Università degli Studi di Cassino e del Lazio Meridionale

Tampere University of Technology

Summer School 2012

«Tecnologie sostenibili per la tutela dell'ambiente»

Treatment of sulfate- and nitrate-containing mine waters in biological fluidized-bed reactors

PhD student: M.Sc. Stefano Papirio

Supervisors: Dr. Giovanni Esposito
Prof. Francesco Pirozzi
Prof. Jaakko Puhakka

POLITECNICO DI MILANO

DIIAR

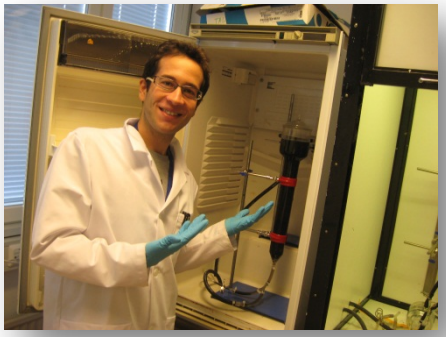
GITISA
Gruppo Italiano di Ingegneria Sanitaria Ambientale

Milano, 25/06/2012

Outline

- Introduction

- Materials and Methods
- Results



- Conclusions

Acid Mine Drainage (AMD)

RAIN WATER

Characterization

FeS_2 **CdS** **ZnS** **CuS**

n, Cu, Co,

- Strongly ACIDIC pH (pH ≈ 2 – 3)
- No organic content

AMD (Zn^{2+}, Fe^{2+}, Cu^{2+}, Cd^{2+}, SO_4^{2-}, H_3O^+)

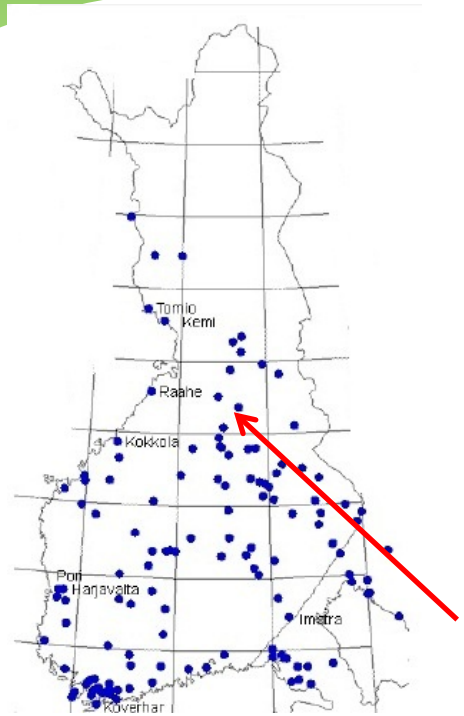
Reactions (Kaksonen and Puhakka, 2007):

$$2FeS_2 + 7O_2 + 6H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H_3O^+$$

$$Fe^{2+} + 4H_3O^+ + O_2 \rightarrow Fe^{3+} + 6H_2O$$

$$Fe^{3+} + 6H_2O \rightarrow Fe(OH)_3 + 3H_3O^+$$

AMD - Finland



e history of mining

Visiting SOTKAMO mine

420 mines have

for the exploita

Bioleaching of Fe, Cu, Ni, Co, As

66% of metal ores has been sulfide

Sulfate

Discharged by several industrial processes:

- Tannery and textile
- Food production and brewery
- Pulp and paper
- Mining activities

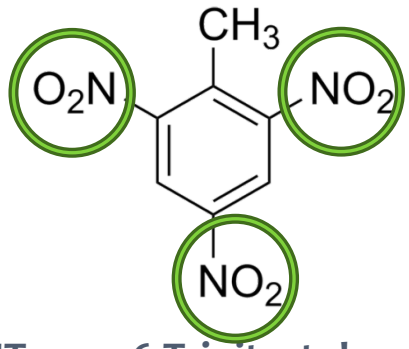
Environmental issues:

- Disturbing the natural sulfur cycle
- Production of sulfide (toxicity and corrosion problems)
- Acidification of the natural water streams
- Leaching of heavy metals

ACID MINE DRAINAGE

Nitrate

Use of BLASTING AGENTS or LEACHING SOLUTIONS during the mining activity

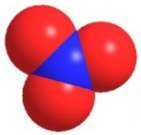


TNT – 2,4,6 Trinitrotoluene

Cyanide (used for GOLD extraction)

Release of NITROGEN compounds into AMD:

- **$N\text{-}NH_4^+$** up to 80 mg/L
- **$N\text{-}NO_3^-$** up to 90 mg/L



(Zaitsev et al., 2008)

Nitrate (2)

Environmental issues due to the release of NO_3^- ions into the environment:

- Change of the NATURAL NITROGEN CYCLE
- EUTROPHICATION and influence on the trophic equilibria of the ecosystems
- Contamination of ground waters used as sources of drinking water
- Human health damages («Blue baby syndrome» and development of other diseases) (Environmental Agency, 2005)

Materials and Methods

DENITRIFICATION

$12N_2 + 20CO_2 + 18H_2O + 24OH^-$

Up-flow fluidized-bed reactors

Batch tests (pH effect and metal toxicity)

OHCOO

SULFATE REDUCTION

Down-flow fluidized-bed reactors

ORGANIC SUBSTRATES ALKALINITY BIOGENIC SULFIDE

Materials and Methods - UniCas

- **Two DFFB reactors –** volume 5,7 L
- **Carrier material:** polypropylene beads
- **Fluidization degree:** 10%
- **Electron donor:** lactic acid
- **HRT:** 24 h
- **Room temperature**

Reactor 1 $COD/SO_4^{2-} = 0,67$
$pH \approx 5$

Reactor 2 $COD/SO_4^{2-} = 3 \div 4$
$pH \approx 3 \div 5$

Goal of the research: optimization of the sulfate-reducing process

- Evaluation of the best COD/SO_4^{2-}
- Robustness test → decrease of the feed pH
- Reliability of the carrier material for the biomass immobilization

Materials and Methods - TUT

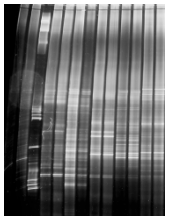
- **Two classical FBRs –** volume 1,1 L
- **Carrier material:** granular activated carbon (GAC)
- **Fluidization degree:** 25%
- **Electron donor:** ethanol
- **HRT:** 6-9 hours

Reactor 1 Temperature ≈ 8÷9°C

Reactor 2 Room temperature ≈ 22°C

Batch assays - Determination of the lowest tolerable pH
- Metal toxicity (Cu, As, Co, Ni)

Bacterial community analysis - DGGE



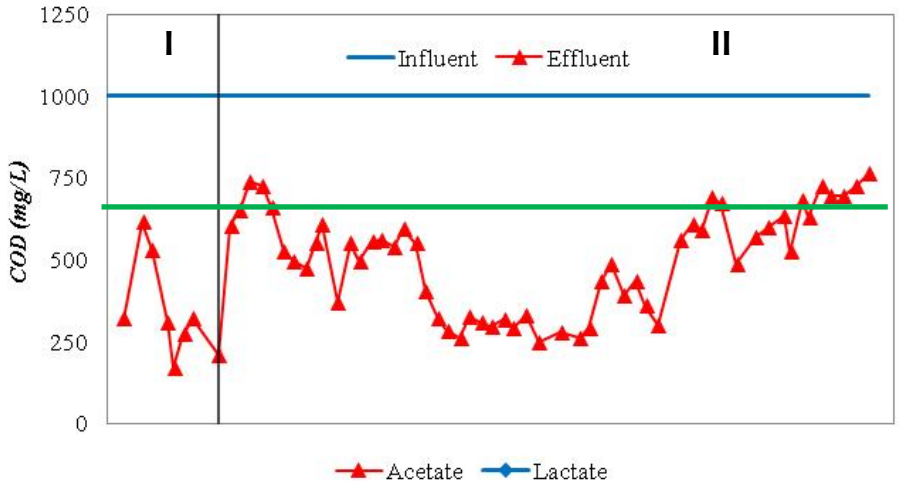
Goal of the research: optimization of the denitrification process

- Amount of ethanol to supply
- Effect of toxic metals on the biological process
- Gradual decrease of the feed pH
- Influence of the temperature

Results – sulfate-reducing reactors (1)

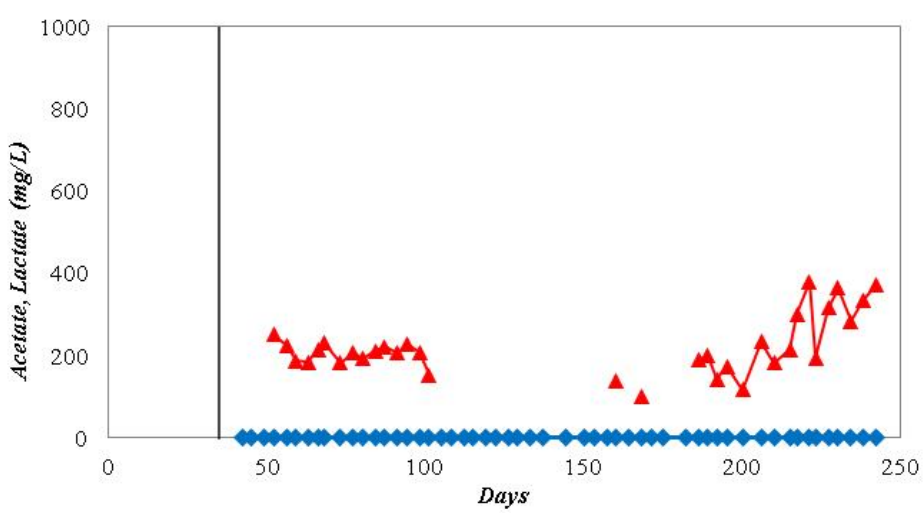
REACTOR 1

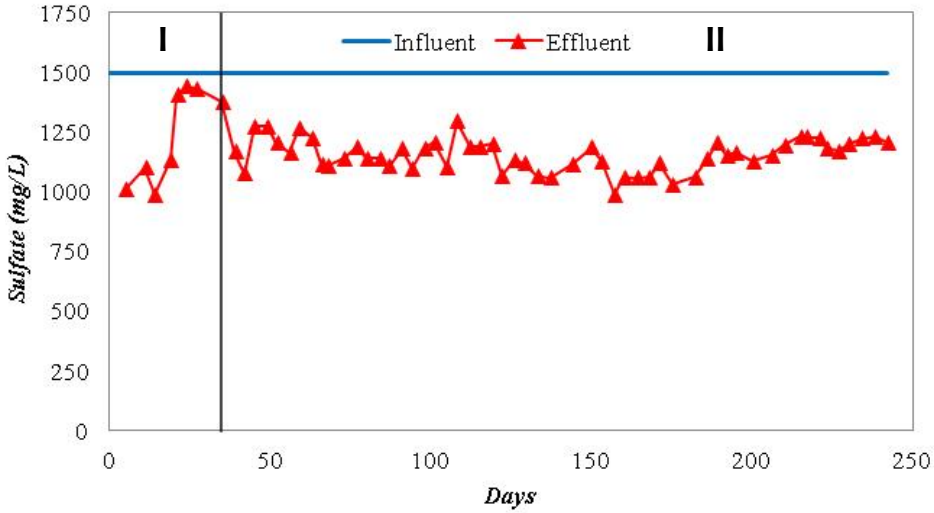
(pH ≈ 5)



Phase 1 (35 days): COD=1000 mg/L, SO_4^{2-}=1500 mg/L

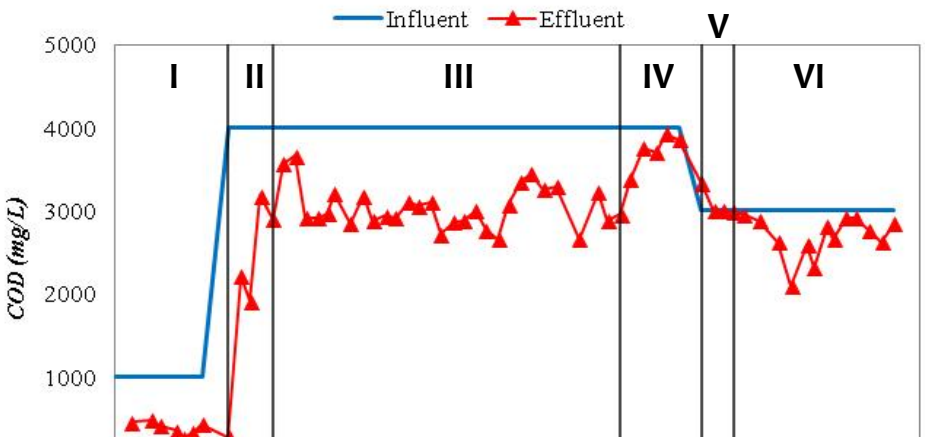
Phase 2 (207 days): COD=1000 mg/L, SO_4^{2-}=1500 mg/L





Results – sulfate-reducing reactors (2)

REACTOR 2



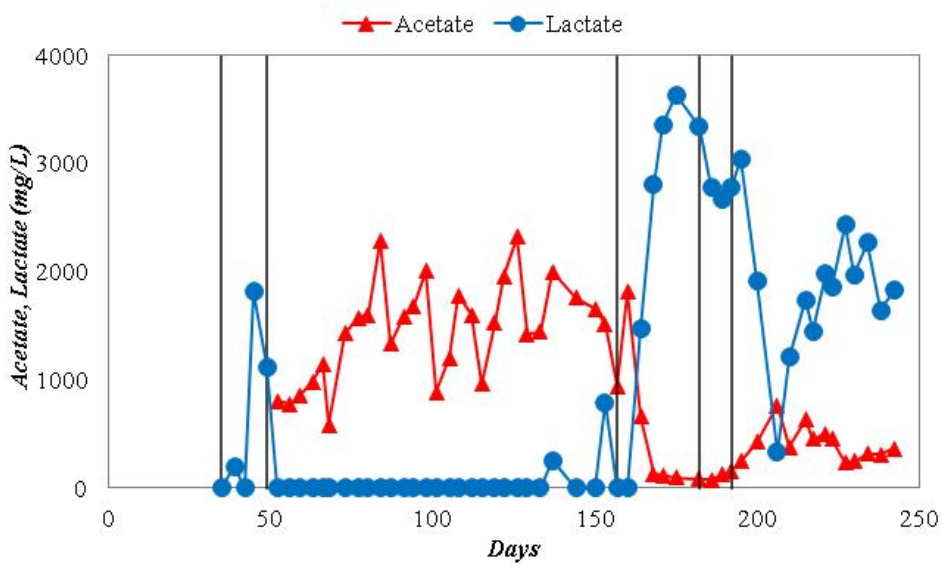
Too low pH → **INHIBITION**

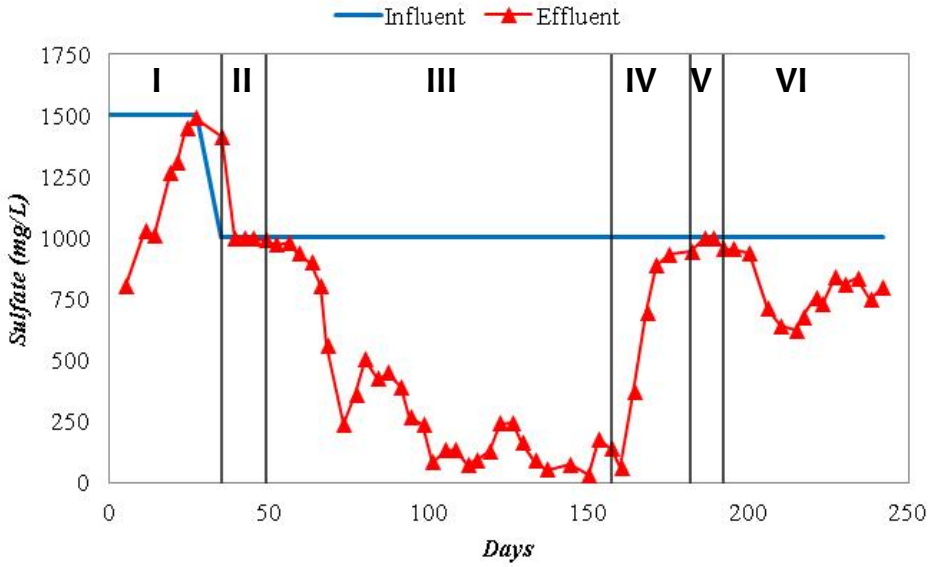
Excess of acetate → **NO INHIBITION**

- low fluidization degree (10%)

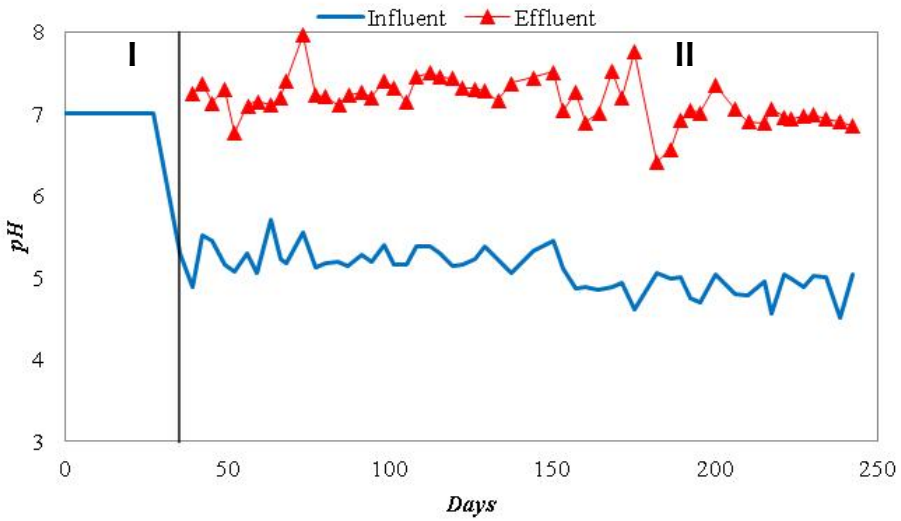
Prevalence of incomplete oxidation reactions

-compounds present as non-dissociated acids



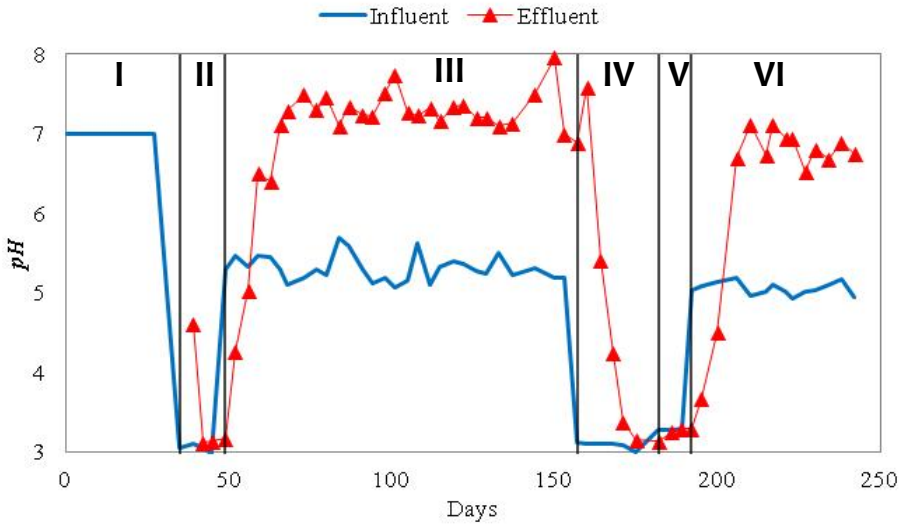


Results – sulfate-reducing reactors (3)



- pH evolution

REACTOR 2



REACTOR 1

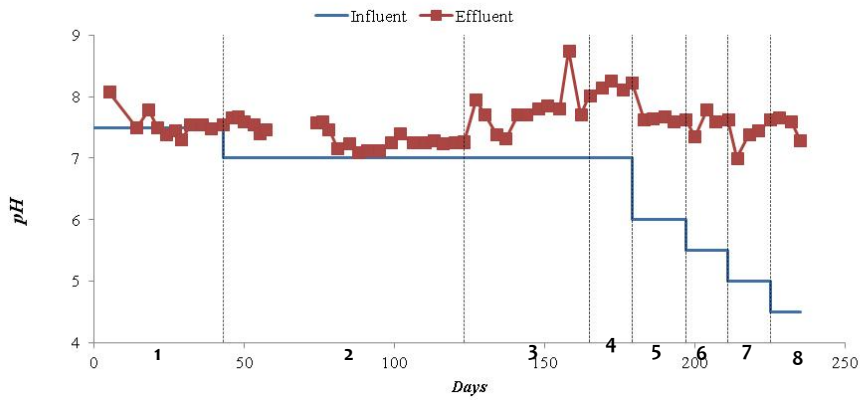
Feed pH ≈ 3 → **INHIBITION**

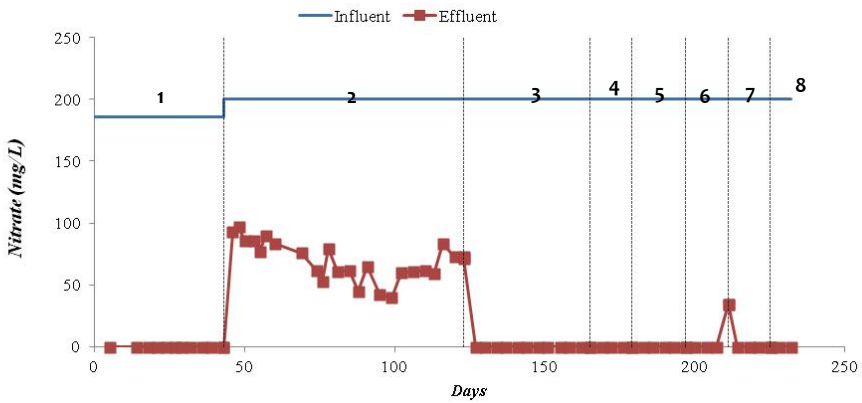
Feed pH ≈ 5 → **NEUTRALIZATION**

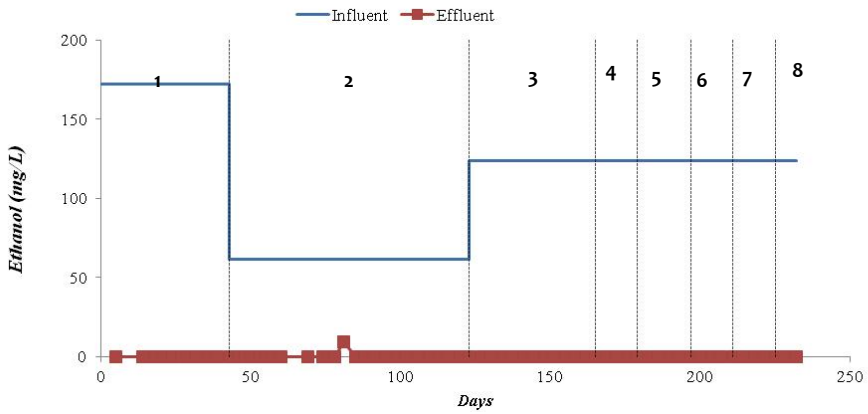
(production of HCO_3^-)

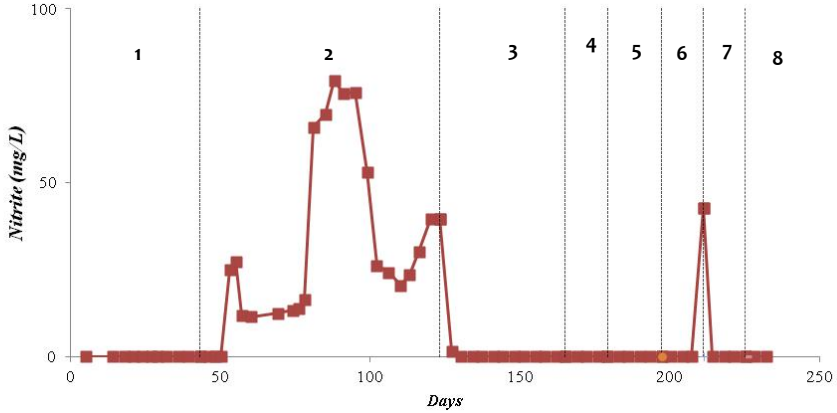
Results – nitrate-reducing reactors (1)

FBR 1 (T ≈ 8÷9°C)









1→2 : batch→ continuous flow

2→3 : ethanol concentration has been doubled

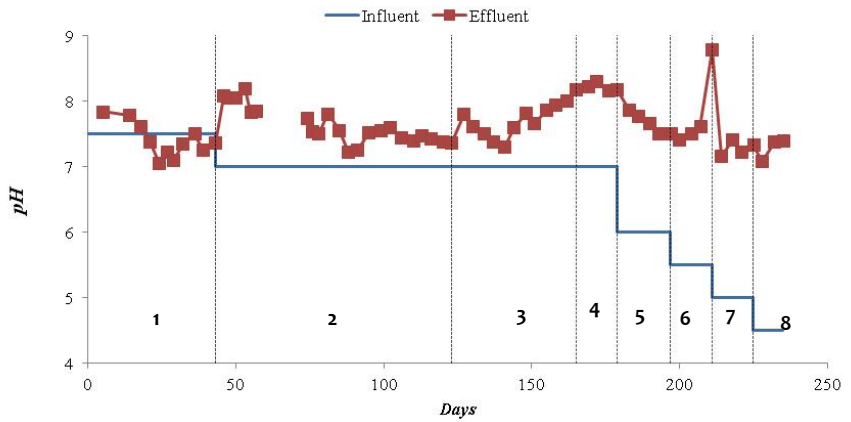
3→4 : decrease of HRT from 9 to 6 hours

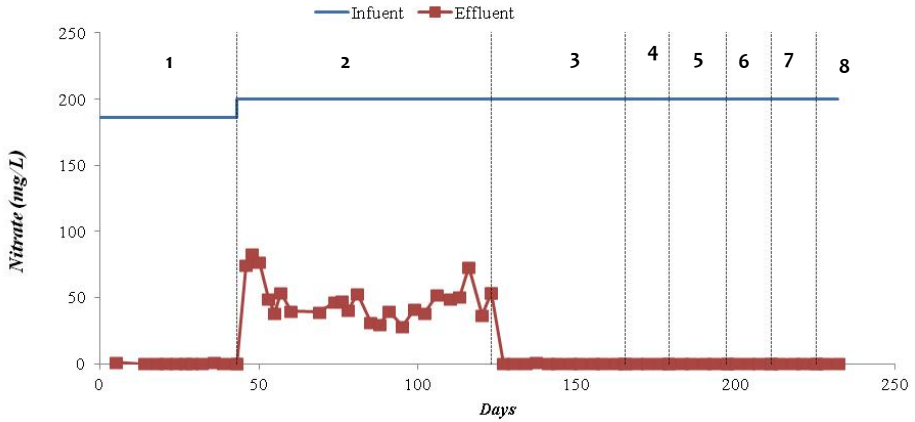
Other phases: decrease of feed pH

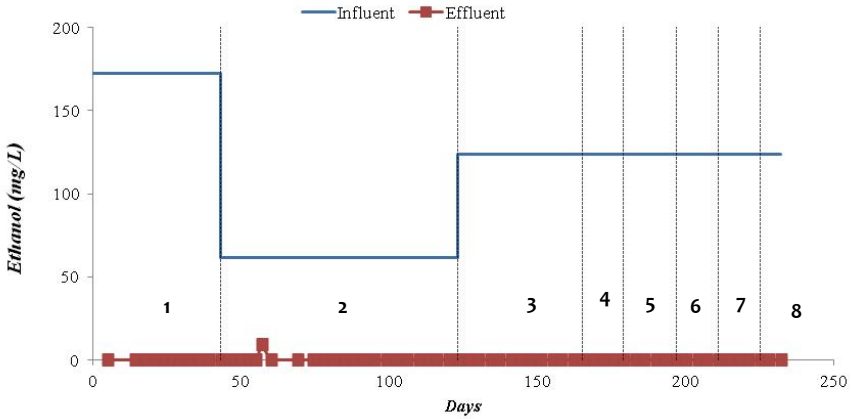
$$6NO_3^- + CH_3CH_2OH \rightarrow 6NO_2^- + 2CO_2 + 3H_2O$$

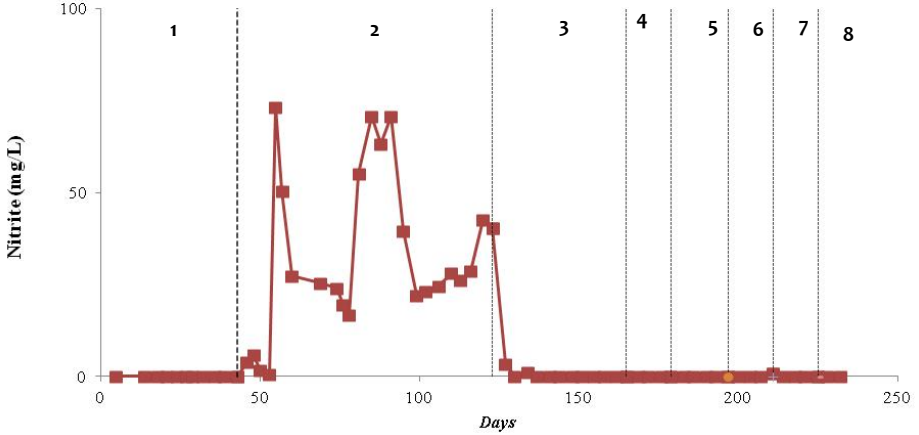
Results – nitrate-reducing reactors (2)

FBR 2 (T ≈ 22÷24°C)

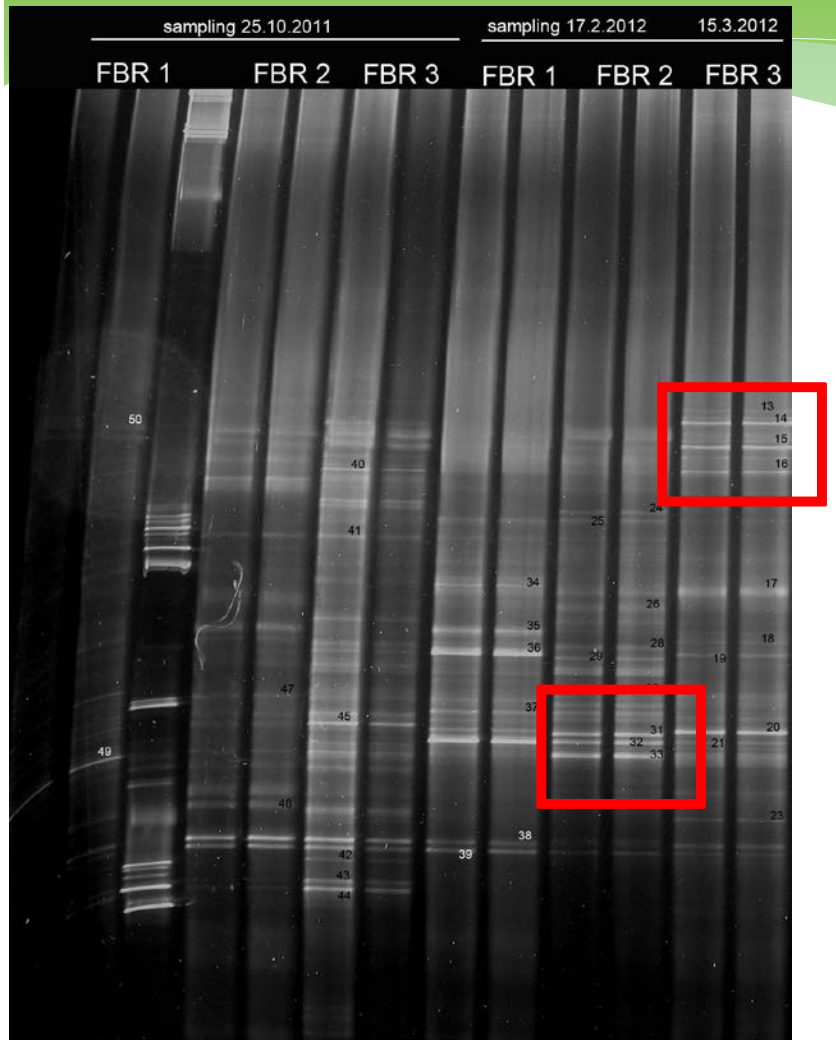








Results – nitrate-reducing reactors (3)



DGGE analysis

- 13. *Niabella* sp. (94%)/Bacteroidetes
- 14. *Niabella* sp. (94%)/Bacteroidetes
- 15. *Terrimonas lutea* (96%)/Bacteroidetes (**denitrification**)
- 16. *Terrimonas lutea* (96%)/Bacteroidetes (**denitrification**)
- 17. β-proteobacteria
- 19. β-proteobacteria
- 20. Azospira restricta (98%)/ β-proteobacteria (**nitrogen-fixing**)
- 21. *Dechloromonas* sp. /β-proteobacteria (**chlorate-reducing**
- 23. *Piscinibacter aquaticus*/ β-proteobacteria
- 30. *Dechloromonas sp.* (98%)/β-proteobacteria (**chlorate-reducing**)
- 31. *Hydrogenophaga caeni* (99%)/ β-proteobacteria (**denitrification**)
- 36. β-proteobacteria
- 38. *Nitrospira moscoviensis* (95%) /Nitrospirae (**nitrite-oxidizing**)
- 39. *Nitrospira moscoviensis* (95%) /Nitrospirae
- 41. Flavisolibacter sp. (93 %) /Bacteroidetes (**denitrification**)
- 43. *Iamia* majanohamensis (99%)/Actinobacteria (**denitrification**)
- 44. *Iamia* majanohamensis (99%)/Actinobacteria(**denitrification**)
- 45. *Ferribacterium limneticum* (99%)/ β-proteobacteria (**Fe(III)-reducing**
- 48. *Nitrospira moscoviensis* (95%) /Nitrospirae
- 49. *Zoogloea caeni* (99%)/β-proteobacteria

Results – batch tests

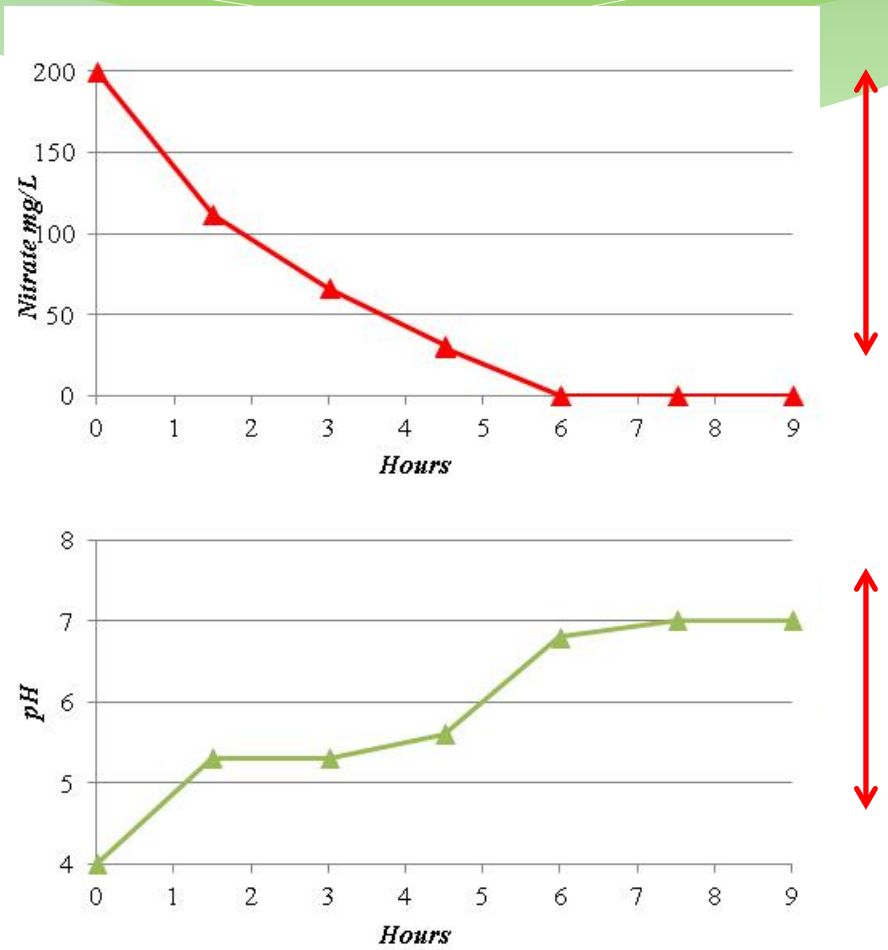
- Determination of the **lowest tolerable pH**
- **Stoichiometric** ethanol/nitrate ratio
- **Lenght:** 9h
- **Shaking velocity:** 200 rpm

Stoichiometric ethanol/nitrate ratio

+

respiking with ethanol after 4.5 hours

pH: 4



Conclusions (1)

- **Unsuitability** of the polypropylene support for the biomass immobilization
- **No dilution** of the inhibitors because of the **low fluidization degrees**

- The stoichiometric **COD/SO_4^{2-} ratio** has been shown to be inadequate to attain a high-efficiency sulfate reduction. However, the feed pH of 5 has always been neutralized.
- **Sulfate reduction efficiencies higher than 95%** have been obtained with a COD/SO_4^{2-} ratio of 4.

- **Acetate accumulation** in both the reactors
- In R1 **acetate accumulation is inhibitory** for the biological process, whereas, in R2, it does not affect the process since the **excess of lactate in the feed solution**.

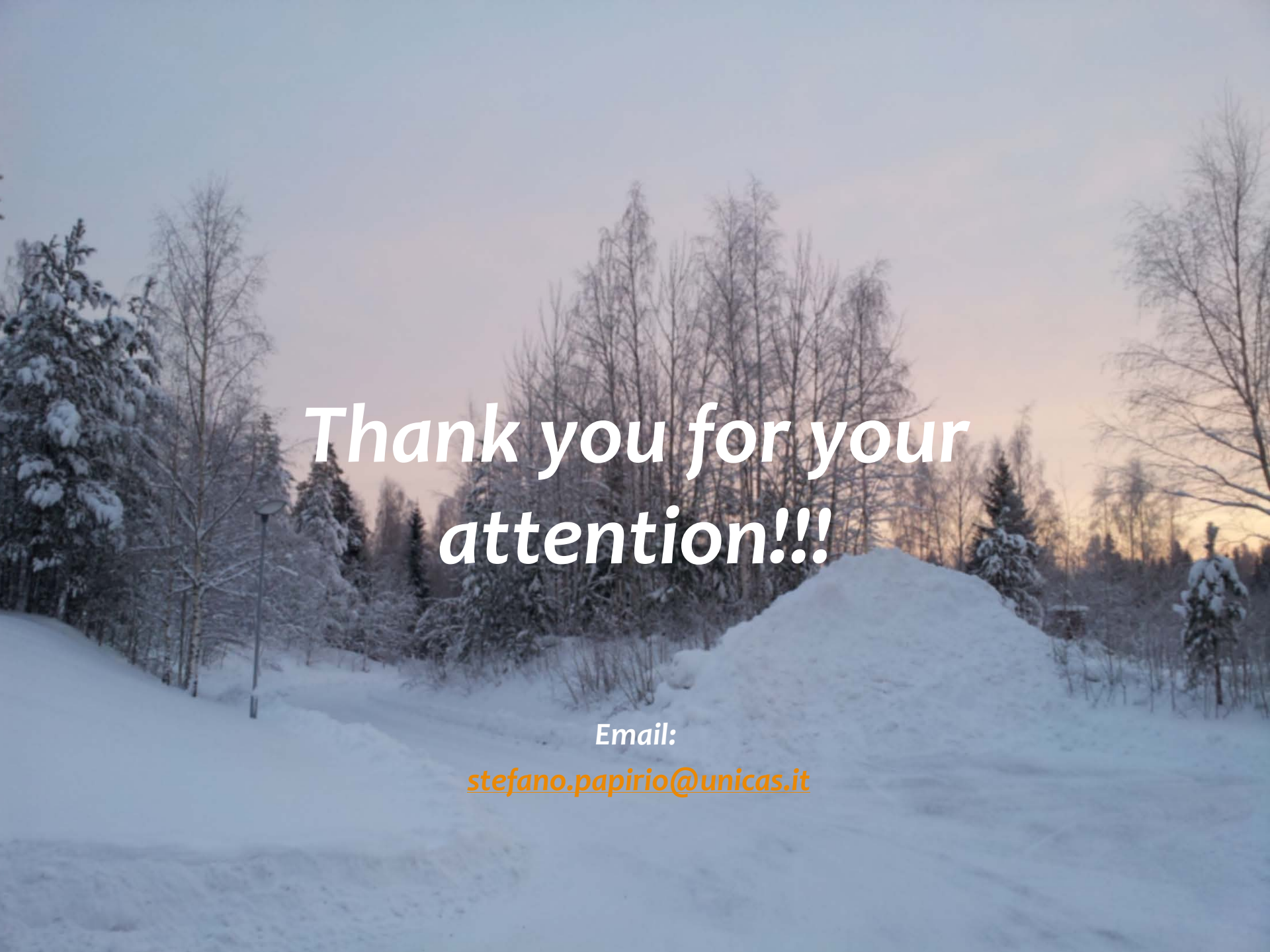
- **Microbial competition for lactate**. Activity tests will be conducted in order to assess the sulfate-reducing activity and other fermentation activities.

Conclusions (2)

- **Quick acclimatization** of the denitrifying bacteria. **Many denitrifying species colonized** the support.
- **Ethanol and nitrate effluent concentrations** are below the detection limit when the ethanol/nitrate ratio is two times higher than the theoretical one.
- The **HRT decrease** from 9h to 6h and the **gradual pH decrease** from 7 to 4.5 do not affect the efficiencies of the reactor.
- The **temperature** has been shown not to affect the process so far.
- Denitrification occurs even at **pH as low as 3.5.**

Future Research

- Still **decreasing the pH** in the feed solutions for the reactors;
- Evaluation of the **metal toxicity** to the denitrifying activity;
- **Add sulfate** to the feed solution and study the **simultaneous removal** of sulfate and nitrate;
- Assess the **toxicity of sulfide** to the denitrifying bacteria;
- **Set-up of a MBR system** for the comparison of the denitrification efficiencies



Thank you for your attention!!!

Email:

stefano.papirio@unicas.it