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Biometals for advanced water treatment

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Topics

A. Microbial carbonate precipitation

B. Microbial interactions with iron
  - B1. Zerovalent iron [Fe(0)]
  - B2. Iron oxides [Fe_xO_y]

C. Manganese oxides [Mn_xO_y]

D. Other bioconversions
  - D1. Concepts
  - D2. Applications

E. Other perspectives

F. Conclusions

A. Microbial Carbonate Precipitation [MCP]

Calcite ($CaCO_3$) precipitation is governed by two parameters (Hammes et al., 2002; ES&T, 1: 3-7) :

1. The presence of nucleation sites

2. The pH of the environment
   and the levels of Ca^{2+} & CO_3^{2-}

A. Microbial Carbonate Precipitation [MCP]

1. The presence of nucleation sites

Microorganisms = Ideal crystal nucleation sites

(Schultze-Lam et al., 1996; Chem Geol, 132: 171-181)

- negatively charged microbial cell wall
- specific funtional groups

Take home :

Microbial cell walls favor binding of divalent cations :

Ca^{2+} and Mg^{2+}

A. Microbial Carbonate Precipitation [MCP]

2. The pH of the environment
and the levels of Ca^{2+} & CO_3^{2-}

Urea hydrolys ediment Geol, 126: 9-23)

$CO(NH_2)_2 + 2\ H_2O$

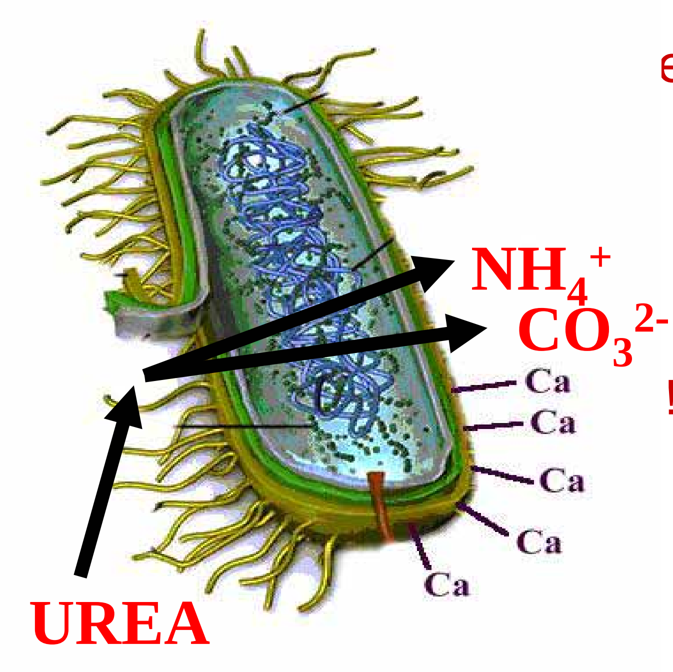
Equilibrium

$H_2CO_3 \leftrightarrow HCO_3^- +$

$2\ NH_3 + 2\ H_2O \leftrightarrow$!

Formation of

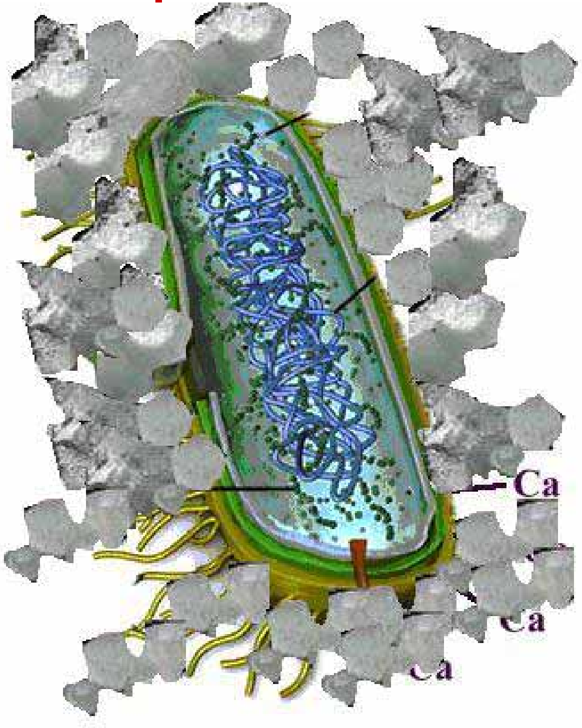
$HCO_3^- + H^+ + 2\ N$ $2\ H_2O$

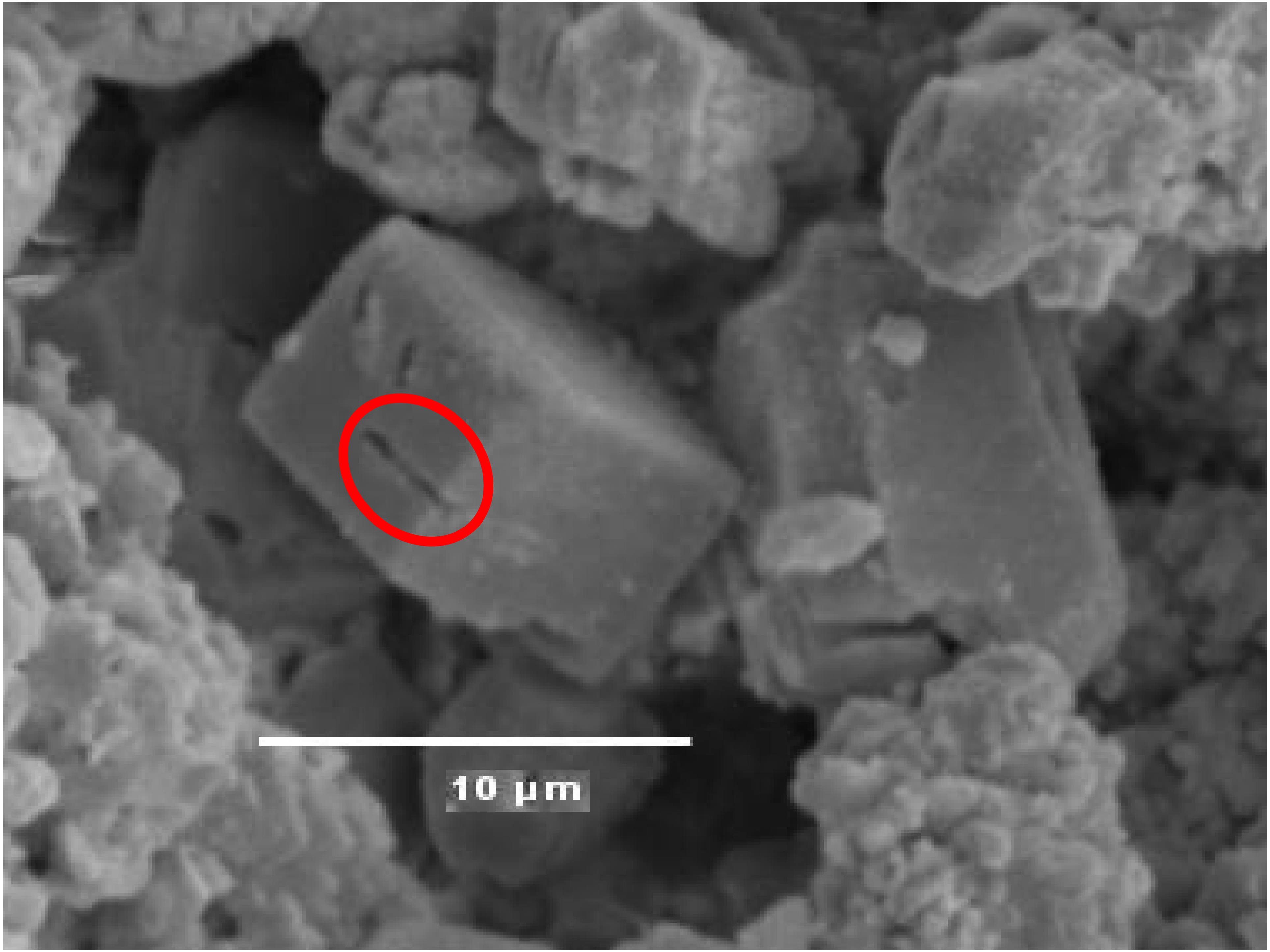


A. Microbial Carbonate Precipitation [MCP]

In the presence of Ca^{2+}

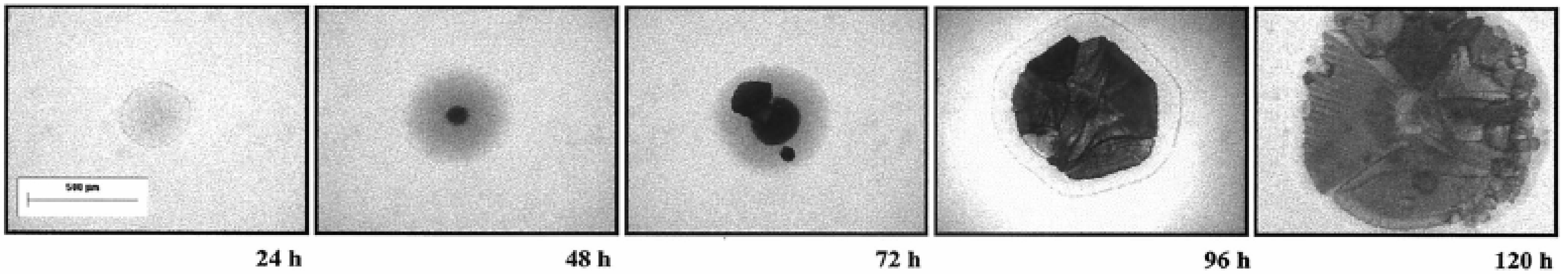
→ precipitation as $CaCO_3$




10 μm

A. Microbial Carbonate Precipitation [MCP]

Kinetics of $CaCO_3$ precipitation sequence :



Quantifications of pH changes can be done by speciation software :

- e.g. MINEQL (http://www.mineql.com)

Indices for carbonate precipitation :

- e.g. Langelier saturation index, Ryznar stability index (You et al., 2001; Res, Cons & Recycl, 32: 73-81)

A. Microbial Carbonate Precipitation [MCP]

MCP = emerging tool in treatment of calcium-rich industrial wastewater (for reuse)

↓

Stimulating and accelerating urease activity by addition of low concentrions of urea

Tested at pilot scale in paper recycling factory

Influent up to 500 mg Ca^{2+}/L
90 % removal (HRT = 8h)

A. Microbial Carbonate Precipitation [MCP]

Take home :

MCP for treatment of calcium-rich wastewater = economic feasible :

- ○ Acceptable economics of urea
- ○ Removal of calcite by sedimentation
- ○ Reuse of calcite to lime farming land or to produce cardboard paper

B. Iron
B1. Zerovalent Iron [Fe(0)]

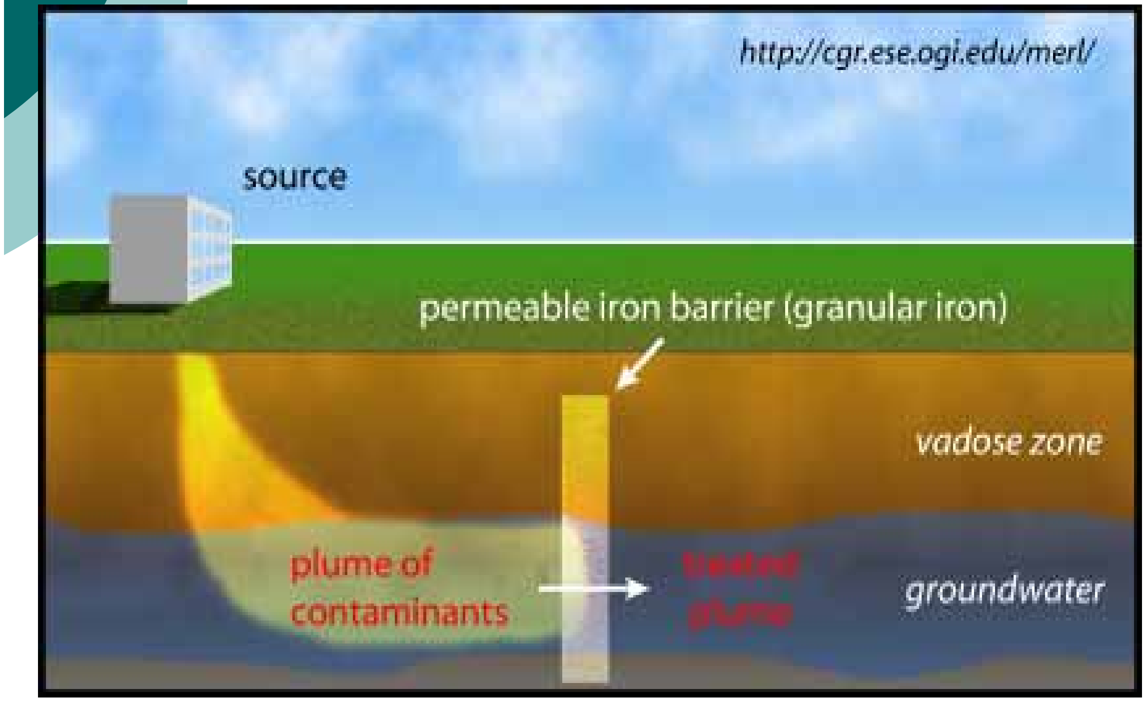
1. Fe(0) can effectively remove viruses
   - Formation of iron(oxyhydr)oxides

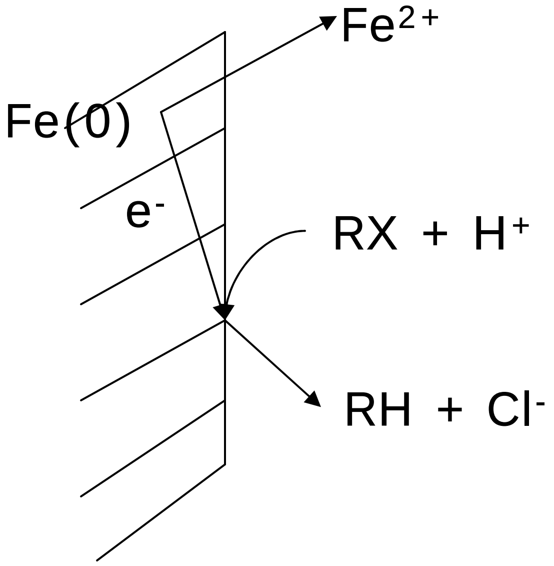
     (You et al., 2005; ES&T, 39: 9263-9269)
   - Adsorption through electrostatic attraction

     (Ryan et al., 2002; ES&T, 36: 2403-2413)
   - Inactivation by strong attachment force

     (Ryan et al., 2002; ES&T, 36: 2403-2413)

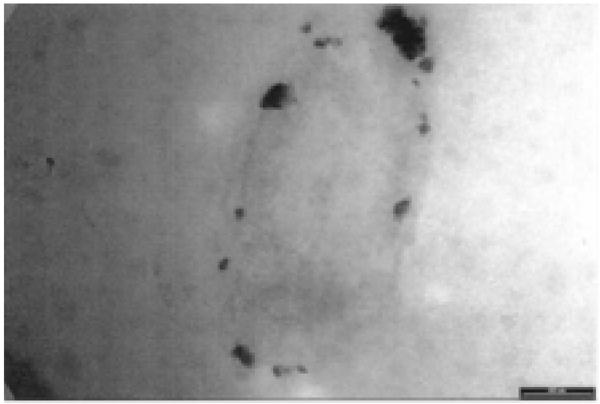
2. Use of Fe(0) in bioactive groundwater barrier system

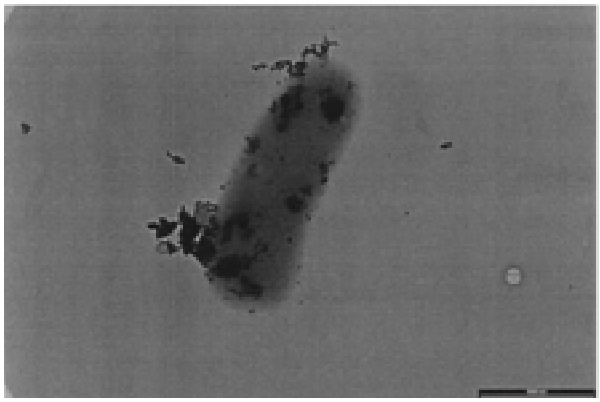




(Matheson & Tratnyek, 1994; ES&T, 28: 2045-2053)

B2. Microbial iron oxides [Fe_xO_y]

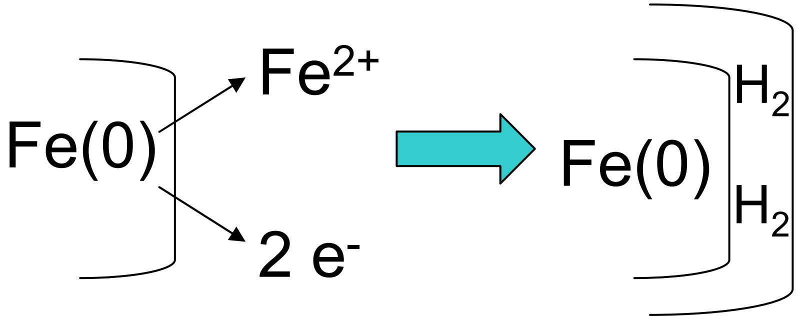




- Biologically precipitated Fe-oxides
- Oxidation of Fe by several bacteria (e.g. *Shewanella, Leptothrix, Geobacter*,...)

B2. Microbial iron oxides [Fe_xO_y] : example

Corrosion of iron



$Fe(0) \rightarrow Fe^{2+}$

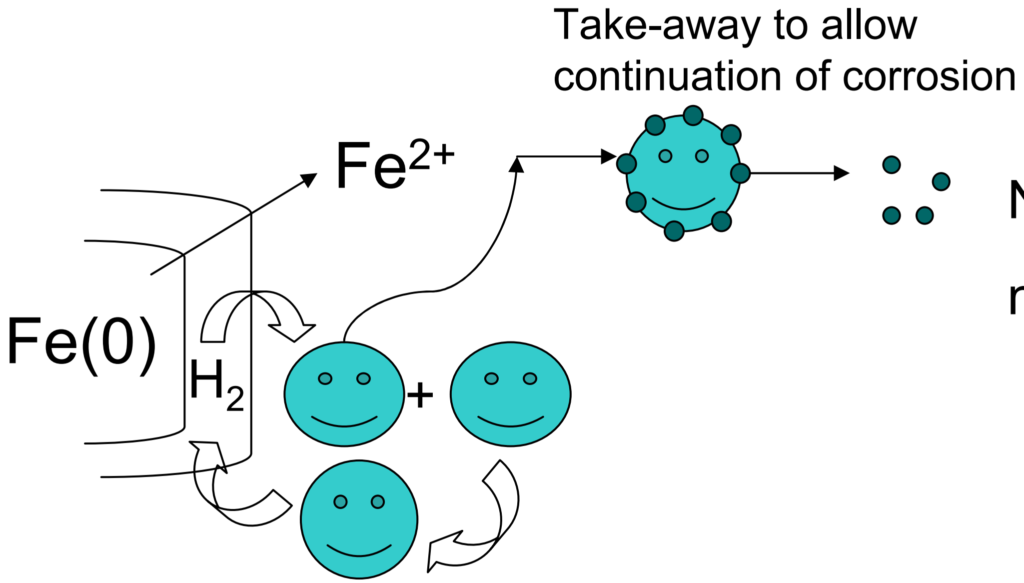
$Fe(0) \rightarrow 2\,e^-$

Fe(0) H_2 H_2

Thin layer of H_2 protects against Fe^{2+} release and corrosion

B2. Microbial iron oxides [Fe_xO_y] : example

Use of H_2 by bacteria and formation of iron precipitates



Take-away to allow continuation of corrosion

Fe^{2+}

Fe(0)

H_2

Nano Fe_xO_y:

new applications

(e.g. De Windt et al., 2003; Environ Microbiol, 5: 1192-2002)

B2. Microbial iron oxides [Fe_xO_y] : characteristics

- Other characteristics compared to chemically produced oxides:
  - Larger specific surface
  - Stronger binding force

↓

Potentially higher removal efficiencies than chemically produced oxides

- Remediation of heavy metals by adsorption with co-precipitation, e.g.:
  - **11,6 g As/kg** biogenic Fe(Katsoyiannis et al., 2002; Chemosph, 47: 325-332)

    ↕

    5,2 g As/kg chemical Fe (e.g. Bayoxide) (Impellitteri and Scheckel, 2006; Chemosph, 64: 875-880)
  - **113 g Pb/kg** biogenic Fe ↔ **38 g Pb/kg** chemical Fe
    (Nelson et al., 2002; ES&T, 36: 421-425)

B2. Microbial iron oxides [Fe_xO_y] : characteristics

- Removal of phosphate or As by adsorption
  (Melitas et al., 2002; ES&T, 36: 3188-3193)

- Removal of natural organic matter
  (= precursor of DBPs) before post-chlorination

  (Gu et al., 1994; ES&T, 28: 38-46)

C. Manganese Oxides (Mn_xO_y)

- Manganese oxidizing bacteria (MOB) produce MnO_2

  Bacillus sp., Leptothrix discophora, Pseudomonas putida

  (Francis et al., 2001; AEM, 67: 4024-4029)

- Biogenic MnO_2 has a higher specific surface area:

  224 m²/g biogenic Mn (Nelson et al., 1999; AEM, 65: 175-180)

  ⇕

  4,7 m²/g Mn for powdered pyrolusite

- Biogenic MnO_2 has higher sorption capacities :
  - **1066 g Pb/kg** biogenic Mn

    ⇕

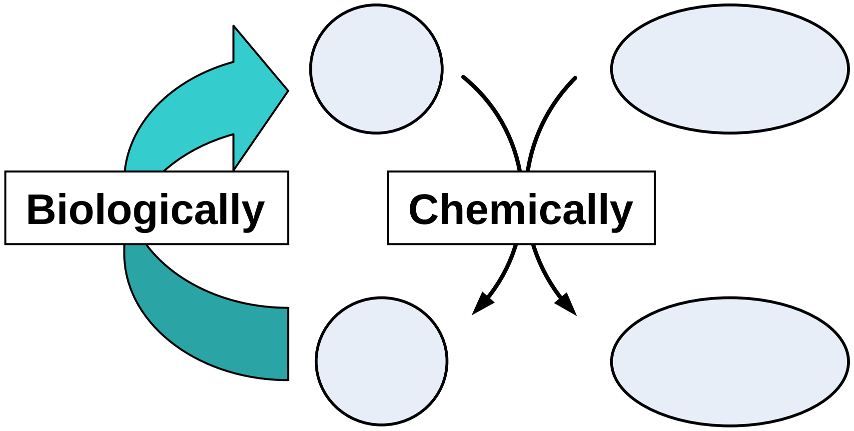
    5,4 g Pb/kg chemical Mn (Nelson et al., 1999; AEM, 65: 175-180)
  - **247 g Co/kg** biogenic Mn (Tani et al., 2004; Env Sci Health, 39: 2641-2660)

    ⇕

    109 g Co/kg chemical Mn (Dong et al., 2007; Microchem J, 85: 270–275)

C. Manganese Oxides (Mn_xO_y)

- Abiotic Mn(II) oxidation is a slow process [$K_s = 10^{-3}$-10^{-5} h^{-1}] (Morgan et al., 2005; Geo & Cosm Actua, 69: 35-48)
- Microbial oxidation of Mn(II) proceeds at several orders of magnitude faster [$K_s = 10$-10^{-2} h^{-1}]



Biologically

Chemically

Take home:

Microbial oxidation of Mn(II) for regeneration of MnO_2 as self-generating oxidative substrate

C. Manganese Oxides (Mn_xO_y)

Mn oxides are powerful oxidants for

- Inorganic compounds
  - As(III) to As(V) (=less toxic)
    (Tebo et al., 2004; Annu Rev Earth Planet, 32: 287-328)
- Organic compounds
  - Humic substances
    (Sunda & Kieber, 1994; Nature, 367: 62-64)
  - Atrazine
    (Panter et al., 1999; Chemosp, 38: 3579–3596)
  - Hydroxylamines
    (Cicchi et al., 2001; Tetrahdron Lett, 42: 6503–6505)
  - Micropollutants such as EE2
    (De Rudder et al., 2004; Wat Res, 38: 184-192)

C. Manganese Oxides (Mn_xO_y)

Application of Mn(III,IV)oxides in combination with MOB: bio-catalytic step after conventional treatment to remove micropollutants such as POPs and EDCs

Example : Upflow aerated bioreactor with MnO_2 and MOB for EE2 removal

- 82 % removal

  [infl: 15 µg EE2/L, HRT: 1h]

  (De Rudder et al., 2004; Wat Res, 38: 184-192)
- 85 % removal

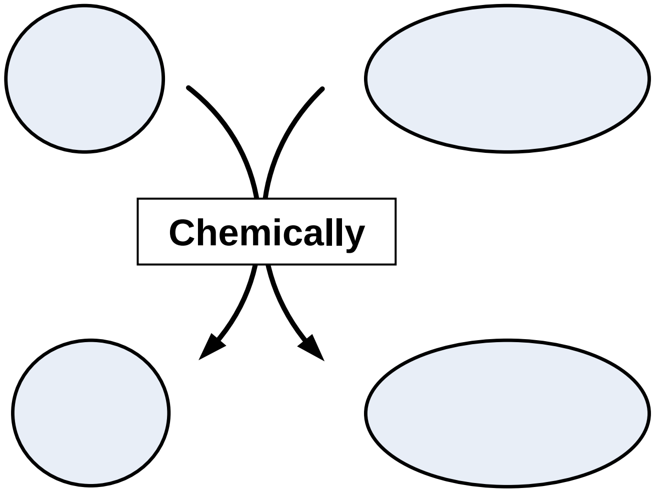
  [infl: 40 µg EE2/L.d, HRT: 1d]

  (Forrez et al., 2008; submitted)]

C. Manganese Oxides (Mn_xO_y)

Take home:

Oxidation of these compounds results in biodegradable, low molecular compounds



and formation of Mn(II)

(Sunda & Kieber, 1994; Nature, 367: 62-64)

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D. Other bioconversions
D1. Concepts

- Use of metals as electron acceptors
  - Growth
  - Maintenance
  - Detoxification mechanism

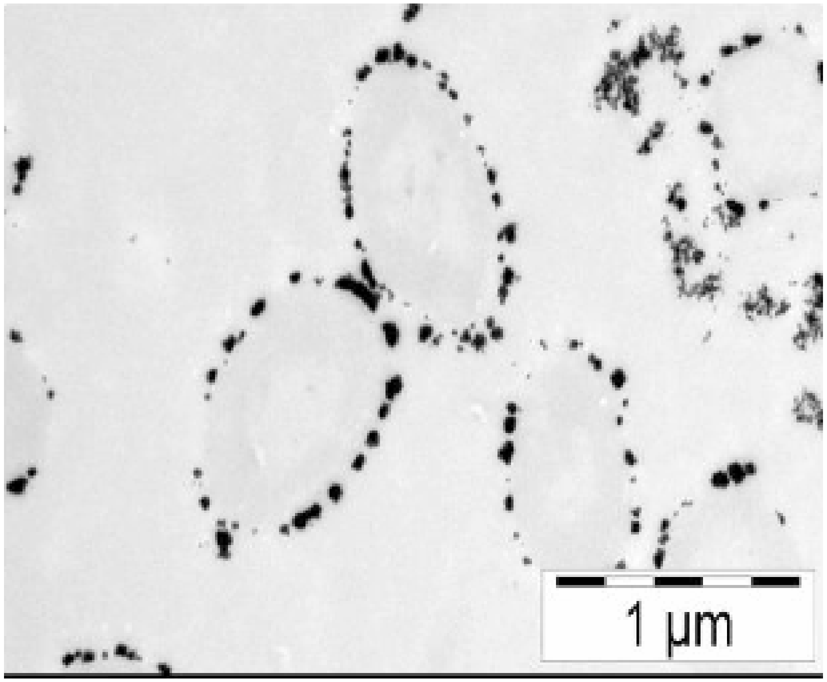
- Reduction of metals by bacteria can increase mobility and recovery, e.g. As(V)→As(III)

- Reduction can produce nanometals

D1. Concepts

"Bio-Pd": microbial precipitated Pd nanoparticles

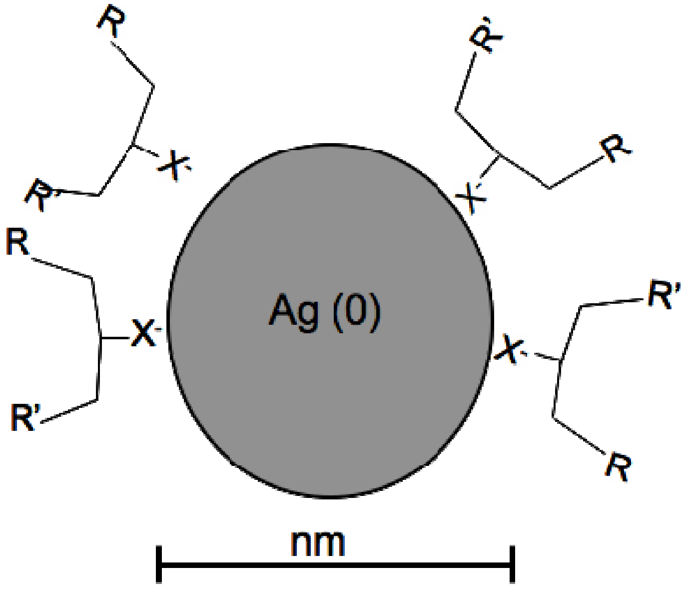
- Microbial reduction of Pd(II) to Pd(0)
- Deposition of this biogenic Pd as nanoparticles
- On the cell wall and periplasmatic space of *Shewanella oneidensis* (De Windt et al., 2005; Environ Biotechnol, 90:377-389)



D1. Concepts

Microsil: Microbial precipitated Ag nanoparticles

- **Small** Ag^0-particles
  - 2 to 50 nm
  - Size controlled by method
  - Particles in the glycocalyx
- On a **biopolymer**
  - Dead probiotic bacteria
  - Chemical post-treatment
  - Still some biopolymer around
  - Different from chemically produced nano-Ag



Patent UGent (LabMET)

D1. Concepts

- Biological production of other nano-scale biocatalyst
  - **Hg**

    (Rasmussen et al., 1997; Appl Environ Microbiol, 63: 3291-3293)
  - **Pt**

    (Rashamuse & Whiteley, 2007; Appl Microbiol Biotechnol, 75: 1429-1435)
  - **Au**

    (Macaskie et al., 2007; Biotechnol Bioeng, 96: 631-639, Konishi et al., 2007; J Biotechnol,128: 648-653)

D2. Applications

Bio-Pd

- Bio-Pd can be used as catalyst for dehalogenation and reduction reactions:
  - **PCB’s, lindane, dioxines, chlorinated solvents, PBDE’s and EE2**
  - **Nitrate, perchlorate and arsenate**

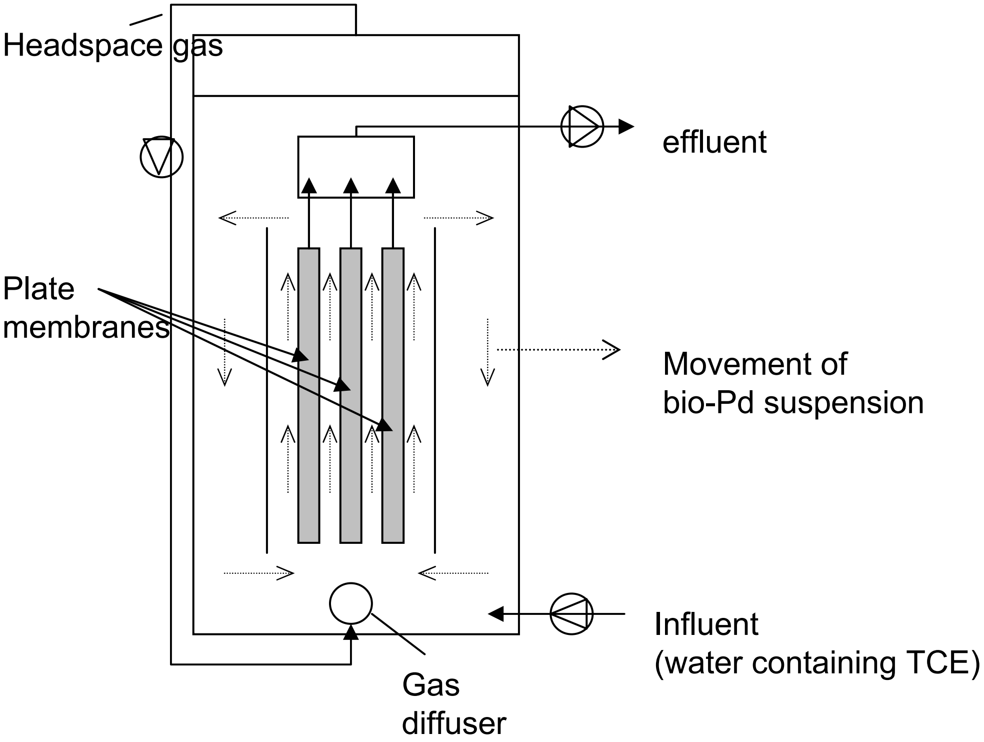
    (De Windt et al., 2006; A v L J Gen & Mol Microbiol, 90: 377-389, Mertens et al., 2007; Chemosph, 66: 99-105, unpublished results)
- Example:

  Biocatalytical removal of TCE by bio-Pd in a membrane reactor (MR) (Hennebel et al., submitted)

D2. Applications

Biocatalytical removal of TCE by bio-Pd in a MR:

2500 mg TCE removed/g Pd.day (Hennebel et al., submitted)



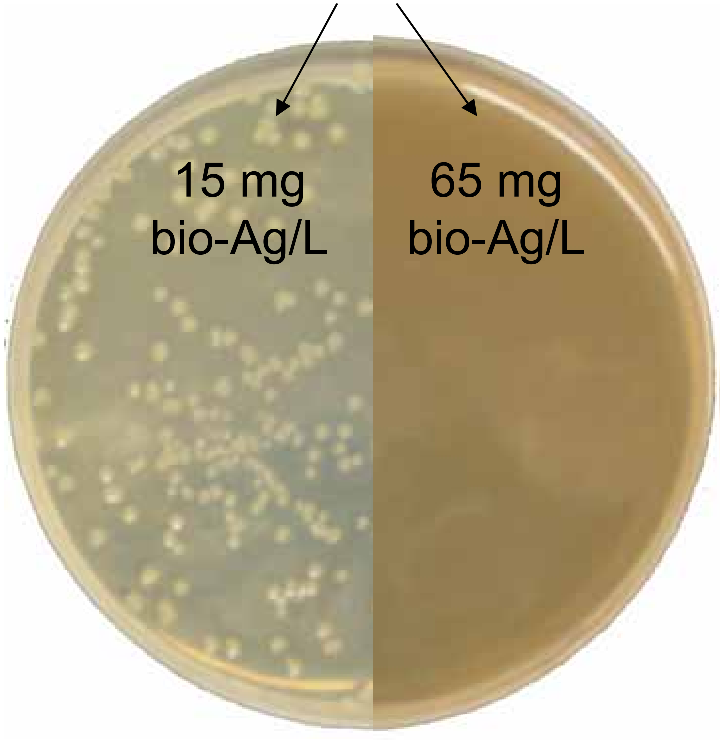
D2. Applications

Microsil

- With **biocidal effect** against
  - Bacteria (MIC ± 25 mg/L)
  - Fungi (MIC ± 100 mg/L)
  - Algae (MIC ± 0,10 mg/L)
  - Viruses ?

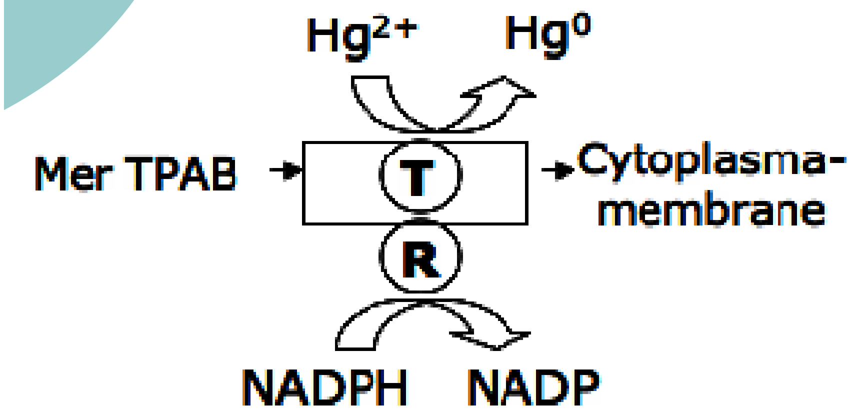
- **Cost effective** method
  - No expensive infrastructure required
  - Easy to grow bacteria
  - Rapid and cheap processing method
  - Tested on pilot-scale

Growth of E. Coli

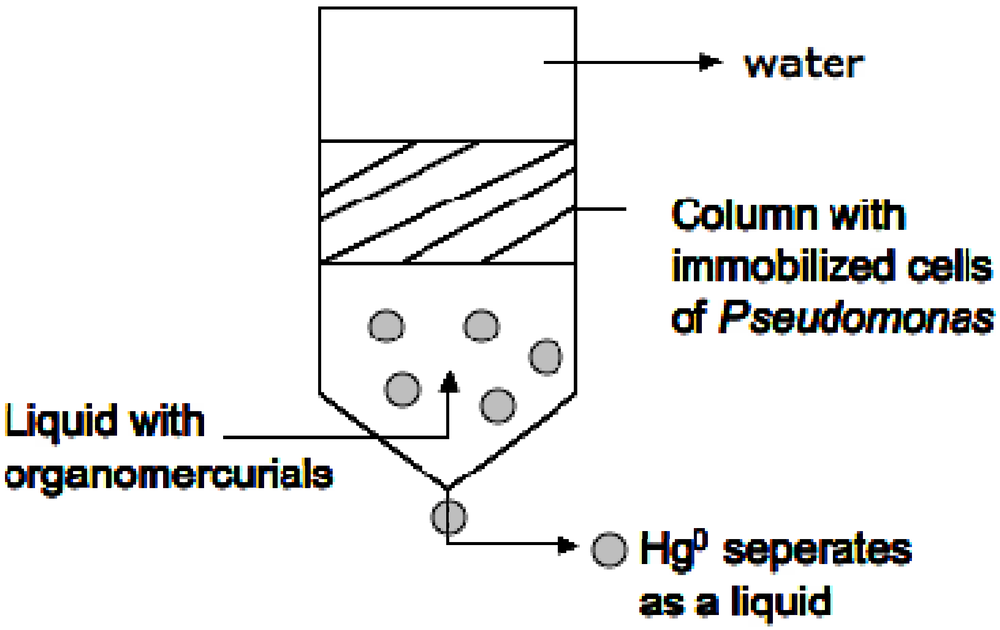


D2. Applications

Use of *Pseudomonas* for detoxification of phenylmercury from the alkaline chlorine electrolyse: production of Hg(0)



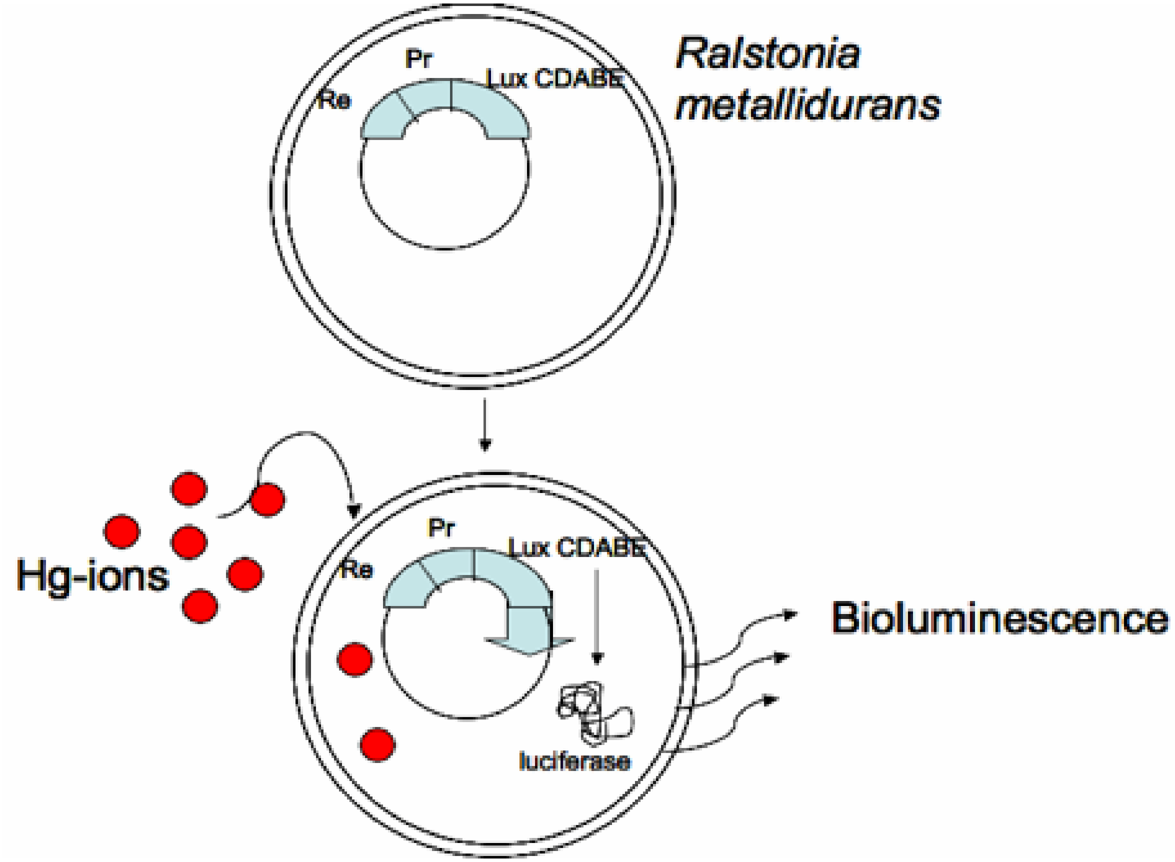
T= Tranportprotein
R=Reductaseprotein



(Brunke et al., 1993; FEMS, 11: 145-152)

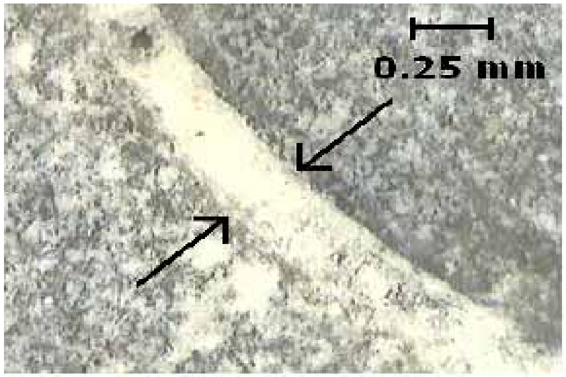
D2. Applications

e.g. Hg: use as a biosensor (Biomet principle, www.vito.be)



E. Other perspectives

- $CaCO_3$: biomortars for microbiologically enhanced crack remediation



- New biometals with specialized microbial species e.g.
  - Cu precipitates (applications as disinfectant)
  - Zn precipitates (applications as catalyst)
  - Rh precipitates (applications as catalyst)

E. Other perspectives

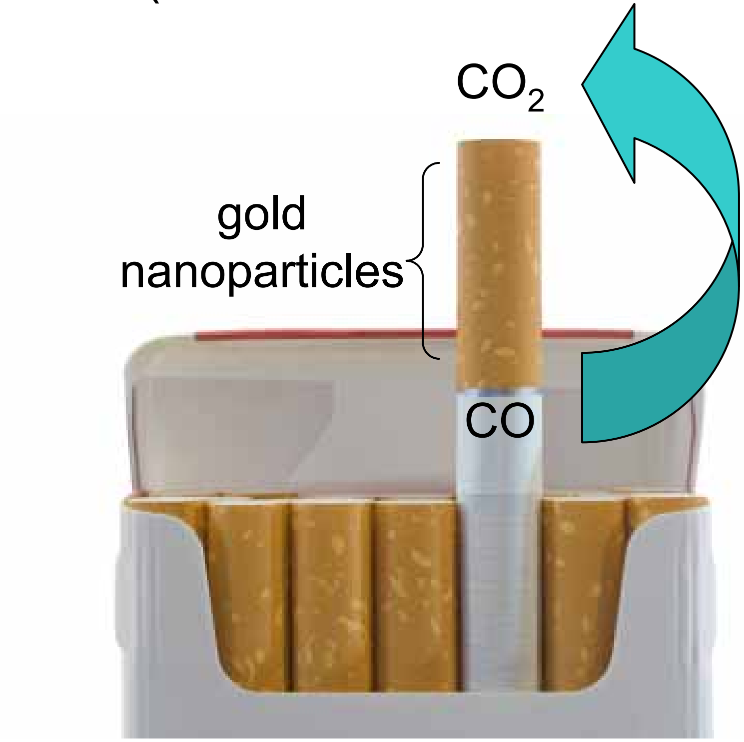
- Bioprecipitation of As on Fe for groundwater treatment
- Nanosilver for electronics:
  - Fine line flexible circuits (Ferro Electronic Material Systems)

  - Mass-produced printed technology
  - Radio frequency identification (RFID), e-books, thin-film batteries, flexible displays,...

E. Other perspectives

- Gold nanoparticels to oxidize CO to CO_2

  Philip Morris (World Gold Counsil, 2006; CatGold news, 11: 4)



F. Conclusions

- Various microorganisms interact with metals and produce mineral resp. metal deposits
- This is a new domain in microbial biotechnology

F. Conclusions

- Biometals have a wide variety of potential uses
  - as depositing materials
  - as sorbents
  - as catalysts
  - as disinfectants
  - …
- These products are of special interest because they are
  - nano-sized

  YET

  - matrix bound

F. Conclusions

“There is plenty of room for startling developments”

Acknowledgements

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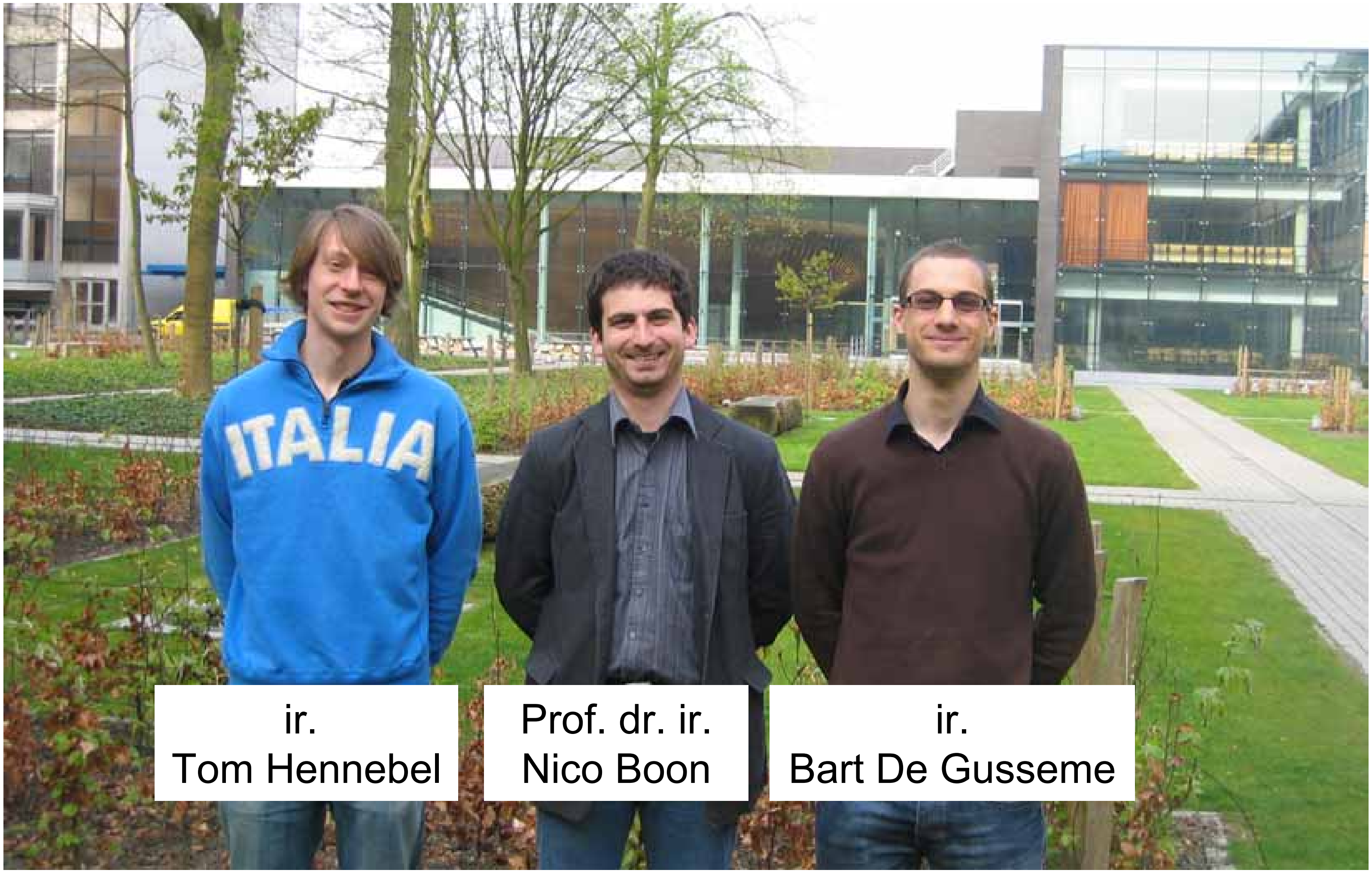
Biometals for advanced water treatment



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