 7.6
- NOM = 1.4 mg/L
- Alkalinity = 318 mg/L as $CaCO_3$
- initial O_3 = 3 mg/L
- molar ratio: $[H_2O_2]/[O_3]$ = 0.5 (optimum), 0.75, 1.0
- H_2O_2 = 1.06, 1.59, 2.12 mg/L
- Br^- = 300 ug/L
- Completely Mixed Batch Reactor (CMBR)

Simulation results – O_3 with H_2O_2 process–



UV/TiO_2

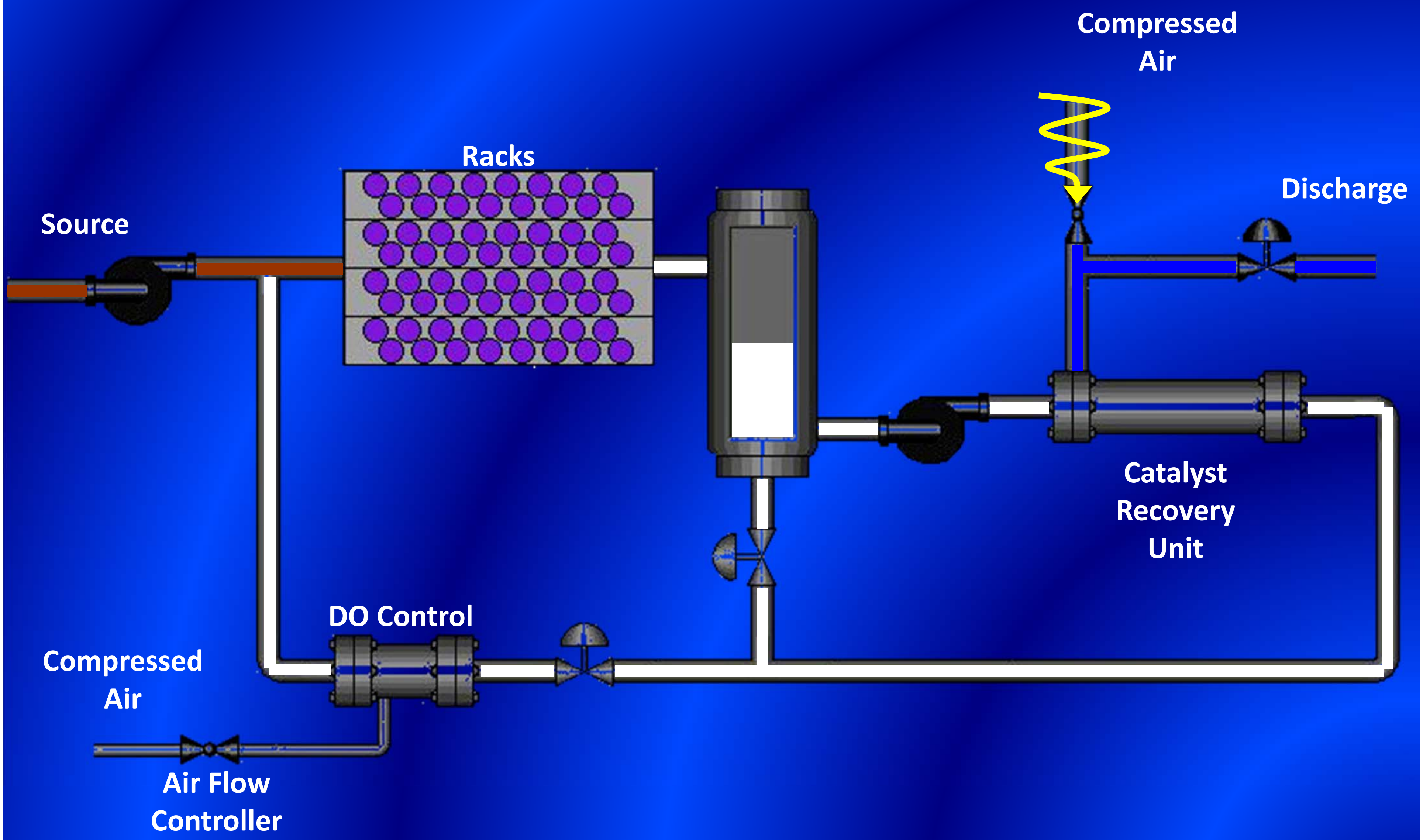
Intro

- TiO_2 catalyst is activated by UV irradiation, resulting in hydroxyl radical formation.

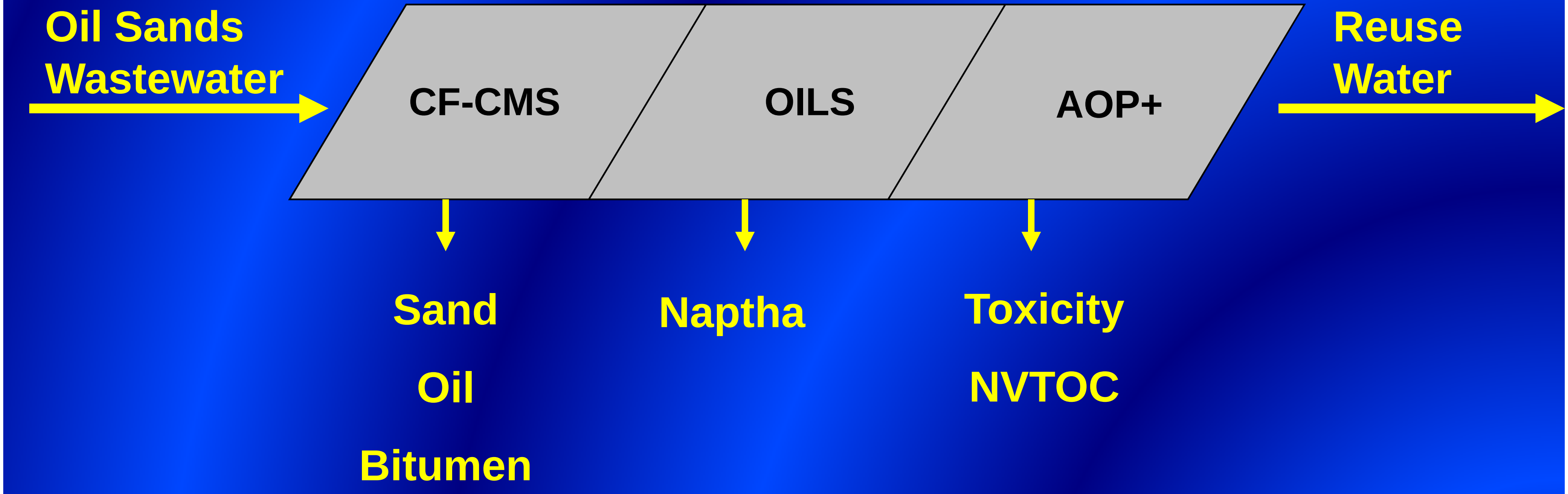
$$TiO_2+UV \rightarrow h^{+}+e_{cb} \qquad h^{+}+H_2O \rightarrow H^{+}+HO\cdot$$

Advantages	Disadvantages
• No additional chemicals for radical formation • TiO_2 is reusable for months even a year • Does not rely on transmittance of photons through the water • No wiper mechanisms are required to avoid fouling in the reactor	• Performance could be affected by pH or inorganic ions • Catalyst recirculation and head loss through the pipeline increase the energy cost • Pretreatment is needed

Process Flow Diagram for UV/TiO2



UV/TiO_2, Photo-Cat OFS



Oil Sands Wastewater

CF-CMS

OILS

AOP+

Reuse Water

Sand

Oil

Bitumen

Naptha

Toxicity

NVTOC

UV/$TiO_{2,}$ Photo-Cat OFS

Before **After**

List of Other AOPs

ElectroOxidation	Modified TiO_2 coating PbO_2 electrode generate HO• from water. $H_2O \Rightarrow HO\bullet + H^+ + e^-$
Ultrasonic/Ozone Oxiadation	Increases the mass transfer efficiency of ozone to destroy bacteria and revitalize contaminated water for reuse. Submerged electrodes create a secondary oxidation process with production of hydroxyl radicals.
Ferrate	FeO_4^{2-} oxidizes contaminants and is reduced to Fe^{3+}, which acts as coagulant and finally flocculent.
Persulfate Oxidation	$S_2O_8^{2-}$ oxidizes contaminants and is reduced to $SO_4^-\bullet$, which attack some non-degradable chemicals by HO•, like PFOA. $S_2O_8^{2-} \xrightarrow{\Delta} 2SO_4^-\bullet$ $Fe(0) + S_2O_8^{2-} \Rightarrow SO_4^-\bullet + Fe^{3+}$
Zero Valent Iron	In the presence of O_2, Low pH, and Fe^0, hydroxyl radical can be created in water. This formation is similar with Fenton reaction. $2H^+ + O_2 + Fe^0 \Rightarrow H_2O_2 + Fe^{2+} \Rightarrow HO\bullet + HO^- + Fe^{3+}$
FBR Fenton (Fenton IV)	Using a fluidized bed reactor (FBR) to introduce a secondary catalyst, iron oxyhydroxide (FeOOH), to the process. $H_2O_2 + Fe^{2+} \rightarrow HO\bullet + HO^- + Fe^{3+} \rightarrow Fe(OH)_3$
ElectroCoagulation	Fe^{2+} and Fe^{3+} are released from iron blades where direct current is applied. Particles neutralization and precipitation occur.

Modeling AOPs:

Simplified Pseudo-Steady-State Model

UV/H_2O_2 H_2O_2/O_3 Simplified pseudo-steady-state model

$$k_R = k_{12}\left[\mathrm{HO\bullet}\right]_{ss,\,0}$$

1. UV/H2O2

$$[\mathrm{HO\bullet}]_{ss,0} = \frac{2\phi_{H_2O_2} I_0 f_{H_2O_2}\ (1-e^{-A})}{k_{10}[H_2O_2]_0 + k_{11}[HCO_3^-]_0 + k_{12}[R]_0 + k_{13}[NOM]_0}$$

2. H_2O_2 and O_3 are added simultaneously

$$[\mathrm{HO\bullet}]_{ss,\,0} = \frac{K_L a\left(P_{O_3}/H_{O_3}\right)}{k_9\left[HO_2^-\right]_0 + k_{10}\left[H_2O_2\right]_0 + k_{11}\left[HCO_3^-\right]_0 + k_{12}\left[R\right]_0 + k_{13}\left[NOM\right]_0}$$

3. H_2O_2 is added to a water containing O_3, i.e. $[O_3]_0$ is known.

$$[\mathrm{HO\bullet}]_{ss,\,0} = \frac{2k_1\left[H_2O_2\right]_0 \times 10^{\left(\mathrm{pH}-\mathrm{p}K_{H_2O_2}\right)}\left[O_3\right]_{res}}{k_{11}\left[HCO_3^-\right]_0 + k_{12}\left[R\right]_0 + k_{13}\left[NOM\right]_0}$$

Flow Models: Ideal flow at steady state (1st order reaction)

1. Plug Flow Reactor (PFR)

$$C = C_0 e^{-k\tau}$$

$$V = \frac{Q}{k} \ln\left(\frac{C_0}{C}\right)$$

2. Completely Mixed Flow Reactor (CMFR)

$$C = \frac{C_0}{(1 + \tau k)}$$

$$V = \frac{Q(C_0 - C)}{-r}$$

3. Tank-in-series (TIS)

$$C = \frac{C_0}{\left(1 + \frac{\tau}{n} k\right)^n}$$

$$V = \left[\left(\frac{C_0}{C}\right)^{1/n} - 1\right]\left(\frac{nQ}{k}\right)$$

Flow Models: Non-ideal flow

4. Dispersed flow model closed system

$$\frac{C_A}{C_{Ao}} = \frac{4a\exp\left(\frac{1}{2}\frac{vL}{E}\right)}{(1+a)^2\exp\left(\frac{a}{2}\frac{vL}{E}\right) - (1-a)^2\exp\left(-\frac{a}{2}\frac{vL}{E}\right)}$$

$$a = \sqrt{1+4k\tau(E/vL)}$$

Group Contribution Method (GCM) for predicting $k_{HO\bullet}$

$$k = Ae^{-\frac{E_a}{RT}}$$

- Essence is same as the GCM for the gaseous phase developed by Dr. Roger Atkinson (EPA software AOPWIN)

Hypothesis

- Observed experimental reaction rate constant for a given organic compound is the combined rate of all elementary reactions involving HO•, which can be estimated using Arrhenius kinetic expression.

- The E_a consists of two parts based on Benson's thermochemical additivity concept (Benson, 1976):
  (1) **Base part** from main reaction mechanisms (i.e., H-atom abstraction, HO• addition to alkenes and aromatic compounds and HO• interaction with S, N, or P-atom-containing compounds).
  (2) **Functional group contribution** partially from neighboring and/or next nearest neighboring functional group.

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- University of Notre Dame Radiation Center and Department of Energy

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