Potassium Persulfate Oxidation vs. Photo Oxidation

Katie Ho
Cornell University

Keith Olson
NELHA
Purpose

- Determine whether photo oxidation or chemical oxidation is the best method to **breakdown** dissolved **organic** materials into **inorganic** materials
  - **Nitrogen** and **Phosphorus**

- Meet EPA and DOH standards
  - Are tenants polluting?
Nutrient Breakdown

- Total Nutrient (Unfiltered)
- Particulate Nutrient (does not pass through filter)
- Total Dissolved Nutrient (0.2 micron filtered)
Total Dissolved Nutrient
(0.2 micron filtered)
Total Dissolved Nutrient (0.2 micron filtered)

Dissolved Inorganic Nutrient

Dissolved Organic Nutrient
Nutrient Concentrations Determined

**Organic**
- Organic N and P Compounds

**Oxidation Methods**
- Photo Oxidation
- Chemical Oxidation

**Inorganic**
- NO₃/NO₂, NH₃, PO₄

**Nutrient Concentrations Determined**
- Segmented Flow Auto-analyzer
What is Oxidation?

- Oxidation: loss of electrons
- Excess oxygen in hydrogen peroxide ($\text{H}_2\text{O}_2$) and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$)
- Converts all organic N and P compound to inorganic forms

Diagram:
- Organic Glutamic Acid
- Oxidizing Agent: Hydrogen Peroxide
- Inorganic Nitrate
**Photo Oxidation Method**

**Photo Oxidation Apparatus Function:** Oxidize organic N and P using UV radiation

- **30 mL sample + 0.3 mL Hydrogen Peroxide**
- **Samples oxidized for 2.5 hours**
- **Nutrient concentrations analyzed via segmented flow auto-analyzer**
Chemical Oxidation Method

**Autoclave Function:** Vessel used to cause chemical reactions to occur under high temperature and pressure

10 mL of sample + 5 mL of potassium persulfate digestion reagent

Samples oxidized for 1 hour

Nutrient concentrations analyzed via segmented flow auto-analyzer
Segmented Flow Auto-Analyzer

**Function:** evaluate nutrient concentrations by measuring the absorbance of solutions at different wavelengths of light
• Specific reagents used to react with oxidized sample to create various colored solutions
• Spectrometer reads 4 nutrient channels
  • Orthophosphate – 880 nm
  • Nitrate/Nitrate – 540 nm
  • Ammonia - 640 nm
  • Silicate – 820 nm
Nutrient Concentration Analysis

- FASPAC Software used to determine nutrient concentrations
Limitations

- Measuring in parts per billion (precision matters)
  - Human error is a large factor
  - Method Detection Limits above accepted DOH values
    - (ex. NH3 expected < 2.5 ppb)
Potassium Persulfate

Potassium Persulfate used as the oxidizing agent in *photo oxidation* rather than chemical oxidation
Theoretical vs. Actual PO4 Concentration
Potassium Persulfate vs. Hydrogen Peroxide Oxidizing Reagent Method in Photo Oxidation

- **100 ppb Hydrogen Peroxide**
  - Average Recovery: 101%
  - n=6

- **20 ppb Hydrogen Peroxide**
  - Average Recovery: 124%
  - n=6

- **20 ppb Potassium Persulfate**
  - Average Recovery: 71%
  - n=6

- **100 ppb Potassium Persulfate**
  - Average Recovery: 91%
  - n=6
Theoretical vs. Actual NO3 Concentration
Potassium Persulfate vs. Hydrogen Peroxide Oxidizing Reagent Method in Photo Oxidation

- **100 ppb Potassium Persulfate**
  - Average Recovery: 69%
  - n=6

- **100 ppb Hydrogen Peroxide**
  - Average Recovery: 40%
  - n=6

- **20 ppb Potassium Persulfate**
  - Average Recovery: 70%
  - n=6

- **20 ppb Hydrogen Peroxide**
  - Average Recovery: 112%
  - n=6
Theoretical vs. Actual PO4 Concentrations
8.35 mg vs. 33.5 mg Potassium Persulfate Concentration Method
In Chemical Oxidation

- **20 ppb, 8.35 mg Potassium Persulfate**
  - Average Recovery: 569%
  - n=2

- **20 ppb, 33.5 mg Potassium Persulfate**
  - Average Recovery: 518%
  - n=3

- **100 ppb, 33.5 mL Potassium Persulfate**
  - Average Recovery: 196%
  - n=3

- **100 ppb, 8.35 mg Potassium Persulfate**
  - Average Recovery: 136%
  - n=3
Theoretical vs. Actual NO3 Concentrations
8.35 mg vs. 33.5 mg Potassium Persulfate Concentration Method In Chemical Oxidation

- **20 ppb, 8.35 mg Potassium Persulfate**
  - Average Recovery: 160%
  - n=2

- **100 ppb, 33.5 mg Potassium Persulfate**
  - Average Recovery: 60%
  - n=3

- **100 ppb, 8.35 mg Potassium Persulfate**
  - Average Recovery: 60%
  - n=3
Potassium Persulfate Photo Oxidation vs. 5 mL Potassium Persulfate Chemical Oxidation
Significant Findings

- **Contamination of potassium persulfate**
  - Giving false values of ammonia and nitrogen concentrations
  - Raised values 1-2 ppm
  - Measuring on a scale of 0-50 ppb

- *Theoretical* nutrient standards do not match *actual* nutrient standards

- Potassium Persulfate as an oxidizing agent in Photo Oxidation yielded more consistent recovery rates
Future Adjustments

- Develop a standard procedure for chemical oxidation and photo oxidation so both processes can be compared directly
  - Test different standards

- Optimize potassium persulfate as oxidizing reagent in photo oxidation
  - Eventual switch from hydrogen peroxide to potassium persulfate
  - More consistent, accurate results once system optimized
Conclusion

- Photo Oxidation using Potassium Persulfate as the oxidizing agent is better for current testing
  - More accurate recovery rate overall compared to chemical oxidation

- Chemical Oxidation
  - Accurate for Nitrogen
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