Reduction of Biochemical Oxygen Demand and Chemical Oxygen Demand of Metalworking Fluid Wastewater by Electrochemical Oxidation

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INTRODUCTION

- Metalworking Fluids are widely used within our industry.
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- Many metalworking fluid exhibit high biochemical oxygen demand (BOD$_5$) and chemical oxygen demand after conventional pre-treatment methods.

- Regulators continue to enforce BOD$_5$ and COD limitations.

- Cost effective and user friendly advanced technology solutions are necessary and in demand to resolve BOD$_5$ and COD issues.
WHAT ARE CONTAMINANTS IN MWF WASTEWATERS?

- **Hydrocarbon Products (Floatable, Suspended / emulsifiable, and Settleable Organics)**
  - Petroleum Oils, Waxes, Fatty Acid Soaps (Ca, Fe Al), Chlorinated esters and paraffins
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- **Dissolved Solids**
  - Salts (Sodium and Potassium Salts)
- **Dissolved Organics**
  - Amines, Amides, Esters, Glycols, Surfactants, Detergents, Fatty Acids, Fatty Alcohols, biocides, phosphate esters
THE ISSUE

Spent Metalworking Fluids

Pre-treatment System

Current Technology is limited

Municipal Sewer System POTW

Fed/State Discharge Controls

State Waters
Current Established Technology Options

**Chemical Treatment**
- Salt Splitting
- Polymer Treatment

**Membrane Separation**
- Ultrafiltration
- Microfiltration

**Evaporation**
- Thermal Evaporation
- Mechanical Vapor Recompression

**Biological**
- Aerobic
- Anaerobic

**Adsorption**
- Carbon
- Clay

Or Combined technologies from above
Current Options
Combined Technologies

- Chemical / Biological
- Chemical / Carbon or Clay Adsorption
Current Options
Combined Technologies

- Chemical / Biological
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- Distillation / Ultrafilter (MVR/ UF)
Current Options
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- Chemical / Biological
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- Distillation / Ultrafilter (MVR/ UF)
- Ultrafiltration / Biological / Ultrafiltration (MBR)
- Ultrafilter / Reverse Osmosis (UF / RO)
- Ultrafiltration / Carbon or Clay Adsorption
Current Options

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Proposed New Option

- Ultrafilter / Electrochemical Oxidative Process
# Separation Effectiveness and Costs

<table>
<thead>
<tr>
<th>Fluid Type @ 5% v/v</th>
<th>Feed BOD5 - mg/L</th>
<th>After Chemical Or Ultrafiltration</th>
<th>Combined Technologies</th>
<th>Combined Technologies Operating Costs USD per Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsions</td>
<td>30K – 300K</td>
<td>600 – 6,000</td>
<td>20-300</td>
<td>$ 0.25 – 0.45</td>
</tr>
<tr>
<td>Semi-Synthetic</td>
<td>4,000 – 25,000</td>
<td>800 – 6,000</td>
<td>30-600</td>
<td>$ 0.25 – 0.45</td>
</tr>
<tr>
<td>Synthetic</td>
<td>3,000 – 9,000</td>
<td>500 – 5,000</td>
<td>30-600</td>
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<tr>
<td>Emulsions</td>
<td>500,000 - 1,100,000</td>
<td>2,000 – 9,000</td>
<td>300 – 900</td>
<td>$ 0.25 – 0.45</td>
</tr>
<tr>
<td>Semi-Synthetic</td>
<td>20,000 – 55,000</td>
<td>3,000 – 6,000</td>
<td>300 - 1,100</td>
<td>$ 0.25 – 0.55</td>
</tr>
<tr>
<td>Synthetic</td>
<td>25,000-35,000</td>
<td>20,000 30,000</td>
<td>250 - 900</td>
<td>$ 0.25 – 0.55</td>
</tr>
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</table>
CURRENT TECHNOLOGY IS LIMITED
Combined technologies are gaining in popularity.

Spent MWF → Primary Method → Secondary Method

- Dissolved Organics And Salts
- Oil Phase For ultimate Recycle
- Separated Organic Sludge Phase

Lower BOD$_5$ and COD

Only Solved $\frac{1}{2}$ the Problem

Low Reuse Potential?
Advanced Oxidation Process Technology Option

Spent MWF → Primary Method → AOP

Dissolved Organics And Salts

Out Gas N₂, CO₂, O₂

No Sludge

Oil Phase For ultimate Recycle

Lower BOD₅, And COD
What are some of the AOP’s

- Sodium Periodate
- Sodium Perborate
- Hydroxyl Radical
- Ultraviolet
- Ozone
- Hydrogen Peroxide
- UV / Titanium Dioxide
- Chlorine
- Electrochemical Oxidation
Relative Oxidation Potential of Selected Oxidants

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidation Potential, Volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3.0</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>2.8</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.1</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.8</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>1.7</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>1.5</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Electrons are Less Expensive

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Cents/Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrons @ 6 cents/KWH, 3.5 V</td>
<td>0.6</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>3.8</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>14</td>
</tr>
<tr>
<td>Sodium Hydrosulfite</td>
<td>25</td>
</tr>
<tr>
<td>Sodium Dichromate</td>
<td>39</td>
</tr>
<tr>
<td>Potassium Permanganate</td>
<td>45</td>
</tr>
<tr>
<td>Sodium Borohydride</td>
<td>170</td>
</tr>
</tbody>
</table>
Ultrafiltration – Size Comparison

- Virus Particle (Diameter 40 Nanometers)
- Protein (Molecular Weight 70,000)
- Sucrose (Molecular Weight 342)
- Water (Molecular Weight 18)

Molecular Weight in Nanometers (10^-9 Meter)

- Membrane
- Porous Support

- Ultrafiltration Membrane
Ultrafiltration Permeate, Typical

BASIC OIL EMULSION
BEFORE ULTRAFILTER

BASIC OIL EMULSION
AFTER ULTRAFILTER
Electrochemical Oxidation
Multiple Reactions

- Direct Oxidation
  - Reaction occurs directly on the anode surface

- Indirect Oxidation
  - Anode oxidizes a chemical which then oxidizes a substance in solution away from the anode surface
Direct Oxidation
Electrode Reactions

- **Desired Anode Reaction**
  - $\text{COOH}^- = \text{CO}_2 + \text{H}^+ + 2 \text{e}^-$

- **Competing Anode Reaction**
  - $\text{H}_2\text{O} = 2 \text{H}^+ + 1/2 \text{O}_2 + 2 \text{e}^-$

- **Typical Cathode Reactions**
  - $2 \text{H}_2\text{O} + 2 \text{e}^- = 2 \text{OH}^- + \text{H}_2$ (Base)
  - $2 \text{H}^+ + 2\text{e}^- = \text{H}_2$ (Acid)

- **May Require Anode with High Oxygen Potential**
More Complex Molecules
More Electrons Required

Methanol

\[ \text{CH}_3\text{OH} + 6 \text{OH}^- = \text{CO}_2 + 5 \text{H}_2\text{O} + 6 \text{e}^- \]

Isopropanol

\[ \text{CH}_3\text{CH}_2\text{CHOH} + 12 \text{OH}^- = 3 \text{CO}_2 + 7 \text{H}_2\text{O} + 12 \text{e}^- \]

Acetone

\[ \text{CH}_3\text{COCH}_3 + 16 \text{OH}^- = 3 \text{CO}_2 + 11 \text{H}_2\text{O} + 16 \text{e}^- \]
Basic Concept
Electrolizer

- Direct Current

Anode
Titanium with Electro-catalytic Coating

High Surface Area Flow-Through

Cathode
Wastewater
Anode Surface Reactions

Direct Electron Transfer
Plus
Mixed Oxidants from
Direct Surface Reactions

e^-
OH^-
O_3
O^·
Laboratory Electrochemical Cell

CATHODE

MULTI-LAYER MESH™ ANODE

BATCH TANK

ELECTROLYZER

CIRCULATION PUMP
Bench Scale Anode

High Surface Area, Flow Through
Bench Scale MLM Anode Test Cell
EXPERIMENTAL SET UP

Sample MWF

Feed Tank

Feed Return

Pump

Ultrafilter

Permeate Storage

Permeate

Electrolyte

As necessary

Electrochemical Cell

Direct Current Power Supply

Analysis for BOD5, COD pH
Wastewater After UF
No Added Electrolyte
44% Reduction COD

COD vs Time

Elapsed Time (min)

COD (mg/L)
Wastewater After UF
No Added Electrolyte
53% reduction BOD

BOD vs Time

Elapsed Time (min)

BOD (mg/L)
INITIAL TESTING SIGNIFICANT VARIATIONS IN WASTEWATER

- Very site dependant
- Variations from day to day
- Difficult to “Prove Concept” with excess feed variation
- Need to try a standard
- Three amine blend
Synthetic Feed Mixture and Additive Ratios
The Three Amines

<table>
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<tr>
<th>Chemical Mixture</th>
<th>CAS #</th>
<th>% - Volume</th>
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<tbody>
<tr>
<td>Monoethanolamine</td>
<td>141-43-5</td>
<td>30</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>102-71-6</td>
<td>30</td>
</tr>
<tr>
<td>Monoisopropanolamine</td>
<td>78-96-6</td>
<td>40</td>
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Then dilute above mixture 99:1 with H₂O
To create COD ≈ 4,000
SYNTHETIC FEED / With Electrolyte  #1
83% reduction COD
SYNTHETIC FEED / With Electrolyte #1

60 Minutes

460 Minutes
UF Permeate
Premium New MWF at 2% with Electrolyte #1
91.0% COD reduction
UF Permeate COD and BOD5 Reduction versus Time. Virgin MWF, 5%; Electrolyte #1

Time, min

mg/L

COD

BOD

75%

73.4%
UF Permeate
COD Reduction Versus Time
Effect of Electrolytes
Virgin MWF, 5%
UF Permeate
Relative and Absolute Reduction of COD Concentration Effect.
Virgin MWF, 7 hours, Electrolyte #1
Relative and Absolute Reduction of COD Concentration and Treated Volume Effect
Used MWF, 7 hours, Electrolyte #3
Process Control Data
Electrolyte #3

Graph showing data over time with lines for Amps, Rec.V, Cell Voltage (V), pH, and Conductivity.
Premium MWF #3 @ 5% 100 ppm hard water, UF Permeate, Electrolyte #3
99.9% Reduction of Phenol (4AAP)
Full Scale Electrolyzer
Skid Mounted System
Some Engineering System Considerations

- Chemical resistance to oxidation
- Current density
- Anode / cathode lifetime
- Current efficiency – electrolyte addition
- Solution concentration
- Mass transfer
  - Fluid velocity
  - Concentration
  - Volume
- Footprint of physical equipment
- Oxidation reduction by-products to air
- Available operating area
- Fits with partner processes and industry comfort factor
  - UF / Chem treat vs. biological
- Ease of operation and maintenance
- Capital and operating cost
Summary

- Additional experimental work still in progress.

- Electrolyte addition increases the efficiency of the overall process - electrolyte cost is insignificant.

- BOD$_5$ and COD reductions in the range of 60% to 80% in 7-8 hours are achievable.

- Operating cost (energy and anode life) to drive electrolytic cell estimated to be $0.012 - $0.017 per liter at rate of $0.06 / KWH, per 8 hours of run time.

- Compact design.

- No sludge to dispose of.

- Can selectively oxidize certain organic compounds (phenol) in the presence of more difficult to oxidize organic compounds.

- Ultrafiltration with Electrochemical Oxidation is a promising method.