Electrochemical Water Treatment Using Boron Doped Diamond Film Electrodes

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Outline

- Background
  - Common treatment technologies
  - Three Electrode cell
  - Electron transfer mechanisms
  - Advantage of BDD electrodes
- Treatment of CMP wastewaters
  - Reduction of Cu^{2+}
  - Oxidation of Citrate
- Treatment of PFOS wastewaters
- Conclusions

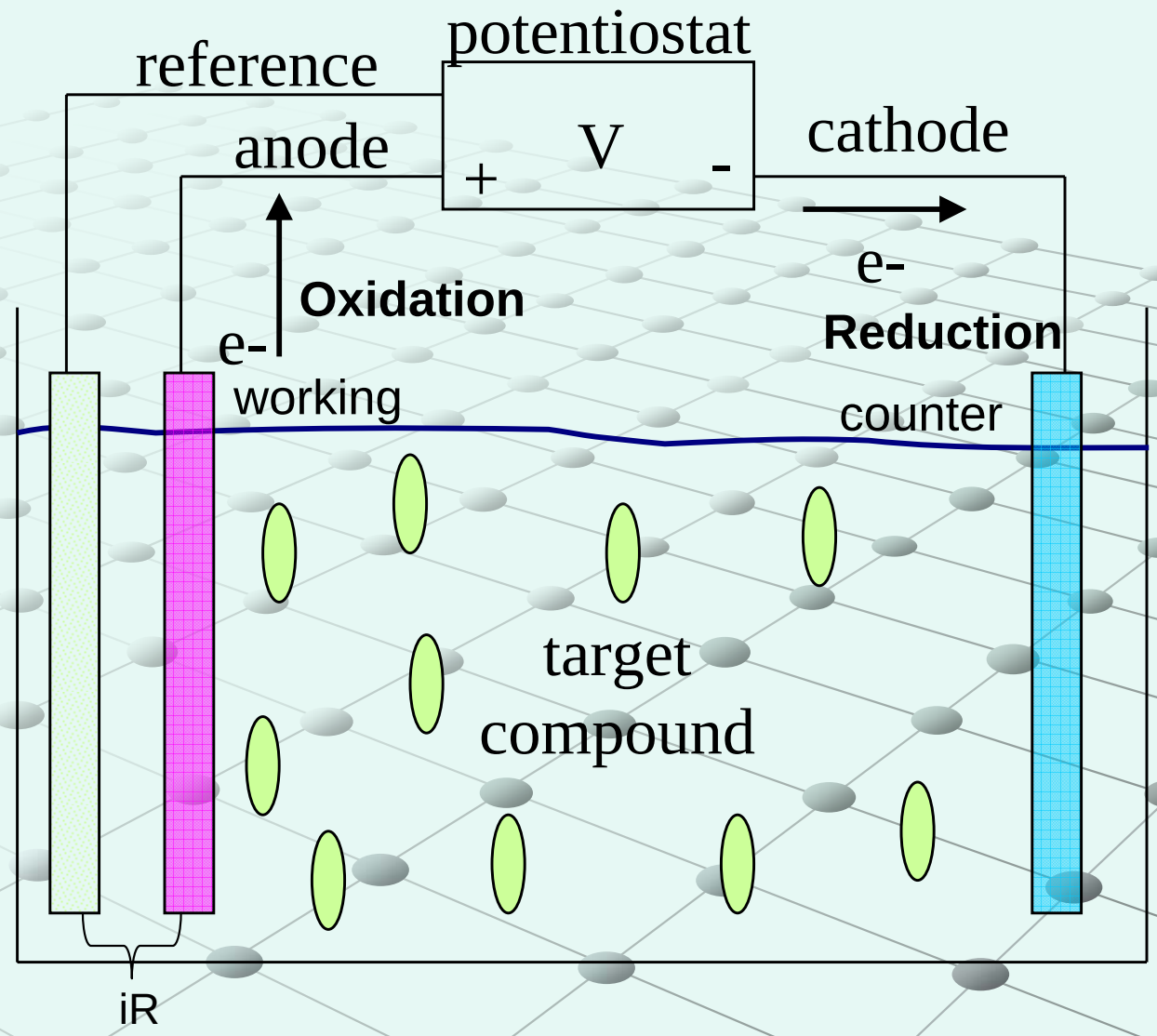
Treatment Technologies

1. Adsorption - activated carbon, zeolites
2. Ion Exchange
3. Air stripping
4. Membranes - reverse osmosis
5. Biological treatment - aerobic, anaerobic
6. Chemical Oxidation – UV or O_3/H_2O_2
7. Electrochemical reduction/oxidation

Disposal issues

Destructive removal

Three Electrode Cell

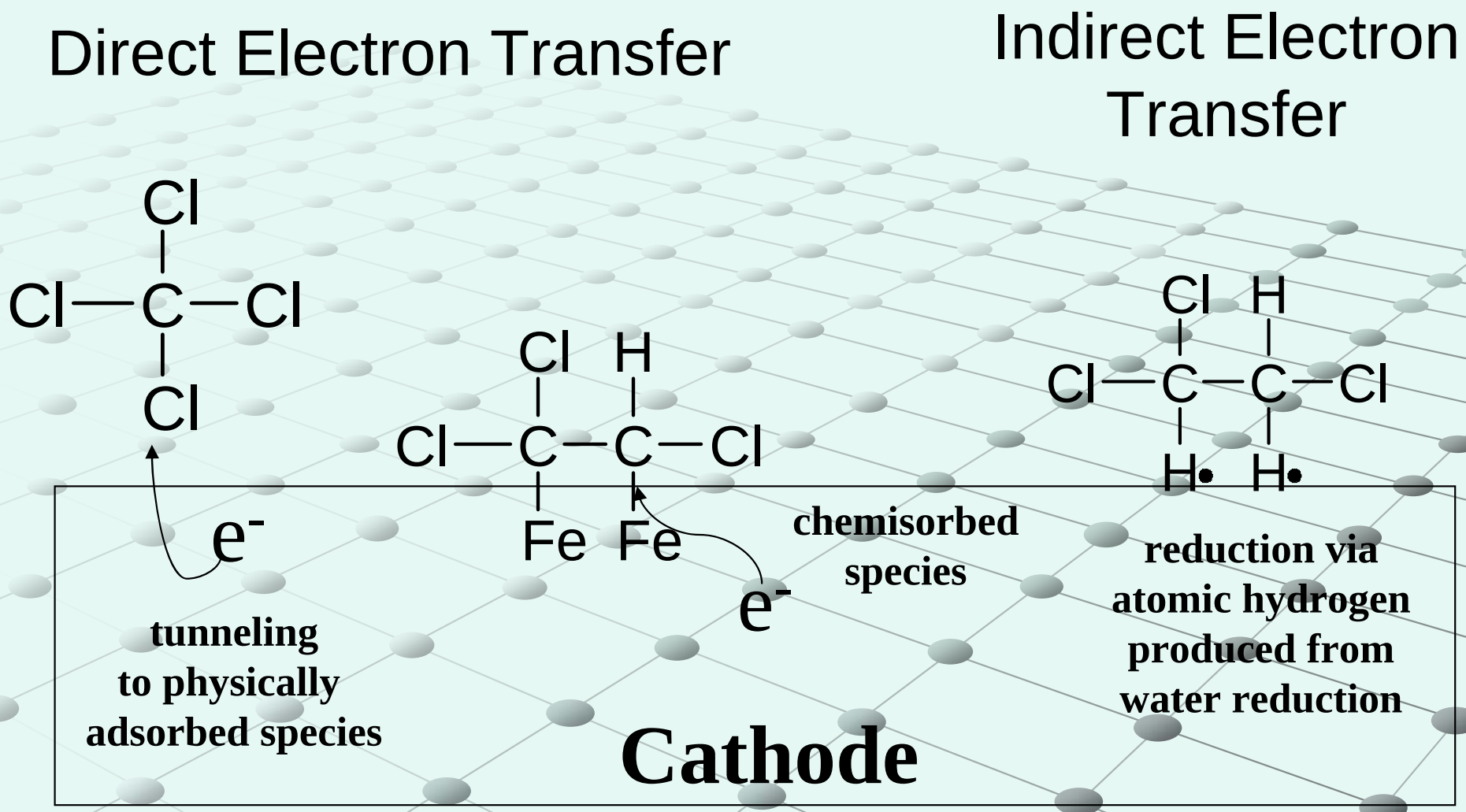


$$H_2O \rightarrow 0.5\,O_2 + 2H^+ + 2\,e^-$$

$$H_2O + e^- \rightarrow 0.5\,H_2 + OH^-$$

Competing Reactions

Reduction - Electron Transfer Mechanisms



Water Oxidation

All Electrode:

$$MO_x + H_2O \rightarrow MO_x(OH^{\bullet}) + H^+ + e^-$$

Active Electrode:
(IrO_2; RuO_2)

$$MO_x(OH^{\bullet}) \rightarrow MO_{x+1} + H^+ + e^-$$

Inactive Electrode:
(BDD; PbO_2; SnO_2)

$$MO_x(OH^{\bullet}) \not\rightarrow MO_{x+1} + H^+ + e^-$$

- MO_x is a metal oxide site on the anode surface.
- Water oxidation produces adsorbed $OH^{\bullet}$ radicals.
- Active oxygen species ($MO_x(OH^{\bullet})$ and MO_{x+1}) may oxidize organic compounds.
- High concentrations of active oxygen species lead to O_2 evolution.

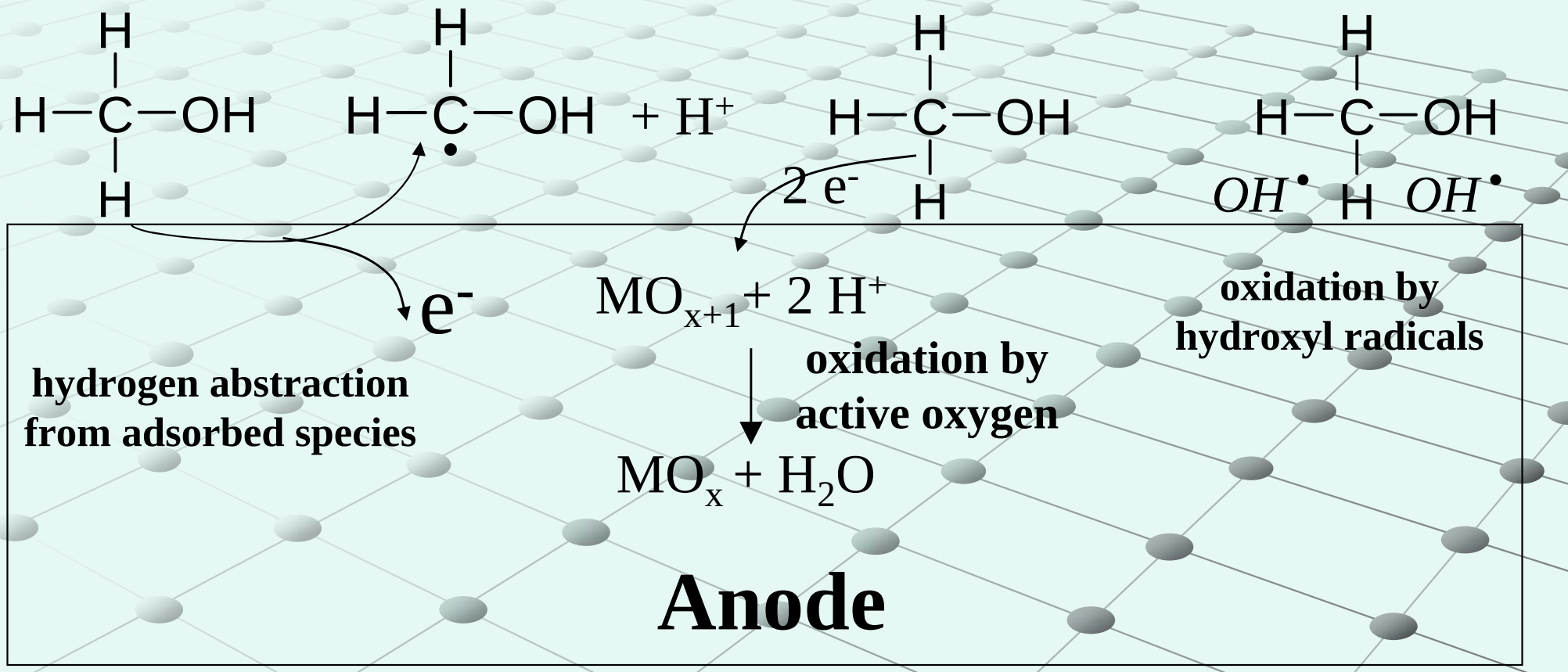
$$MO_x(OH^{\bullet}) \rightarrow 0.5\,O_2 + H^+ + e^- + MO_x$$ Inactive Electrode

$$MO_{x+1} \rightarrow 0.5\,O_2 + MO_x$$ Active Electrode

Oxidation - Electron Transfer Mechanisms

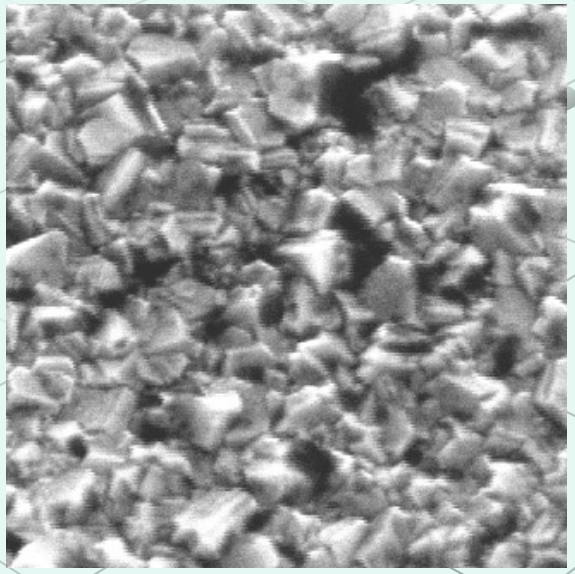
Direct Electron Transfer

Indirect Electron Transfer



Boron-Doped Diamond Film (BDD) Electrodes

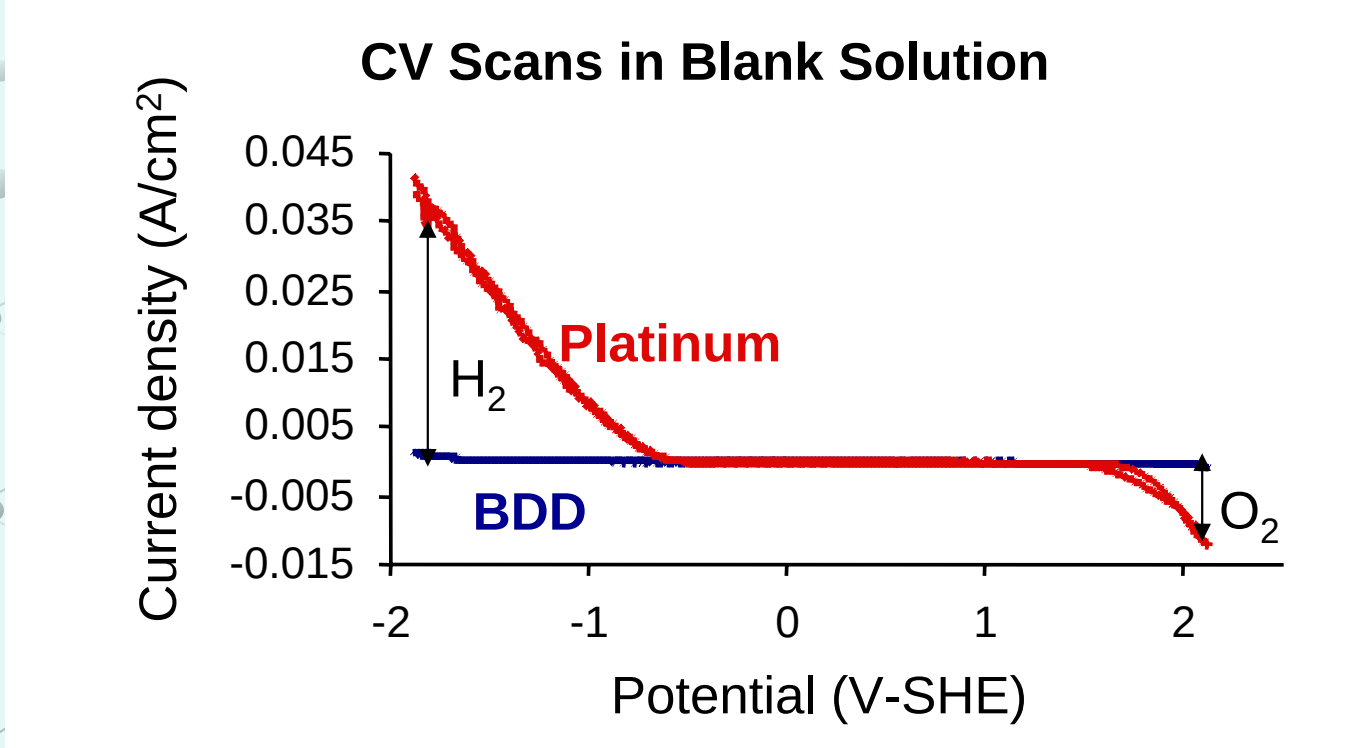
- Diamond film grown on p-silicon substrate using chemical vapor deposition (CVD) technique
  - P-silicon polished with a diamond containing paste, serving as nucleation sites
  - Microwave radiation or a hot filament used to decompose gas mixture of methane and hydrogen
  - Boron doping: B_2H_6
- Boron doping provides electrical conductivity



Scanning electron micrograph of BDD electrode. The individual diamond crystals are ~0.5 μm in size.

BDD Electrodes: Advantages

- Nonactive electrodes: capable of complete mineralization to CO_2.
- Highly stable under anodic and cathodic polarization
- Very low catalytic activity for oxygen and hydrogen evolution: wide electrochemical window for water oxidation and reduction.
- High mechanical strength and resistance to chemical attack
- Hydrophobicity



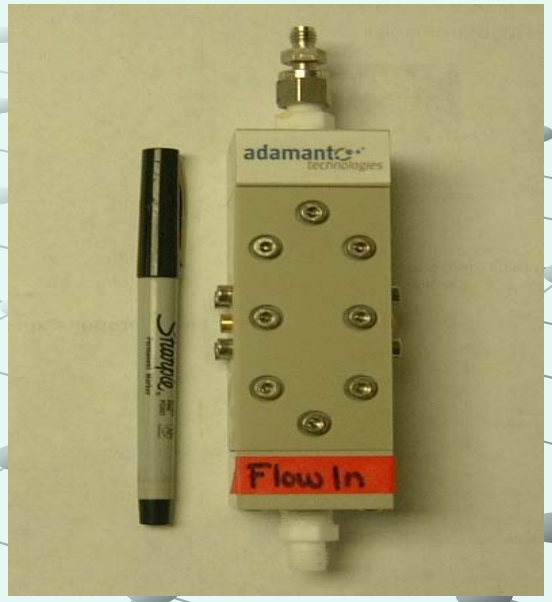
BDD Electrode: Applications

- nitrate reduction to ammonia (Bouamrane, *et al*., 1996)
- organic compound oxidation in wastewater (Gyorgy *et al*., 1999)
- metal ion quantification (Ramesham, 1999)
- metal ion removal (Perret, *et al*. 1999)
- cathodic hydrogen peroxide generation (Goeting, *et al*., 1999)
- ozone generation (Katsuki, *et al*.,1998)
- peroxodisulfuric acid generation (Michaud, *et al*., 2000)
- glucose, ethanol and COD sensors (Rychen, et al., 2001)

Experimental Systems

Rotating disk electrode (RDE) in batch reactor.

- no mass transfer limitations
- electrode surface area = 1 cm^2
- solution volume = 350 mL
- a_s = 0.00286 cm^2/mL



Parallel plate flow-cell.

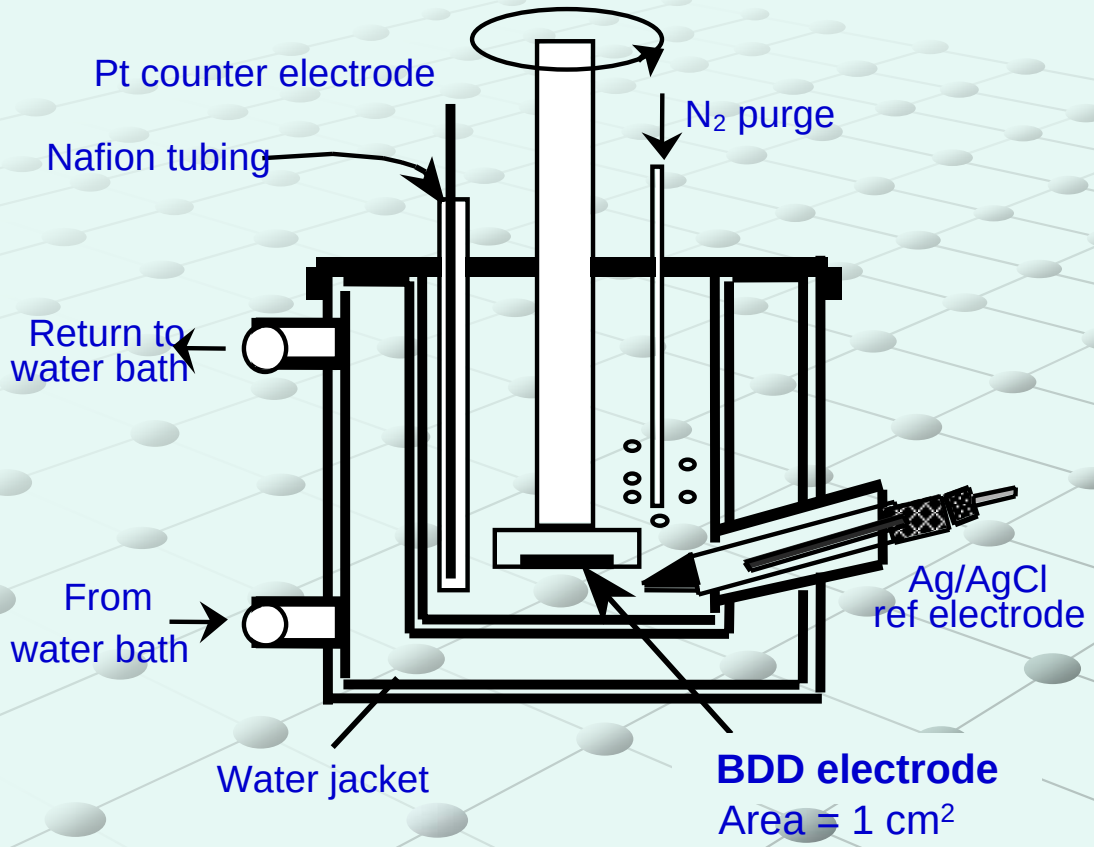
- rates similar to real treatment process
- electrode surface area = 25 cm^2
- solution volume = 15 mL
- a_s = 1.67 cm^2/mL

Example: Treatment of CMP Wasetwater

- Chemical-mechanical planarization (CMP): key technology in ultra large-scale integration devise manufacturing
- Complex waste mixture consisting of suspended solids, Cu^{2+} ions, chelating agents, corrosion inhibitor and other additives
- Current treatment technologies:several sequential unit operations (Expensive)
  - Coagulation/flocculation (additional chemicals introduced)
  - Filtration
  - Ion-exchange
  - Regenation of the ion exchange resin (secondary waste stream)
- Electrochemical methods: simpler and cost effective
  - Cathodic decomposition to remove Cu^{2+} ions
  - Anodic decomposition to remove corrosion inhibitors and organic complexing agents.
  - Filtration after coagulation induced by acidic environment generated by anodic reaction

Tamilmani, S.; Hung, W. H.; Raghavan, S.; Farrell, *J. IEEE transactions on Semiconductor manufacturing*, 17, 448-454 (2004).

CMP Wastewater Treatment: Batch Experiments



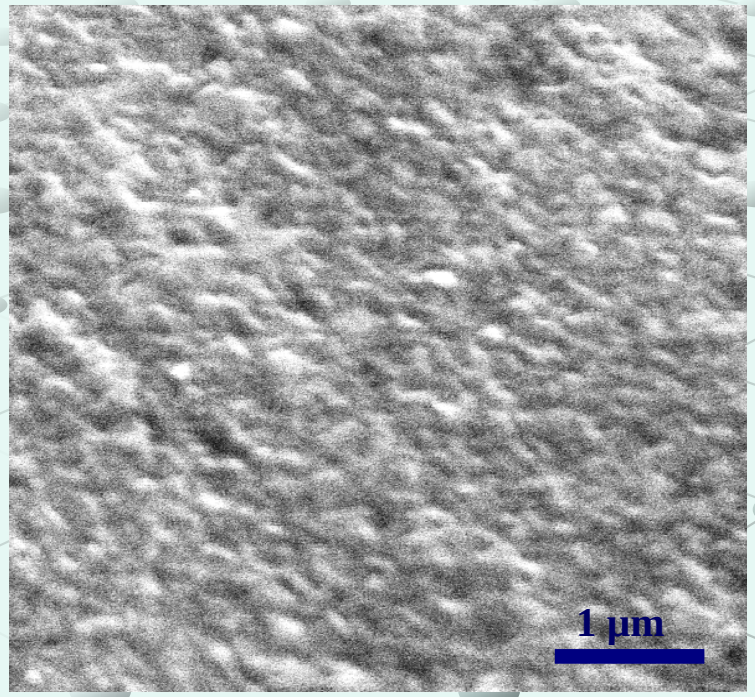
- Electrode rotated at 100 rpm
- Reactor volume = 30 mL
- EG&G model 273 A potentiostat
- Copper ions determined by AAS
- Citrate ions determined by IC
- TOC removal determined by combustion /IR

Rotating Disk Electrode (RDE) Reactor

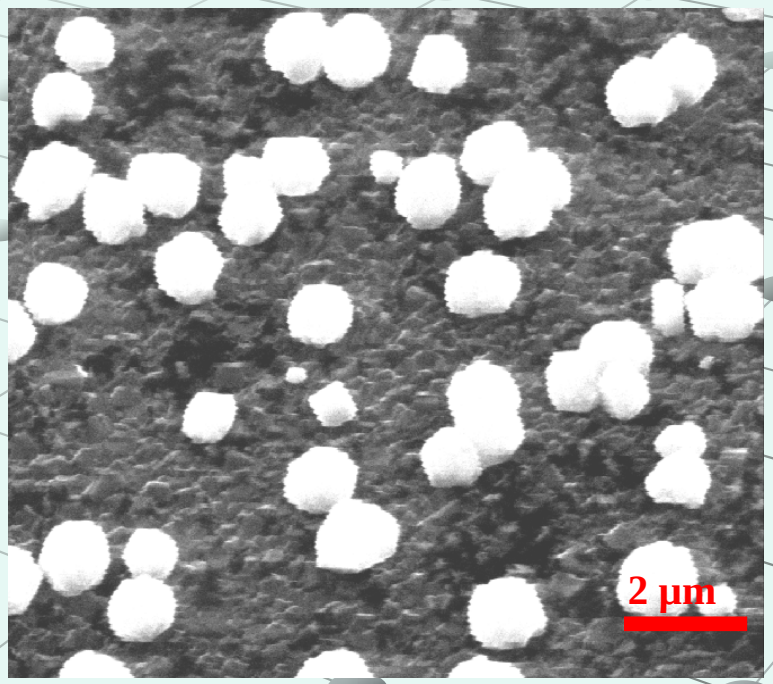
SEM Micrographs of Copper Deposits

Copper deposits obtained after 90 minutes of polarization at -200 mV-Ag/AgCl in a 50 mM K_2SO_4 solution containing 20 mg/L copper.

Copper on Copper Electrode



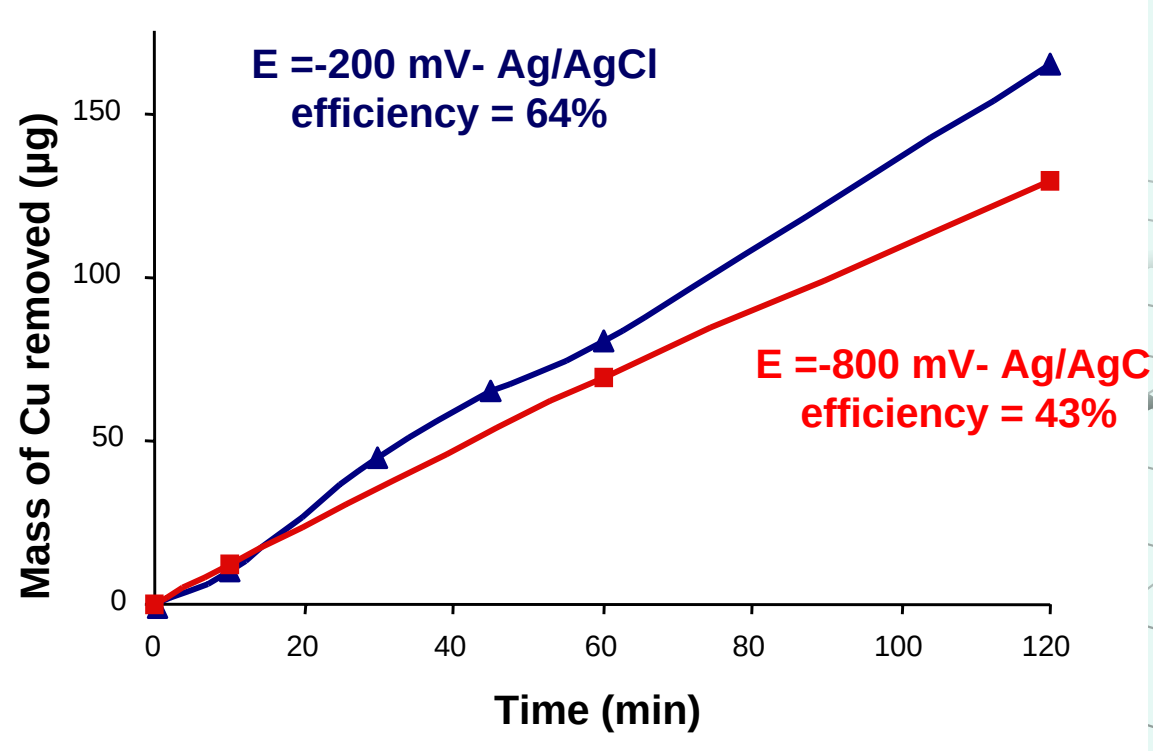
Copper on BDD Electrode



Discrete particles suggests discrete active sites.

Effect of Potential on Cu^{2+} Removal

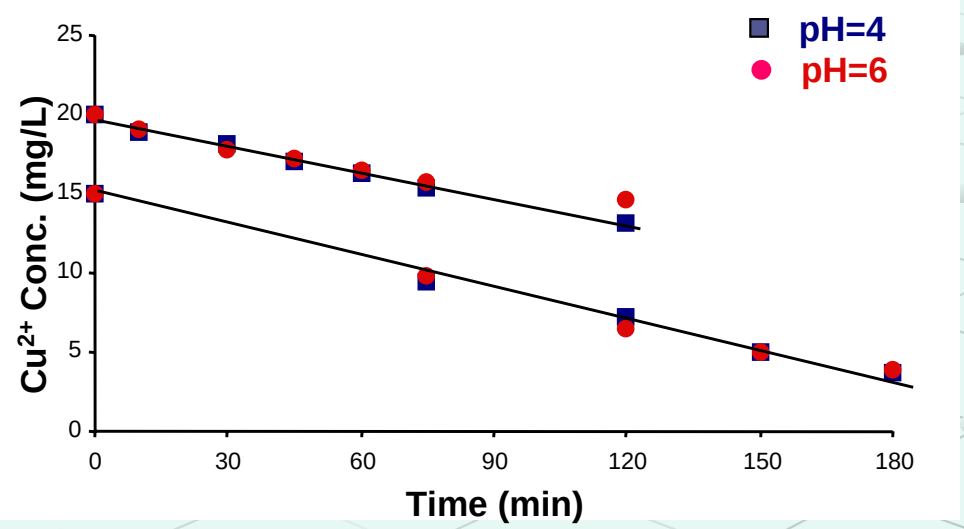
Cu^{2+} removal in batch RDE reactor at 100 rpm.



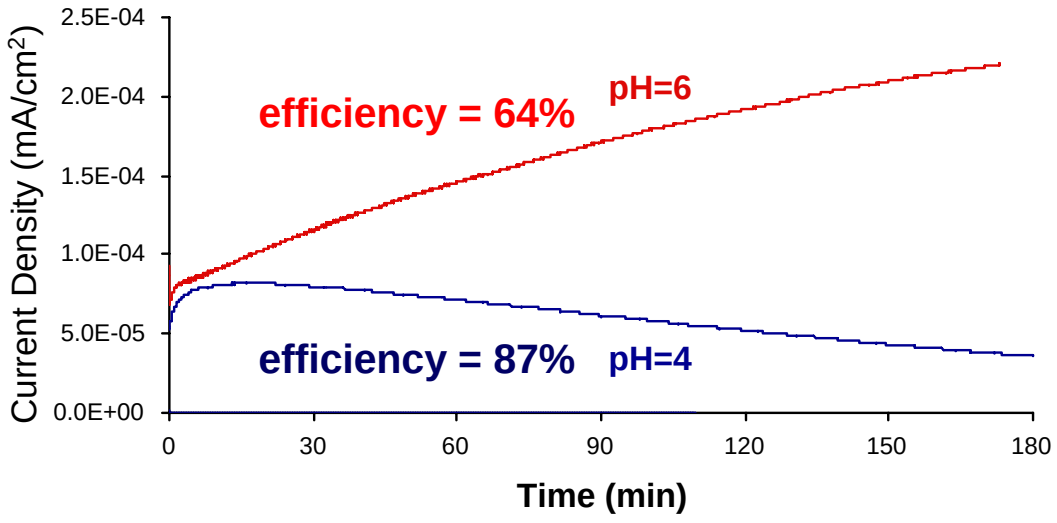
- Slower removal at lower potential due to increased blocking effect of hydrogen bubbles.
- Weak effect of potential suggests mass transfer limited removal.
- Removal rate = mass transfer limited flux for d=45 µm.

Effect of pH on Cu^{2+} Removal

Concentrations in batch RDE reactor at 100 rpm for E = -200 mV-Ag/AgCl.



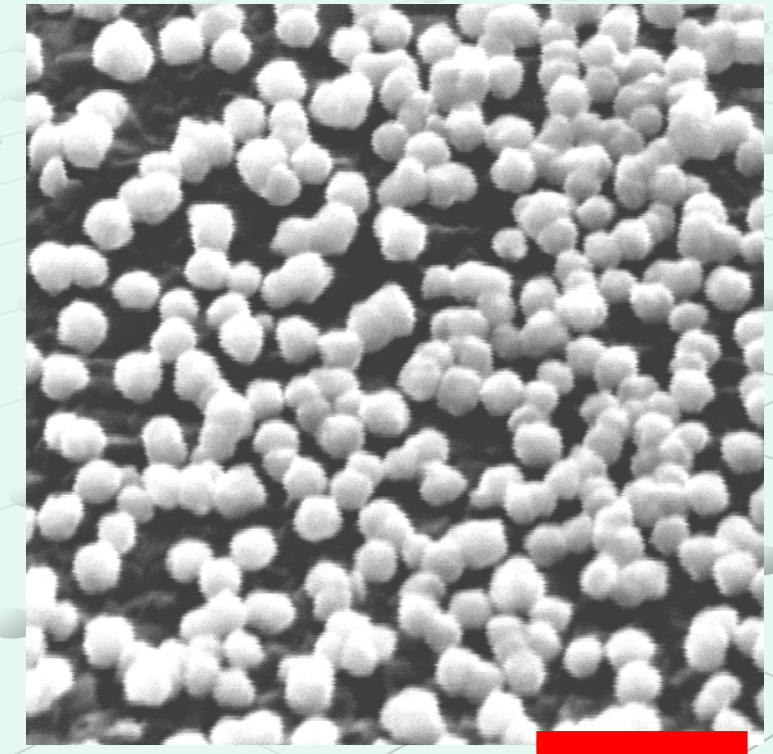
Current for 15 mg/L initial concentration.



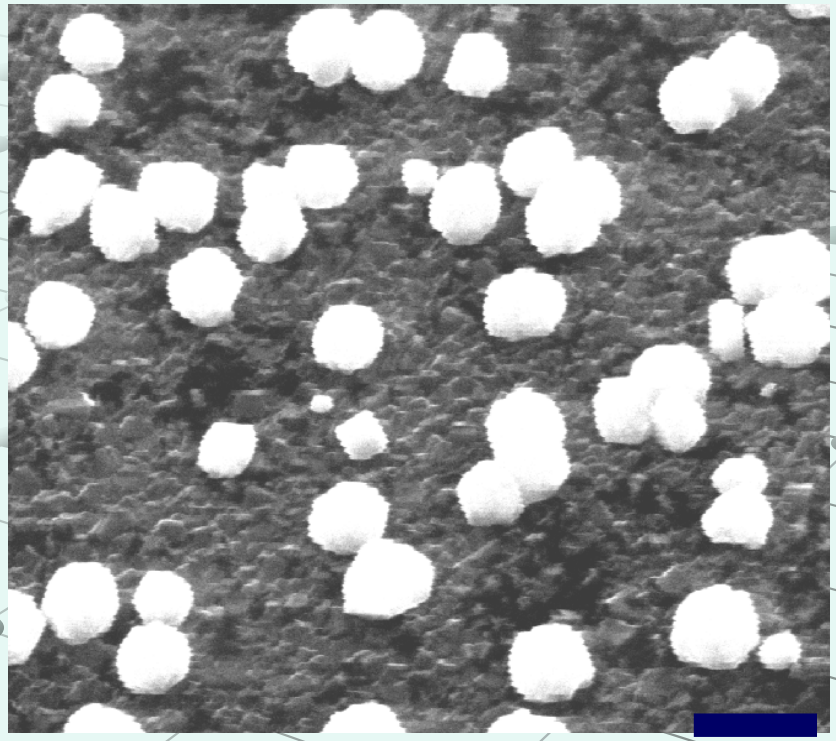
- Cu^{2+} removal rates are independent of the pH value.
- Current efficiency for Cu deposition is greater at pH=4.
  - Same amount of Cu^{2+} removal
  - Lower rate of water reduction
  - Smaller electroactive surface area

Effect of pH on Cu Morphology

pH=6

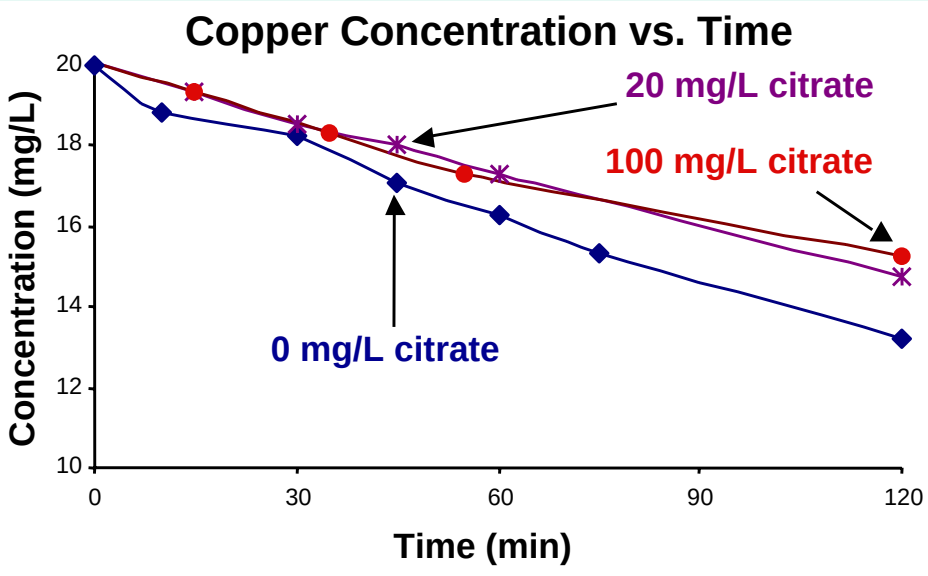


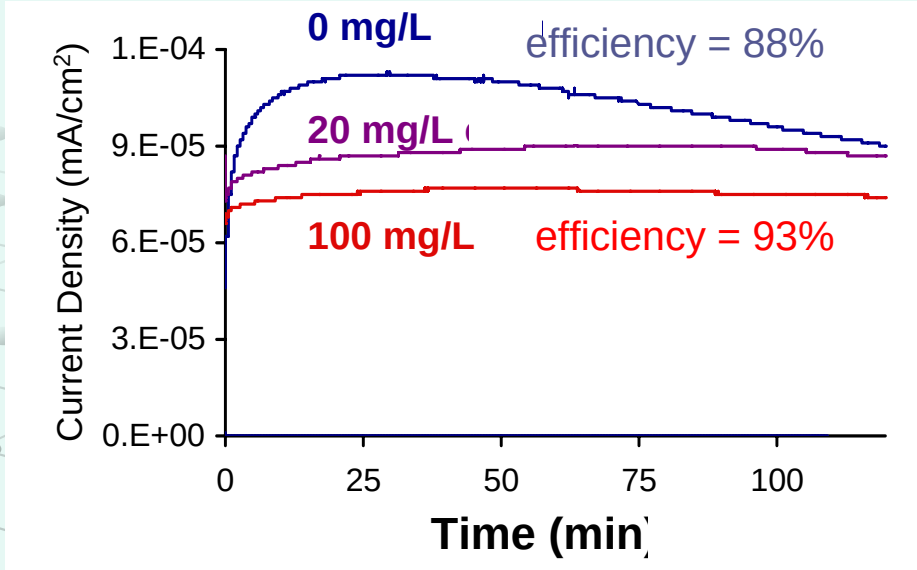
pH=4



- Fewer but larger spheres at pH=4: overall smaller electroactive surface area than that at pH=6 leading to higher current efficiency.
- Lower pH may decrease the number of active sites by protonating oxygenated active sites.

Effect of Complexing Agents on Cu^{2+} Removal

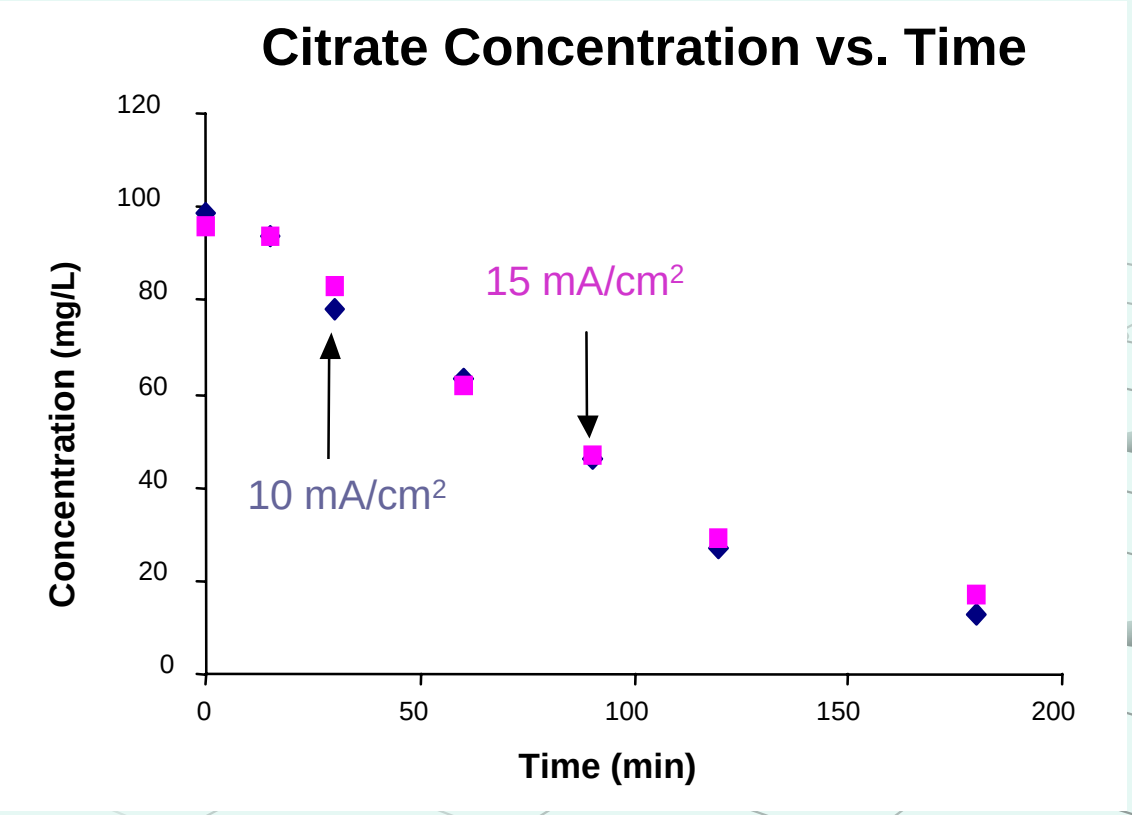




- Citrate had a minor effect on the Cu^{2+} removal rate.
- Citrate increased the current efficiency for Cu^{2+} removal.
- Adsorbed citrate may block sites for O_2 reduction.

Citrate Oxidation

$$\frac{dc}{dt} = -k_0$$

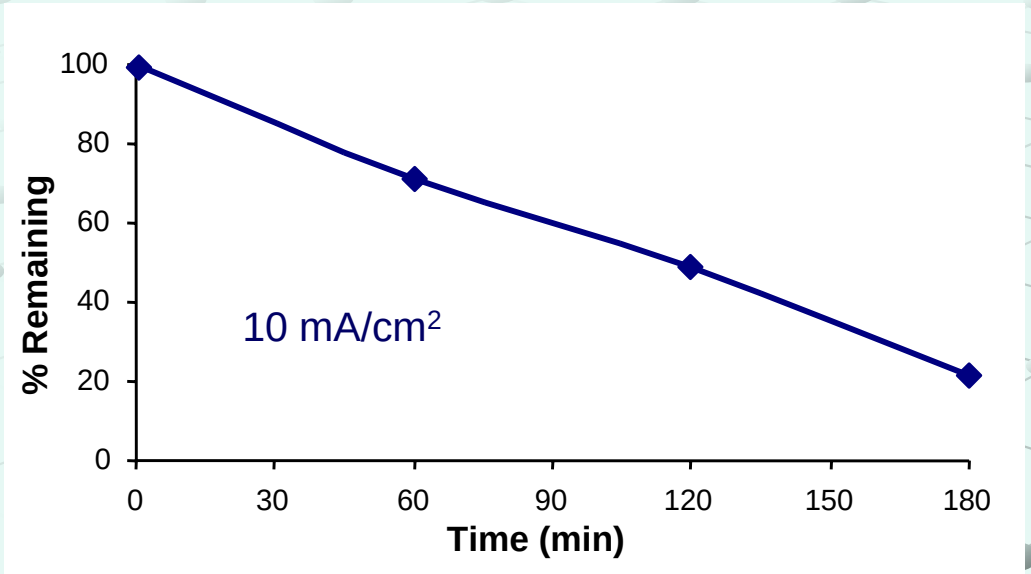


$$\frac{dc}{dt} = -k_1 c$$

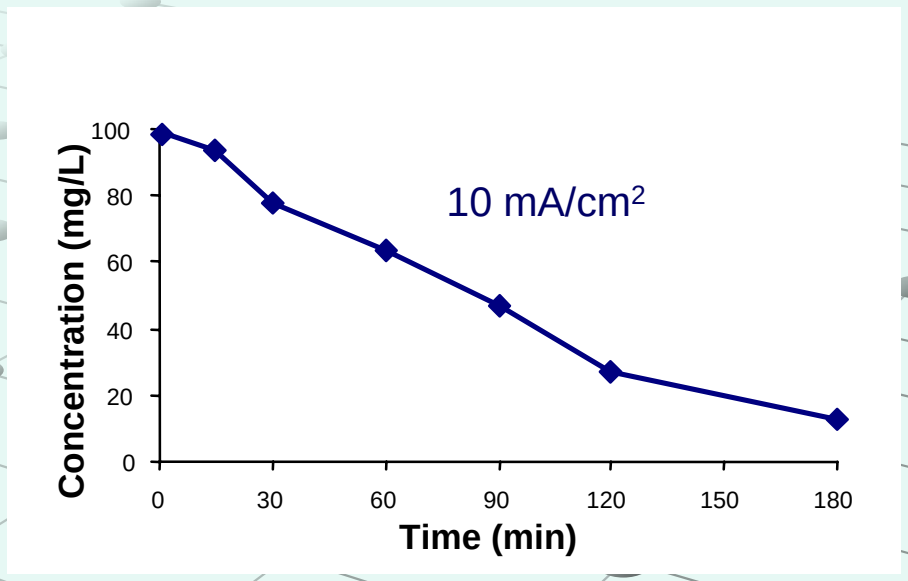
Citrate removal was independent of the current density, suggesting indirect oxidization by HO•

Citrate Destruction and TOC Removal

TOC Remaining vs. Time

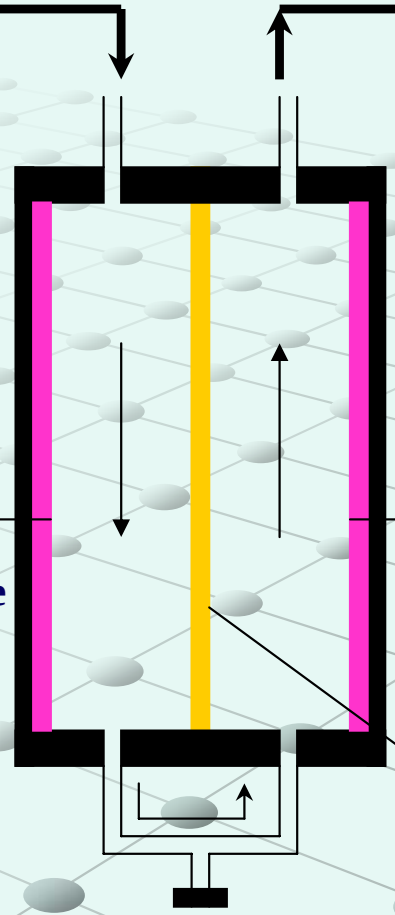


Citrate Concentration vs. Time



Similar TOC and citrate removal indicates mineralization to CO_2.

Proposed Treatment Scheme



Inlet of CMP waste water

complexed Cu^{2+}, free organics, alumina & silica colloids

Treated water

<1ppm Cu^{2+}

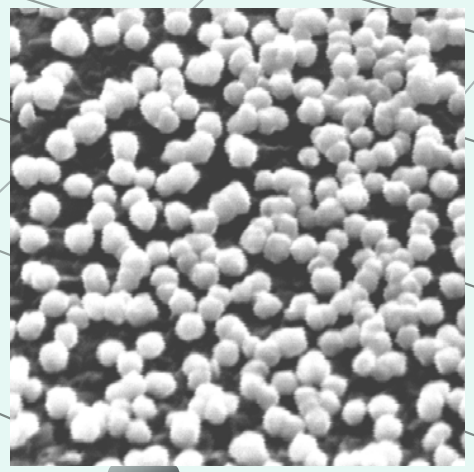
Anode - BDD electrode

Cu-complexes are broken, organics are oxidized, water oxidation reduces pH, low pH destabilizes colloids

Cathode - BDD electrode

NAFION membrane

metallic copper deposits on cathode



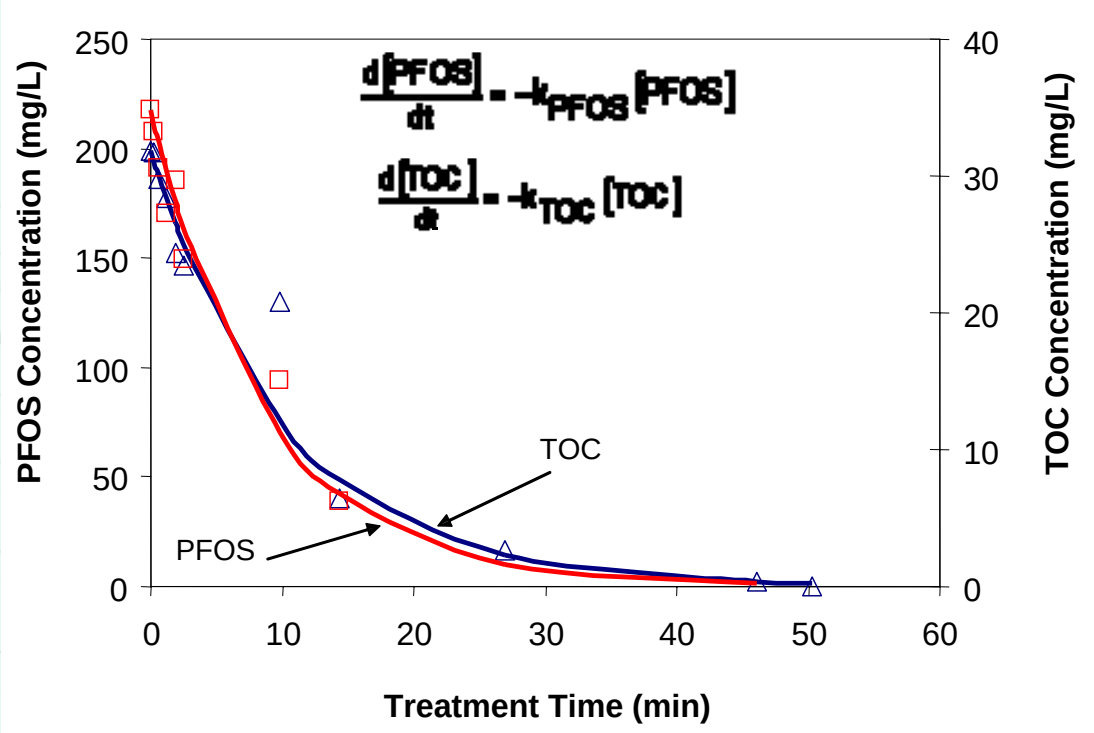
Sampling point

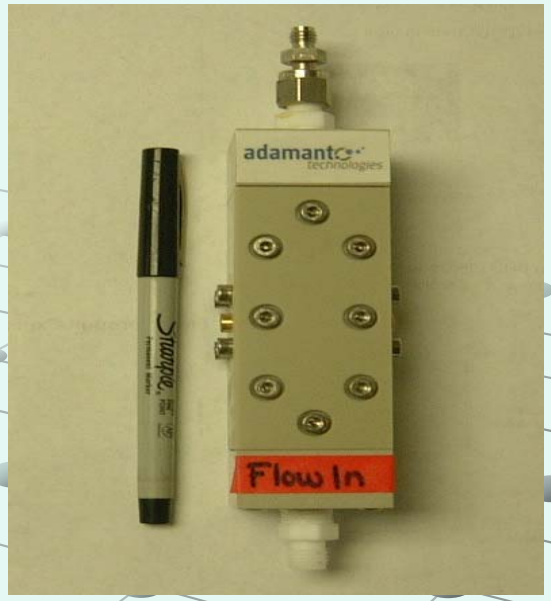
A single elctrochemical reactor could be used in place of the multiple step process that is presently being used for treating CMP wastewater

Example: Destruction of PFOS

- Perfluorooctyl Sulfonate (PFOS) is a perfluorinated surfactant: hydrophilic and hydrophobic
- Extremely low surface tension (2 dynes/cm^2)
- Widely used in commercial products and industry process
  - Pharmaceuticals, adhesives, Teflon coatings
  - Stain-resistant coatings for fabrics, upholstery, and carpet
  - Paper protectors for food products
  - Semi-conductor industry –
    - Electroplating and electronic etching baths
    - Photographic emulsifiers
    - Surface treatment agents for photolithography
  - Fire extinguishing foams
- Problems with the compound
  - Very stable in environment and accumulate in human body
  - Not degradable by conventional advanced oxidation processes
  - Not biodegradable in wastewater treatment plant
- New technology is needed to remove PFOS from dilute aqueous solutions

Destruction of PFOS: Experimental Results



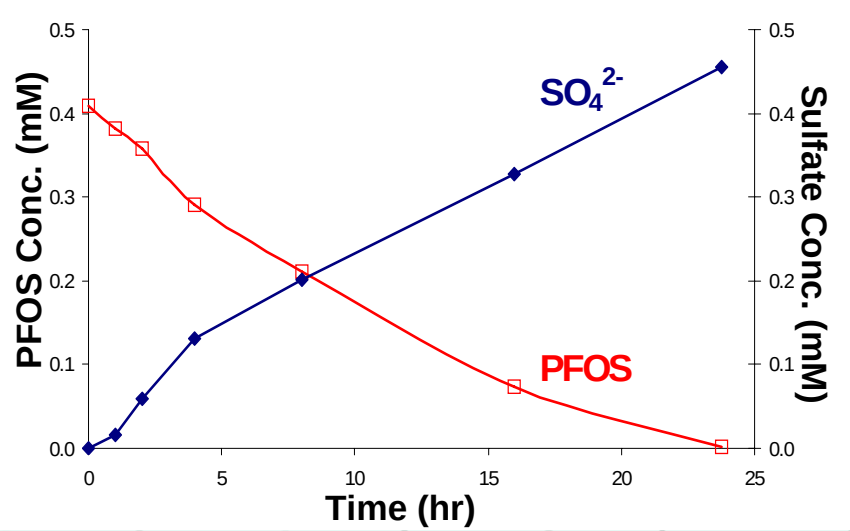


PFOS and total organic carbon concentration (TOC) in flow-cell operated at a current density of 15 mA/cm^2.

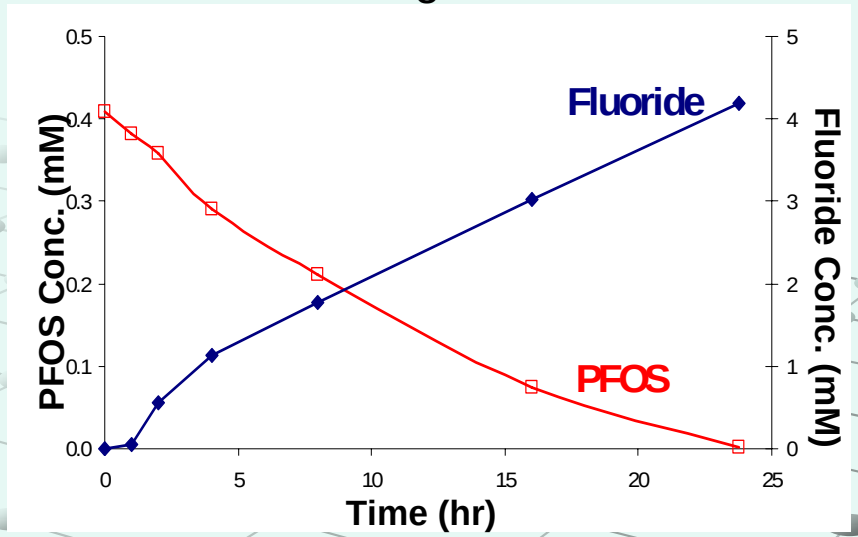
- PFOS can be rapidly removed from water
- Reaction rates are first order
- Treatment half-life less than 10 minutes
- No build-up of fluorinated organic reaction products

Destruction of PFOS: Reaction Products

Comparison of sulfate released to PFOS degradation



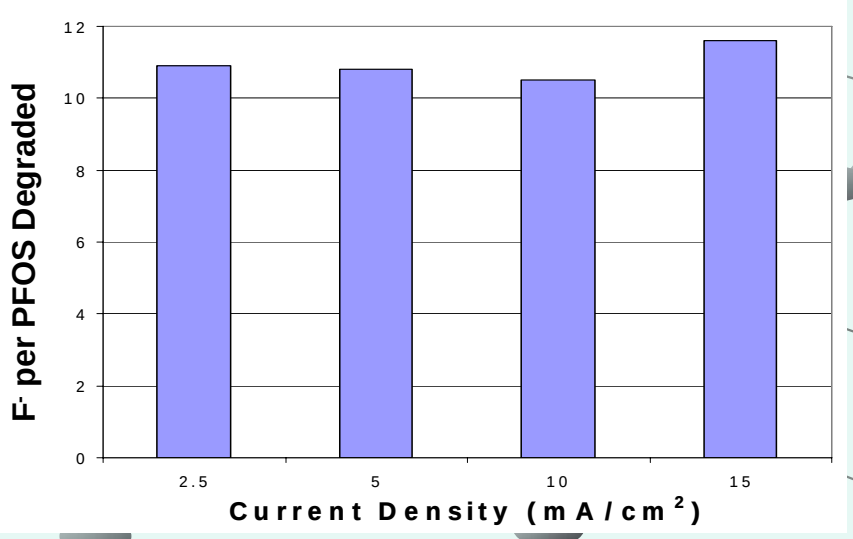
Comparison of fluoride released to PFOS degradation



Only trace quantities of:

- Perfluorooctanoic acid
- Perfluoroheptanoic acid
- Perfluorohexanoic acid

Fluoride per PFOS degradation for different current densities.



Proposed Reaction Sequence

PFOS → PFOA

$$C_8F_{17}SO_3H + 3H_20 \rightarrow C_7F_{15}CO_2H + SO_4^{2-} + 4H^+ + 2F^- + 2H_2$$

$$C_7F_{15}CO_2H + 2\,H_2O \rightarrow C_6F_{13}CO_2H + CO_2 + 2H^+ + 2F^- + H_2$$

PFOA → $C_5F_{11}CO_2H$

$C_4F_9CO_2H$

$C_3F_7CO_2H$

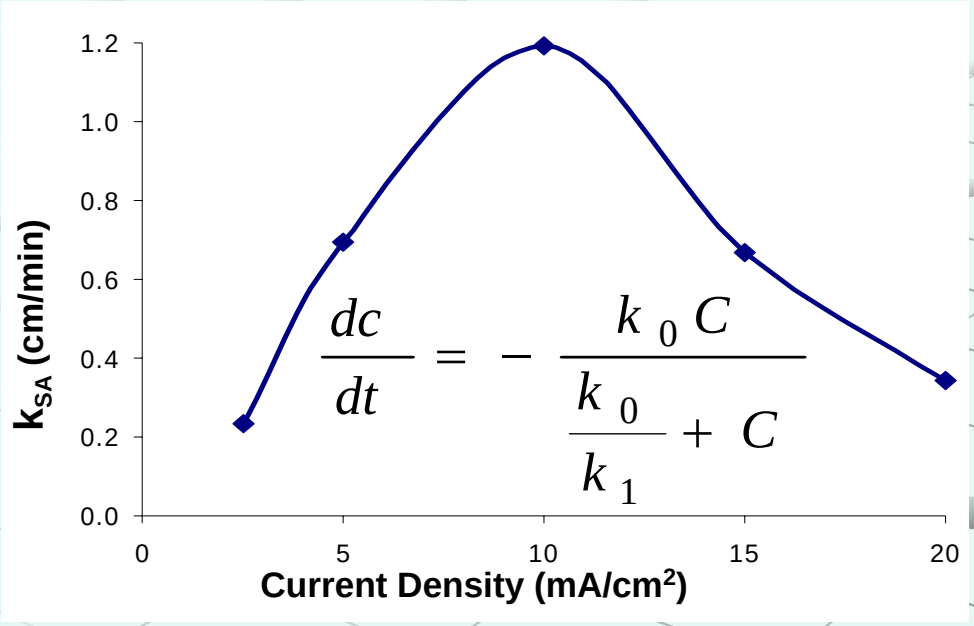
Pentafluoropropionic acid $C_2F_5CO_2H$ Volatile species

Trifluoroacetic acid CF_3CO_2H Volatile species

- Fluoride mass balance of 11 F^- released per PFOS degraded suggests that volatile species are lost from solution.
- Only trace levels of intermediate products suggests near complete FPOS destruction in a single interaction with the electrode surface.

Effect of Current Density on Reaction Rates

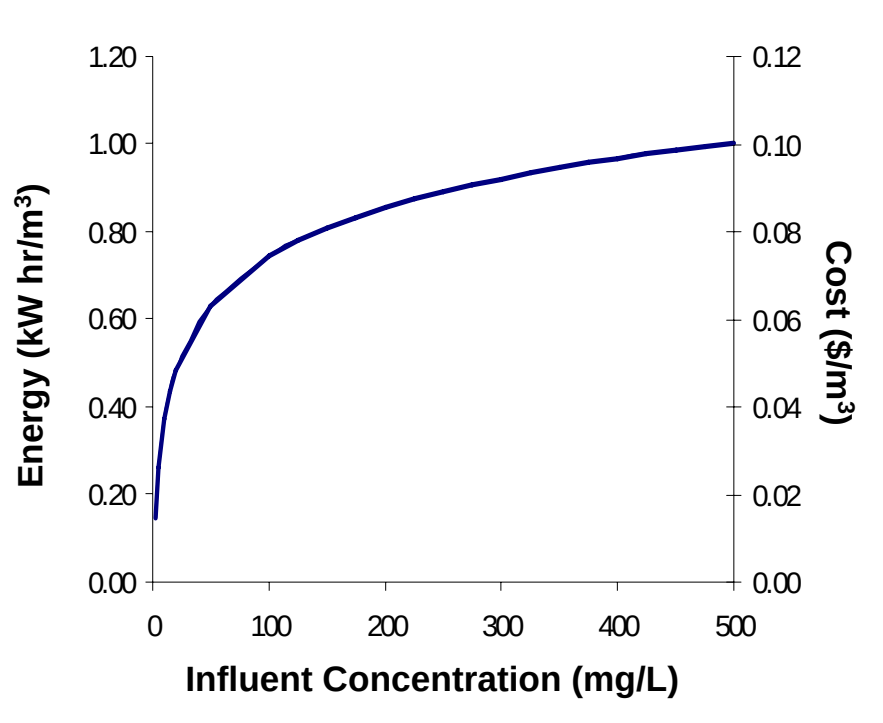
The effect of current density on the RDE surface area normalized rate constants (k_{sa}) for PFOS oxidation.



- Oxygen gas bubbles at high current densities reduce the wetted surface area of the electrode and interfere with PFOS oxidation.
- Maximum practical reaction rates are limited by the competing reaction of oxygen evolution.

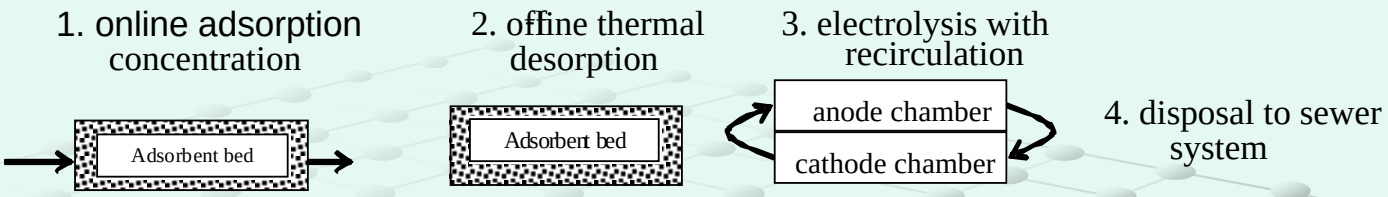
PFOS Treatment Costs

Electrical power requirements and costs required to reach a final PFOS concentration of 1 mg/L (2.5 µM) as a function of the influent concentration. Costs based on flow-cell operated at a current density of 20 mA/cm^2.



- Electrical power costs are small compared to other treatment methods.
- Capital costs for a 10 liter per minute flow-cell are ~$5000.

Proposed Treatment Scheme



Multi-step treatment scheme:

1. Concentrate target compounds from dilute aqueous solutions on an adsorbent.
2. Thermally desorb PFOS into a concentrated solution.
3. Recirculate concentrated PFOS solution through a BDD electrode reactor for electrolytic destruction.
4. Dispose of biodegradable electrolysis products to the sanitary sewer system.

Conclusions

- **Electrochemical treatment at BDD electrode can be used for destructive removal of both inorganic and organic contaminants.**
- **Electrochemical treatment of CMP wastewater at BDD anodes is capable of removing Cu^{2+} ions, decomposing organic compounds and decreasing pH in one single reactor.**
- **Organic compounds such as PFOS that cannot be oxidized by chemical and biological treatment process can be treated by electrochemical process.**

Acknowledgements

- James Farrell, Srini Raghavan, Kimberly Carter, Subramanian Tamilmani, Wayne H. Huang
- NSF/SRC ERC 2001MC425
- NSF Chemical and Transport Systems CTS-0522790
- Petroleum Research Fund 43535-AC5

Industrial Collaboration

• Tim Yeakley	Texas Instruments
• Thomas P. Diamond	IBM
• Jim Jewett	Intel
• Laura Mendicino	Freescale Semiconductor