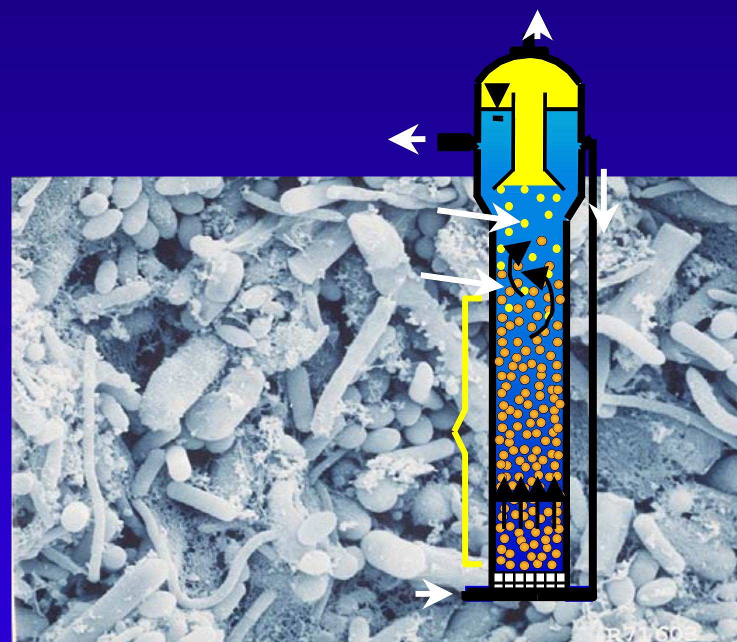
Biological Removal of Copper & Organic Contaminants from Chemical-Mechanical Planarization (CMP) Effluents



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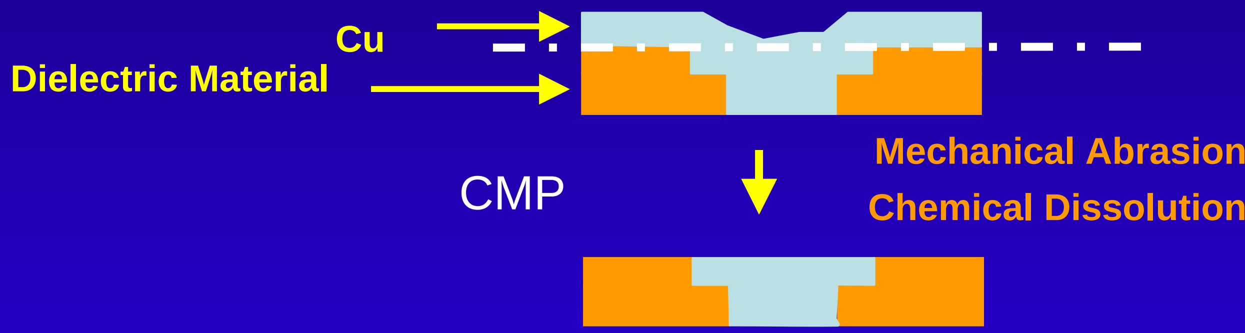
Thrust C:
Factory Integration

Task C-1:
Novel Processes for Water Purification and Wastewater Treatment

Subtask C-1-2:
Bio-treatment of Waste Streams Containing Organic Compounds and Copper

Background

- Cu interconnect technology is rapidly replacing traditional processes for the metallization of semiconductor devices



- Cu-Chemical Mechanical Planarization (CMP) effluents ~ 30-40% water consumed in a fab

- Cu-CMP effluents contain significant quantities of soluble copper and organic contaminants

CMP Wastewater Components

Inorganic

Copper:	Soluble Cu^{+2} (1-50 mg/l)
Inorganic solids:	Abrasives (eg. SiO_2, Al_2O_3, CeO_2)
Oxidizers, strong acids/bases:	H_2O_2, NO_3^-, $KMnO_4$, HF, NH_3, OH^-, etc

Organic

Metal chelators / acids:	Citric acid, oxalic acid, EDTA, peroxy acetic, etc.
Corrosion inhibitors:	Benzotriazoles
Surfactants/dispersants:	PFOS, alkyl sulfates, etc.

Source: Golden et al. 2000. Semiconductor Int. **23**: 85-98.

Why Treat CMP Effluents?

- **To meet environmental standards;** eg:

Cu limit : - discharge to POTWs: 1- 2 mg Cu/l

- direct discharge: 5-10 µg Cu/l

- **Enable water reuse**

Treatment of CMP Effluents:
Physico-Chemical Methods

- **Coagulation / flocculation / clarification**

  (Removal of solids, metals, fluoride, soluble silica)

  Requires large tanks, high chemical addition

  Generates (toxic) sludges

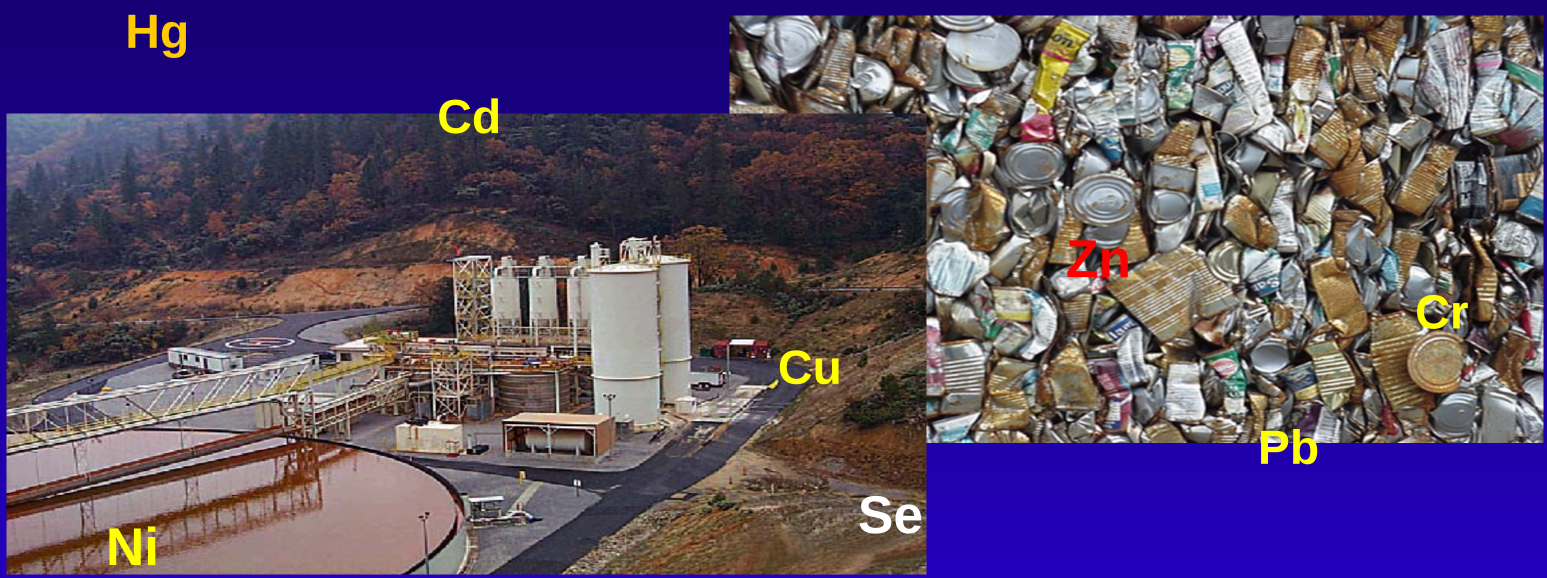
  High residual Cu and suspended solids content

- **UF / oxidant removal/ Ion exchange**

  (Removal of solids, oxidants, copper)

  Expensive; No removal of organic fraction

Bioremediation of Heavy Metals



- **Environmental biotechnologies offer interesting potentials for metal removal and recovery (Zn^{+2}, Pb^{+2}; Se(V); U(VI), etc.)**

- **Biological treatment could also provide an attractive approach to effectively meet regulatory challenges associated with Cu-CMP.**

Anaerobic Biotechnology

Expanded Granular Sludge Bed (EGSB) reactors

High-Rate Bioreactors

Biological Wastewater Treatment System at Philips,

(Stadskanaal, The Netherlands) for the removal of heavy metals (Ni, Pb, Cr, Al, Fe), nitrate and acetate.

Removal of Metal by Sulfate Reducing Bacteria (SRB)

$$SO_4^{2-} + 4\ H_2 + H^+ \longrightarrow HS^- + 4\ H_2O$$

(Electron donor)

$$S^{=} + M^{2+} \longrightarrow MS \downarrow$$

Metal Sulfide

Metal Sulfides: very low solubility products (K_{sp})

eg. 10^{-49} for CuS

Biologically Formed ZnS in a Sulfate Reducing Biofilm

Labrenz et al. 2000 Sience 290:5497

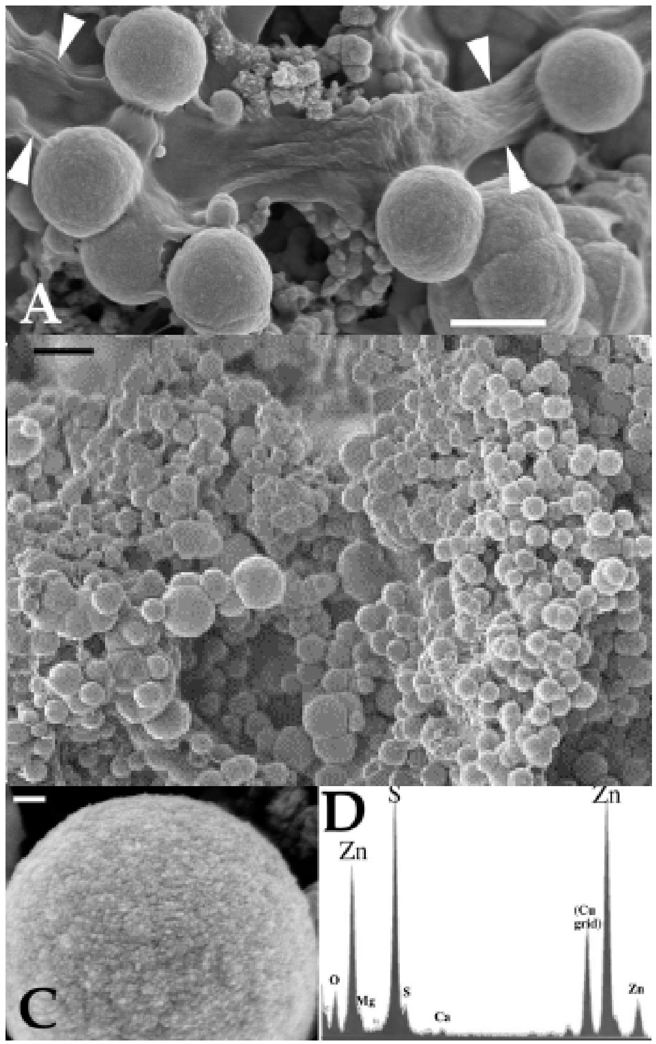


Fig. 2. (**A**) SEM image of a chain of filamentous cells (width indicated by white arrowheads; dehydrated because of the vacuum) and associated micrometer-scale mineral aggregates. Bar, 1 µm. (**B**) TEM image of a chain of cells (low contrast; bar, 1 µm) and aggregates (dark contrast). (**Inset**) Selected area electron diffraction pattern from aggregates with interplanar spacings (in nanometers). (**C**) High-resolution SEM image showing that the aggregates in (A) and (B) consist of few-nanometer-diameter particles (indicated by surface roughness). Bar, 0.1 µm. (**D**) Energy-dispersive x-ray spectrum. Data indicate that micrometer-scale objects are aggregates of randomly oriented, few-nanometer-diameter crystals of sphalerite (ZnS).

Treatment of Heavy-Metal Containing Wastewaters in Single-phase Anaerobic Sulfidogenic Bioreactors

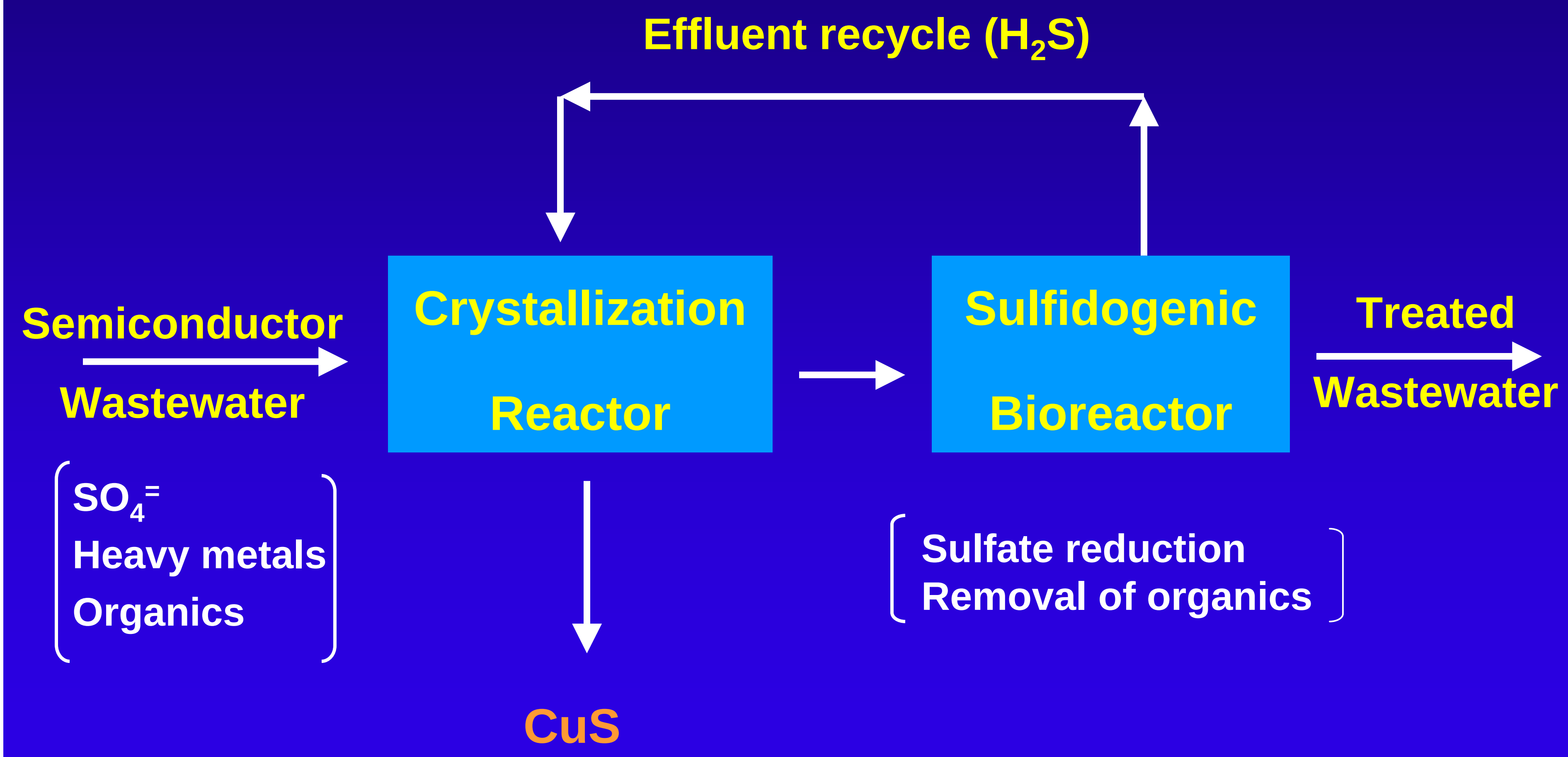
Advantages

- Very low effluent Cu concentrations
- Simultaneous removal of organics
- Low maintenance & operational costs (low energy input / chemical requirements)
- Rapid application at the industrial scale due to widespread full-scale experience with core technology

Drawbacks

- Possible microbial inhibition by heavy metals
- Contamination of biosolids with heavy metals
- Selective recovery of Cu not feasible

Anaerobic Sulfate Reducing Bioreactor – Crystallization Reactor (ASBR-CR)

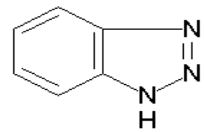
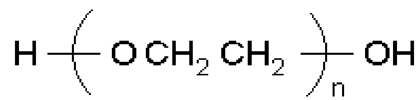
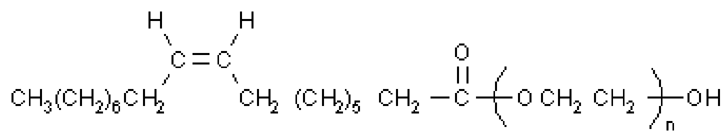
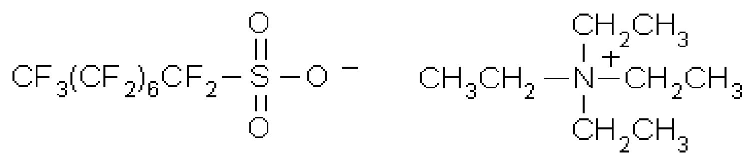
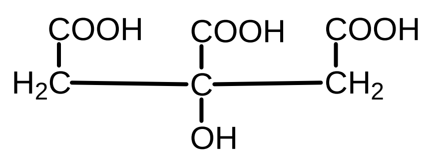


Research Objectives

Investigate the feasibility of a novel treatment system consisting of an **anaerobic sulfate-reducing bioreactor – crystallization reactor** for the simultaneous removal of copper and organic contaminants in CMP effluents.

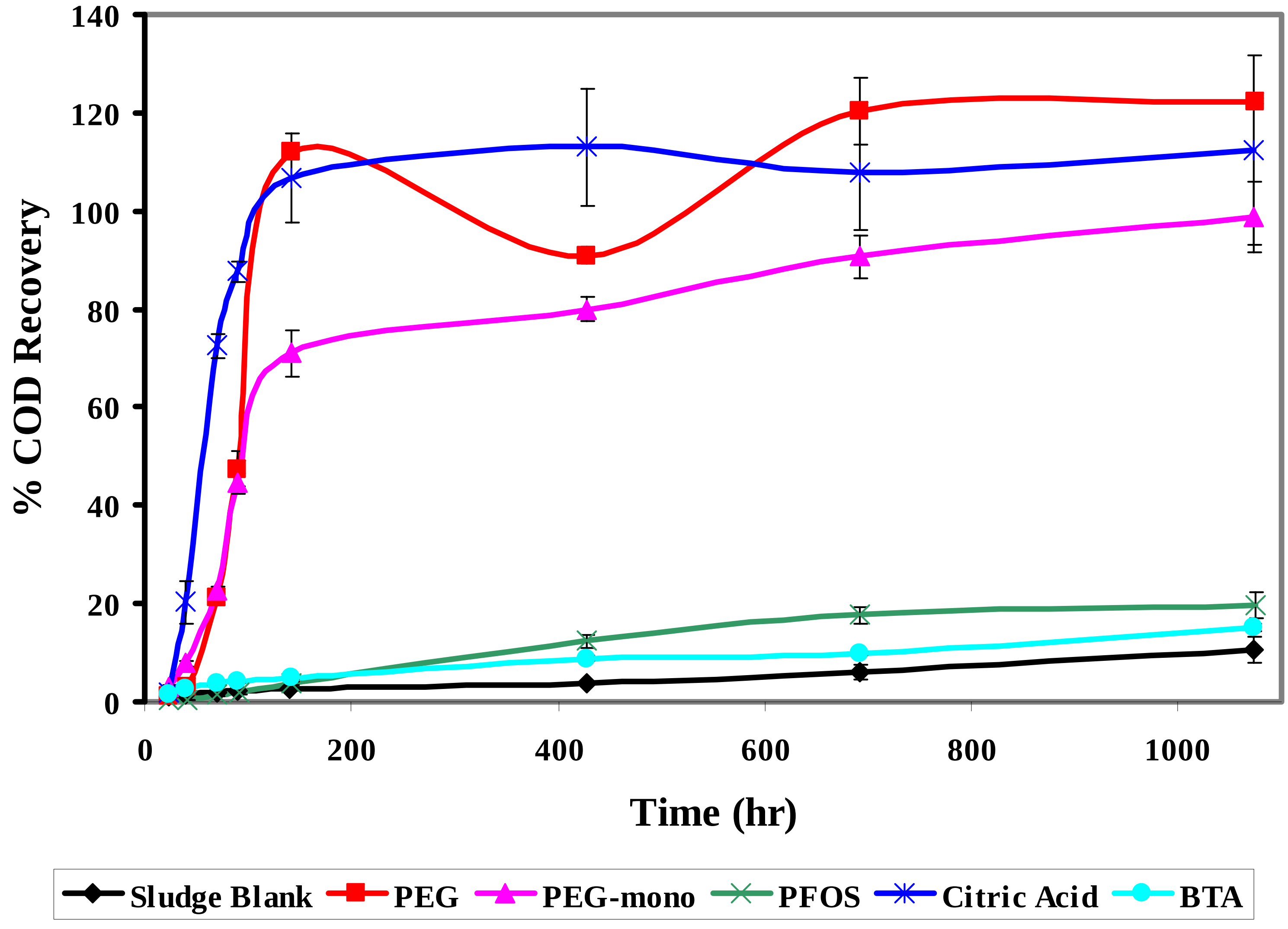
- Susceptibility of CMP wastewater components to anaerobic biodegradation
- Inhibitory effects of CMP wastewater components to anaerobic microorganisms
- Evaluate the treatment of CMP effluent containing varying Cu levels in the two-reactor system

Results - Microbial Inhibition

Compound	Structure	IC_{50} (mg/l)
Copper (II)	Cu	20.6 mg/l
Benzotriazole [BTA]		NT (<310 mg/l)
Poly(ethylene glycol) [PEG]		NT (<349 mg/l)
PEG monooleate [PEG-mono]		NT (<1000 mg/l)
Perfluoro-1-octanesulfonic acid tetraethylammonium salt [PFOS]		NT (<612 mg/l)
Citric Acid		NT (<1237 mg/l)

NT - Non-toxic at concentrations less than the maximum tested concentration, as indicated

Anaerobic Biodegradability

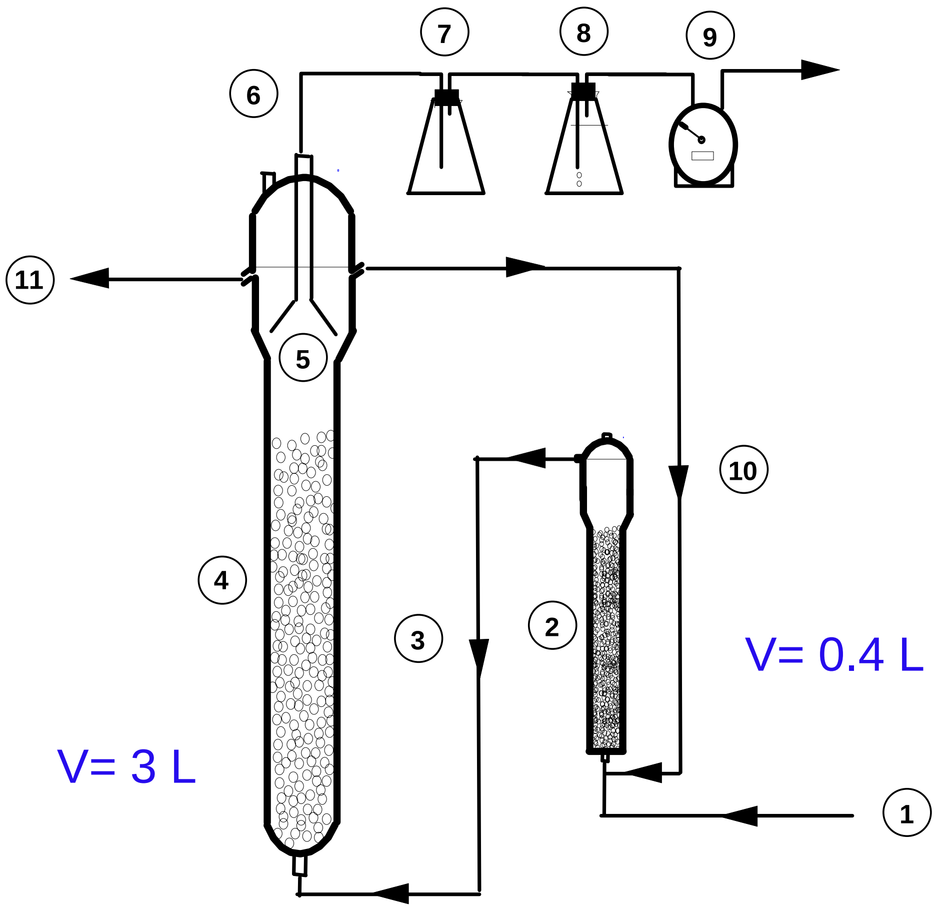


Anaerobic Biodegradability

Compound	Biodegradability	
	Methanogens	SRB
Polyethylene glycol	Yes	Yes
Polyethylene glycol monooleate	Yes	Yes
Isopropyl alcohol	Yes	Yes
Citric Acid	Yes	Yes
Oxalic acid	Partial	Yes
Triton X-100	No	Yes
Fluorinated Surfactant (PFOS)	No	No
Benzotriazole	No	No
Hydro-benzotriazole	No	No

SRB - Sulfate Reducing Bacteria

Anaerobic Sulfate-Reducing Bioreactor – Crystallization Reactor System

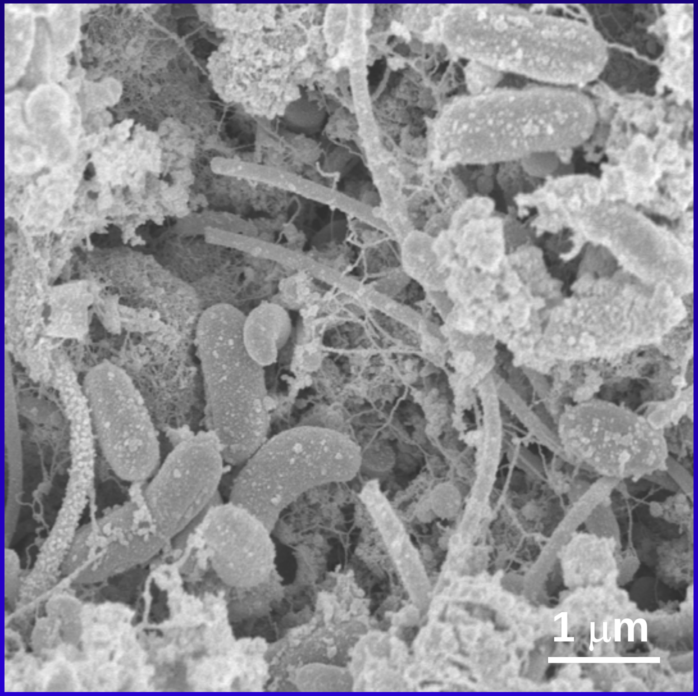


Schematic representation of the anaerobic bioreactor - crystallization reactor system

1 - Influent
2 - Crystallization reactor (CR)
3 - Effluent CR
4 - Mesophilic bioreactor (MR)
5 - Gas cap
6 - Biogas
7 - Safety flask
8 - Sodium hydroxide
9 - Gasmeter
10 - Liquid effluent recirculation
11 - Liquid effluent

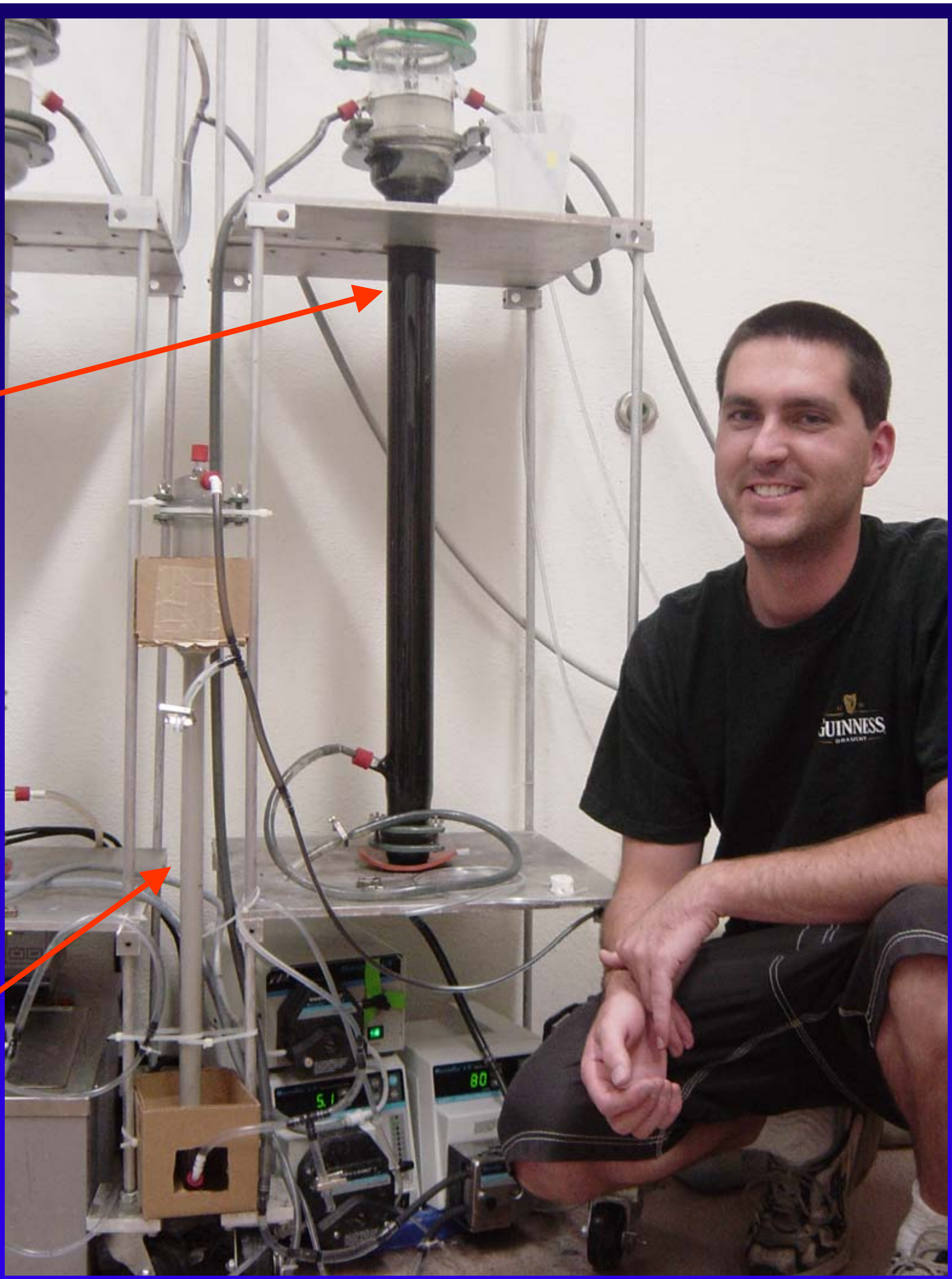
T =	30°C
HRT =	8 h
Recycle ratio =	15
Influent COD =	3 g/l
COD/sulfate =	0.55
Cu conc. =	0-65 mg/l

Anaerobic Sulfate-reducing Bioreactor



Electron scanning micrograph of microorganisms in the anaerobic biofilms

Bioreactor



Crystallization Reactor

(sand bed)

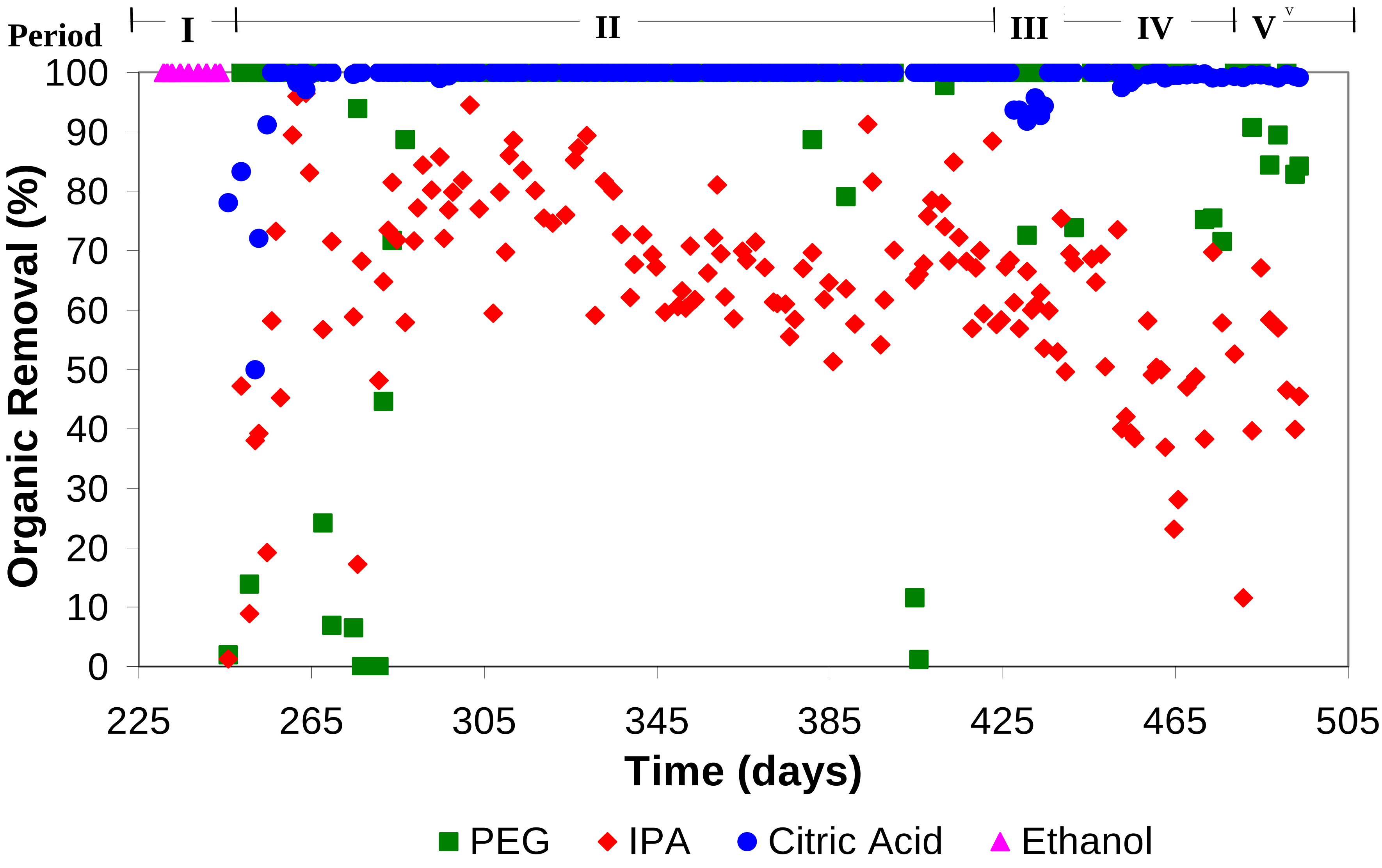
Experimental periods

Period	Cu(II) (mg/l)	Organic matter (g COD/l)	
I	0	**3**	**(ethanol)**
II	0	**3**	**(simulated CMP waste)***
III	5	**3**	**“ “**
IV	25	**3**	**“ “**
V	65	**3**	**“ “**

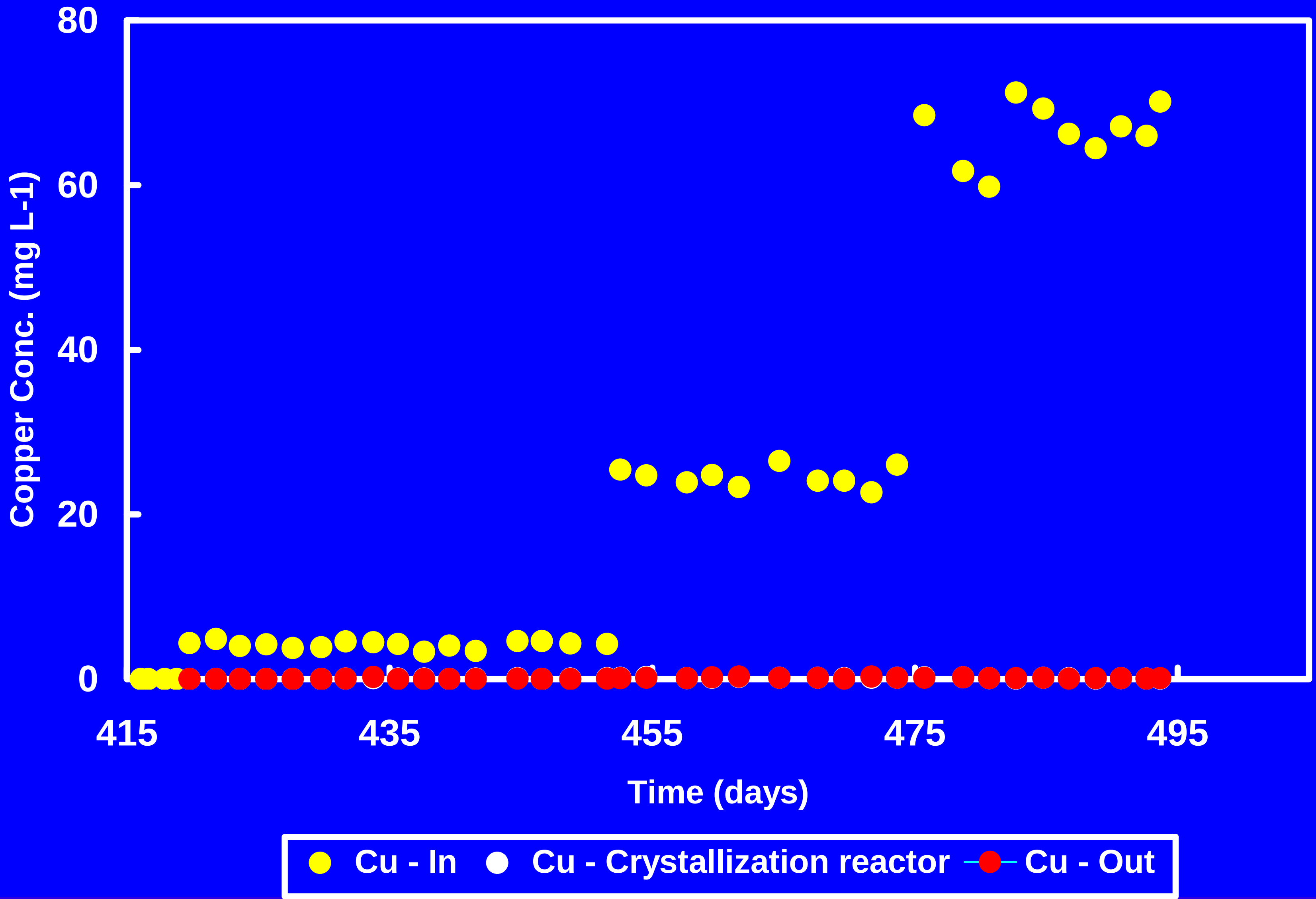
*** Simulated CMP waste:**

Citric acid / poly(ethylene glycol) (PEG Mn=400) /isopropanol (IPA) (1 g COD/L each)

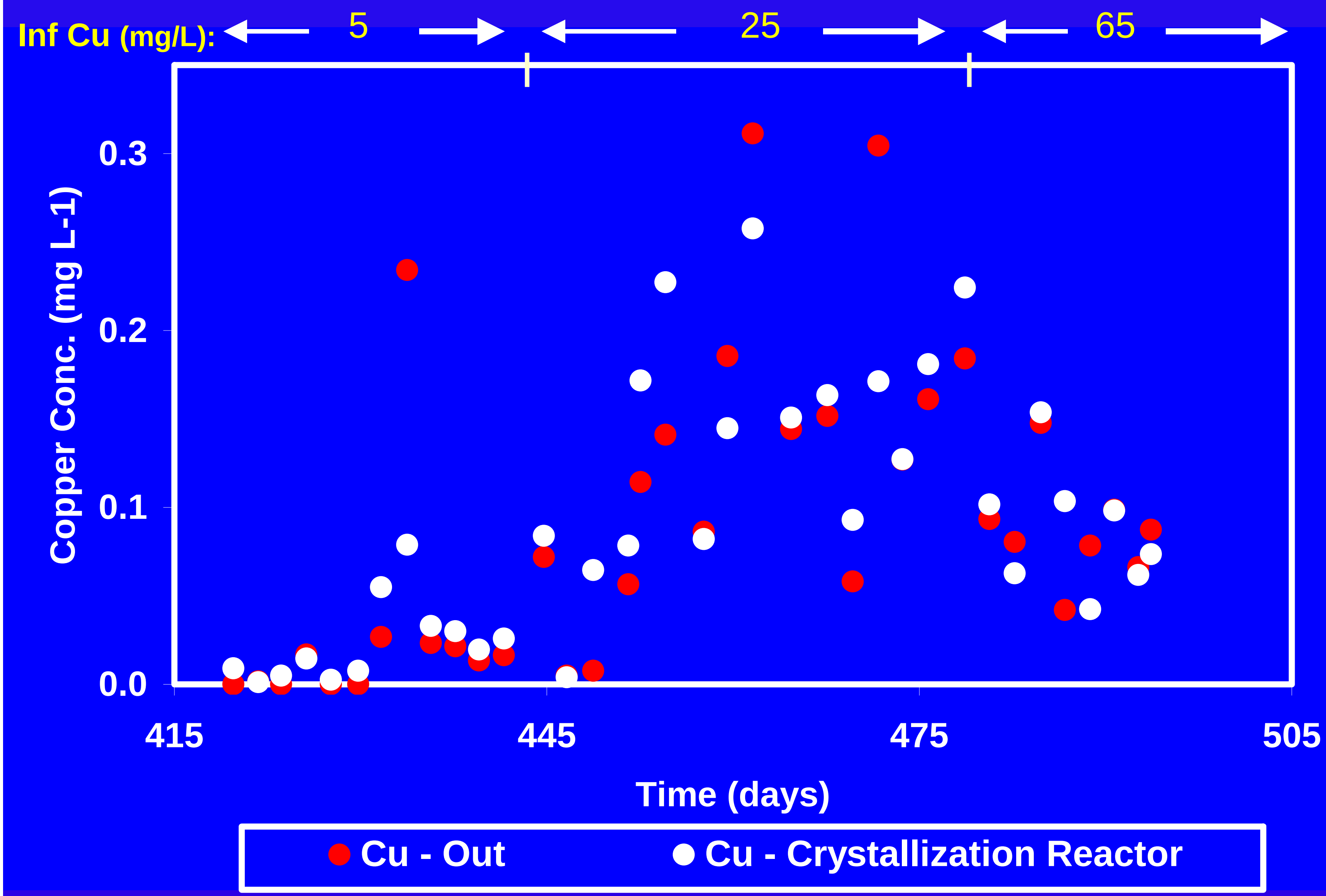
Organic Removal



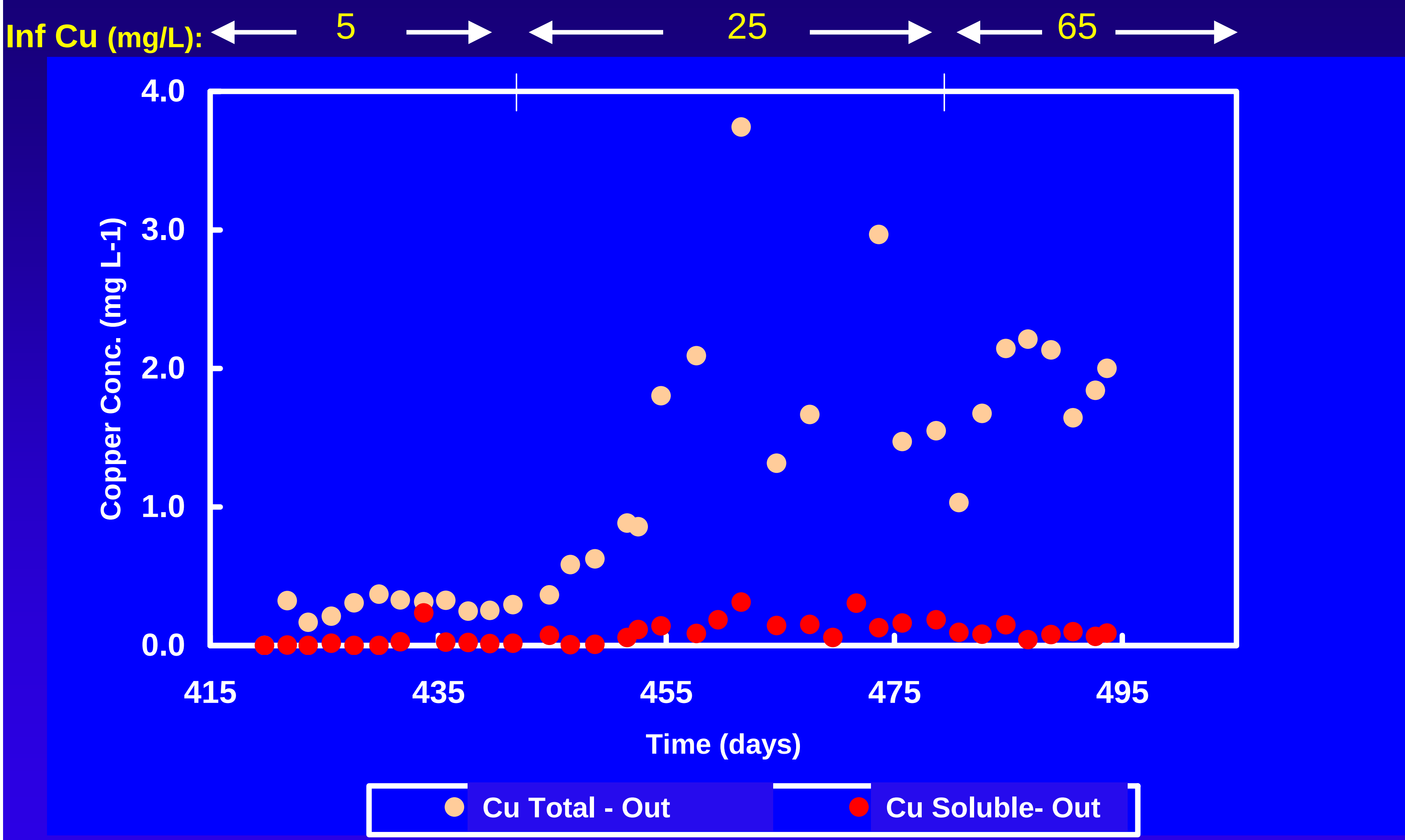
Cu Concentrations in the Effluent of the Two-reactor System and the Effluent of the Crystallization Reactor



Cu Removal by the Two-reactor System

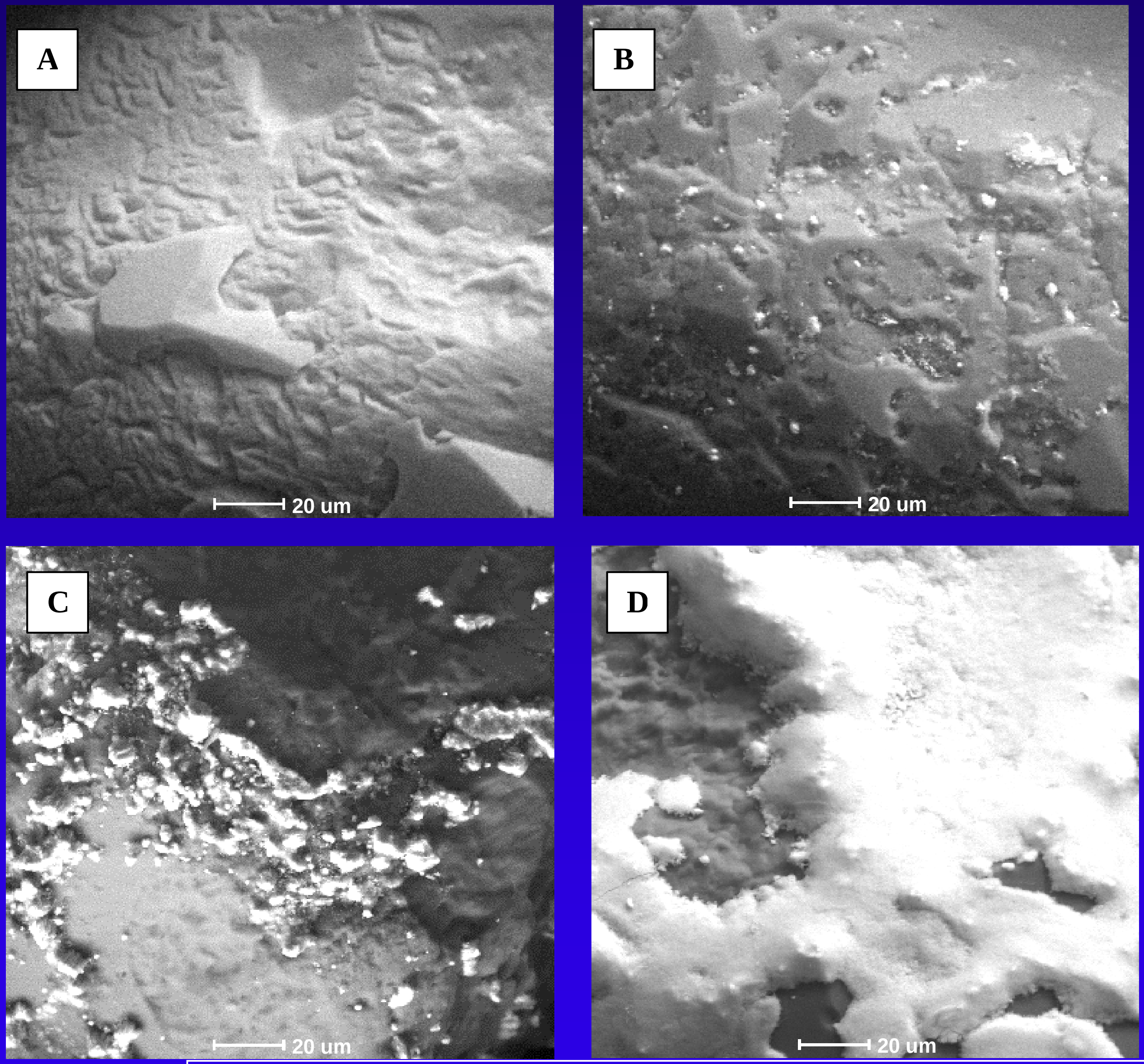


Total and Soluble Cu in the Effluent of the ASRB - CR System



Detail of the crystallization reactor during the first day (*left*) and after 5 days of operation (*right*) with an influent containing 5 mg Cu/l.

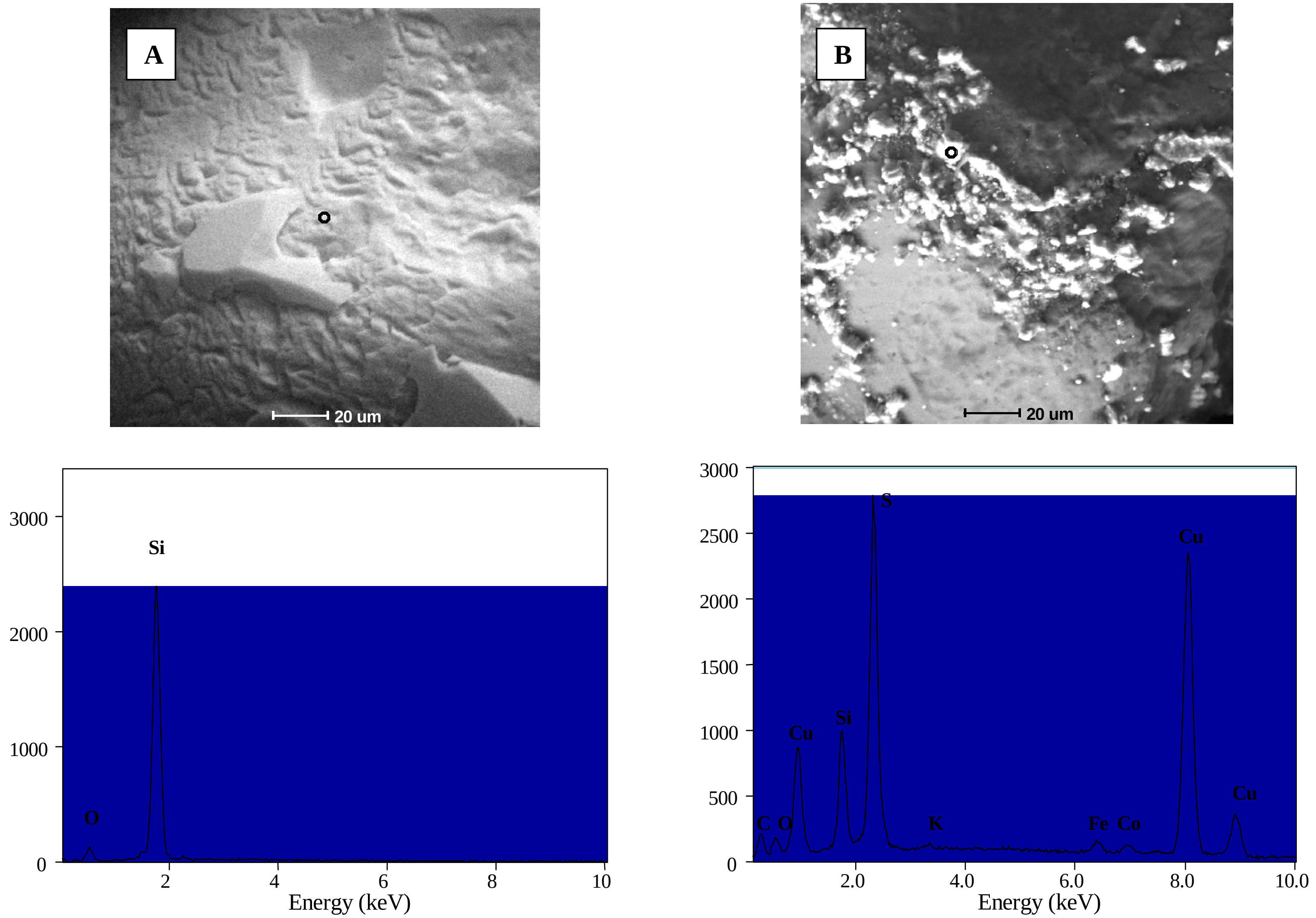
SEM Images of Crystallization Sand



(500x Magnification)

A - Acid washed quartz
B - After Period III
C - After Period IV
D - After Period V

SEM-EDS Analysis of Sand



System Performance:

Removal of Organic Contaminants

Influent	COD removal (%)
Ethanol	94.7 +/- 3.0
Simulated CMP	66.8 +/- 9.8
Simulated CMP + 5 mg Cu/l	65.7 +/- 8.1
Simulated CMP + 25 mg Cu/l	60.4 +/- 7.4
Simulated CMP + 75 mg Cu/l	66.6 +/- 7.5

Organic loading rate: 9.1-10.6 g COD/l/day

System Performance:

Copper Removal

Period	Cu^{2+} -in (μg/l)	Cu^{2+} -out (μg/l)	Cu removal (%)	Cu Removal (%) CR only
III	5,000	16 (+/- 19)	99.4 (+/-1.3)	99.3 (+/-0.6)
IV	25,000	162 (+/-84)	99.3 (+/-0.5)	99.3 (+/- 0.2)
V	65,000	104 (+/- 45)	99.9 (+/-0.2)	99.8 (+/- 0.1)

Conclusions

- Results from batch bioassays indicated that typical components in CMP effluents were amenable to anaerobic treatment

- The proposed system was shown to be highly effective to remove Cu from a simulated CMP wastewater.

  Very high Cu removal efficiencies (99.4-99.9% soluble Cu) were obtained for wastewaters containing 5-65 mg Cu/L.

  Elimination of total copper ranged 88.6-97.3%.

- Cu removal occurred chiefly in the crystallization reactor as a result of copper sulfide precipitation onto the sand surface

- COD removal averaged 60.4-66.8% using simulated organic waste (Citric acid/IPA/PEG).

  Low removal efficiencies of IPA and acetone resulted in incomplete COD removal

Future Research

- Optimize the removal of Cu and organic contaminants
- Determine the maximum Cu loading capacity of CR packing material
- Develop a model for the CR to assist with predicting and improving Cu removal rates and efficiencies
- Evaluate methods for metal recovery from the sand particles and evaluate potential for bed regeneration
- Evaluate performance of the bioreactor - CR system treating actual CMP wastewater

Acknowledgements

<u>**Jeremy Hollingsworth**</u>

Mike Zhou

Matt Yocum

Matt Wilkinson

Dr. Jim A. Field

Dr. Kimberly Ogden

Dr. Farhang Shadman

Mike Kopplin

NSF Advance grant (BES 0137368)

NSF/SRC Center for Environmentally Benign Semiconductor Manufacturing